รายงานวิจัยฉบับสมบูรณ์

โครงการ การเพิ่มความสามารถในการรับแรงกระแทกในวัสดุทดแทนไม้จากเมตริกชนิดพอลิไวนิลคลอไรด์โดยใช้สารเพิ่มการรับแรงกระแทกกลุ่มสไตรินิคโคพอลิเมอร์

โดย รศ.ดร. ศราวุธ ริมดุสิตและคณะ

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คณะผู้วิจัย	สังกัด
1. รศ.ดร. ศราวุธ ริมดุสิต	คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
2. รศ.ดร. ศิริพร ดำรงค์ศักดิ์กุล	คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
3. น.ส. ดลหทัย อัตถากร	คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
4. น.ส. ปฏิมา วงษ์มานิตย์	คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

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การเพิ่มความสามารถในการรับแรงกระแทกในวัสดุทดแทนไม้จากเมตริกชนิดพอลิไวนิลคลอไรด์โดยใช้สารเพิ่มการรับแรงกระแทกกลุ่มสไตรินิคโคพอลิเมอร์

โครงการการเพิ่มความสามารถในการรับแรงกระแทกในวัสดุทดแทนไม้จากเมตริกชนิดพอลิไวนิลคลอไรด์โดยใช้สารเพิ่มการรับแรงกระแทกกลุ่มสไตรินิคโคพอลิเมอร์ โดยการสนับสนุนของ สำนักงานกองทุนสนับสนุนการวิจัย (สกว.) และบริษัท วีนิไทย จำกัด (มหาชน) ได้จัดทำรายงานวิจัยฉบับสมบูรณ์ (ส.ค. 2552 – ส.ค. 2554) ประกอบด้วยรายงาน 2 ส่วน ส่วนแรกเป็นรายงานวิจัย เรื่อง *"การเพิ่มความสามารถในการรับแรงกระแทกในวัสดุทดแทนไม้จากเมตริกชนิดพอลิไวนิลคลอไรด์โดยใช้เอบีเอสเป็นสารเพิ่มการรับแรงกระแทก"* ส่วนที่สองเป็นรายงานวิจัย เรื่อง *"การเพิ่มความสามารถในการรับแรงกระแทกในวัสดุทดแทนไม้จากเมตริกชนิดพอลิไวนิลคลอไรด์โดยใช้อะคริโลไนไตรล์ สไตรีน อะคริเลต"*

ผลการศึกษาในส่วนแรก งานวิจัยนี้พัฒนาวัสดุคอมพอสิตทดแทนไม้ ซึ่งประกอบด้วยเมทริกซ์พอลิเมอร์ผสมระหว่างพีวีซีและเอบีเอสและสารเติมชนิดผงไม้ โดยมีการศึกษาผลของปริมาณพอลิเมอร์ชนิดเอบีเอสตั้งแต่ร้อยละ 0-50 โดยน้ำหนัก ในพอลิเมอร์ผสมระหว่างพีวีซีและเอบีเอสต่อสมบัติทางกล สมบัติทางความร้อน และสมบัติทางกายภาพ พบว่า พอลิเมอร์ผสมที่อัตราส่วนเอบีเอสร้อยละ 50 โดยน้ำหนัก จะเกิดงานร่วมขึ้นในสมบัติการทนแรงกระแทก โดยความแข็งแรงภายใต้แรงกระแทกมีค่าสูงถึง 65 กิโลจูลต่อตารางเมตร ซึ่งสูงกว่าค่าความแข็งแรงภายใต้แรงกระแทกของพีวีซีซึ่งมีค่าเท่ากับ 6.5 กิโลจูลต่อตารางเมตร สำหรับสมบัติทางกล คือ ค่าความแข็งเกร็งและค่าความแข็งแรงภายใต้แรงดึงและแรงดัดโค้งมีแนวโน้มเพิ่มขึ้นเมื่อปริมาณพีวีซีในพอลิเมอร์ผสมมากขึ้น ส่วนสมบัติทางความร้อนของเมทริกซ์พอลิเมอร์ผสมระหว่างพีวีซีและเอบีเอส ในด้านอุณหภูมิที่มีผลต่อการเสียรูปของชิ้นงาน เช่น อุณหภูมิโก่งตัวด้วยความร้อน (เอชดีที) และอุณหภูมิอ่อนตัวไวแคตมีแนวโน้มเพิ่มขึ้นเมื่อปริมาณเอบีเอสในพอลิเมอร์ผสมเพิ่มขึ้น นอกจากนี้ชิ้นงานที่มีอัตราส่วนเอบีเอสร้อยละ 50 โดยน้ำหนักจะมีค่าอุณหภูมิโก่งตัวด้วยความร้อนเท่ากับ 73 องศาเซลเซียสและมีค่าอุณหภูมิอ่อนตัวไวแคตเท่ากับ 84 องศาเซลเซียส ในขณะที่ชิ้นงานพีวีซีมีค่าอุณหภูมิโก่งตัวเท่ากับ 68 องศาเซลเซียสและค่าอุณหภูมิอ่อนนิ่มเท่ากับ 77 องศาเซลเซียส จากนั้นศึกษาวัสดุคอมพอสิตทดแทนไม้โดยใช้เมทริกซ์ที่เป็นพอลิเมอร์ผสมระหว่างพีวีซีและเอบีเอสที่อัตราส่วนของเอบีเอสเท่ากับร้อยละ 50 โดยน้ำหนัก โดยศึกษาผลของการเติมผงไม้ในอัตราส่วนระหว่างร้อยละ 10-50 โดยน้ำหนัก จะได้ว่าคอมพอสิตมีสมบัติทางกลและทางความร้อนที่ดีขึ้นเมื่อปริมาณผงไม้เพิ่มสูงขึ้น และที่อัตราส่วนผงไม้ร้อยละ 50 โดยน้ำหนัก วัสดุคอมพอสิตทดแทนไม้ที่ได้จะมีสมบัติทางความร้อนและสมบัติทางกลที่ดีที่สุด โดยจะมีค่าอุณหภูมิโก่งตัวด้วยความร้อน (เอชดีที) และอุณหภูมิอ่อนตัวไวแคตสูงถึง 87 องศาเซลเซียสและ 98 องศาเซลเซียสตามลำดับ โดยวัสดุคอมพอสิตยังมีค่าสตอเรจมอดูลัสที่อุณหภูมิห้องสูงถึง 5.44 จิกกะปาสคาล นอกจากนี้วัสดุคอมพอลิตทดแทนไม้ที่ใช้พอลิเมอร์เมทริกซ์ผสมระหว่างพีวีซีและเอบีเอสนี้ยังมีค่าความสามารถในการรับแรงกระแทกที่ดีกว่าวัสดุคอมพอสิตทดแทนไม้ที่ใช้พอลิโอเลฟิน เช่น พอลิเอทิลีนและพอลิพรอพิลีนเป็นเมทริกซ์อีกด้วย

ผลการศึกษาในส่วนที่สอง งานวิจัยนี้มีวัตถุประสงค์เพื่อพัฒนาวัสดุคอมพอสิตทดแทนไม้จากพีวีซีและเส้นใยมะพร้าว โดยใช้อะคริโลไนไตรล์ สไตรีน อะคริเลต (เอเอสเอ) เป็นสารเพิ่มสมบัติการรับแรงกระแทก โดยศึกษาปริมาณสารเพิ่มสมบัติการทนแรงกระแทกชนิดเอเอสเอตั้งแต่ร้อยละ 0-50 โดยน้ำหนัก ในพอลิเมอร์ผสมระหว่างพีวีซีและเอเอสเอ ที่ส่งผลต่อสมบัติทางกล สมบัติทางความร้อน และสมบัติทางกายภาพ พบว่าการทนแรงกระแทกของพอลิเมอร์ผสมมีการเพิ่มขึ้นอย่างรวดเร็วที่ปริมาณเอเอสเอ 30-40% โดยน้ำหนัก และที่ปริมาณเอเอสเอ 50% โดยน้ำหนัก พอลิเมอร์ผสมจะมีค่าความแข็งแรงภายใต้การรับแรงกระแทกสูงที่สุดถึง 77 กิโลจูลต่อตารางเมตร ซึ่งมีค่าสูงกว่าค่าความแข็งแรงภายใต้การรับแรงกระแทกของพีวีซีซึ่งมีค่าเพียง 6.8 กิโลจูลต่อตารางเมตร นอกจากนี้ยังพบว่า ความแข็งแกร่งและความแข็งแรงภายใต้แรงดึงและแรงดัดโค้งมีแนวโน้มเพิ่มขึ้นเมื่อปริมาณพีวีซีในพอลิเมอร์ผสมมากขึ้น สำหรับสมบัติทางความร้อนของพอลิเมอร์ผสมระหว่างพีวีซีและเอเอสเอพบว่าอุณหภูมิโก่งตัวด้วยความร้อน (เอชดีที) และอุณหภูมิอ่อนตัวไวแคตมีแนวโน้มเพิ่มขึ้นเมื่อปริมาณเอเอสเอในพอลิเมอร์ผสมเพิ่มขึ้น โดยพอลิเมอร์ผสมที่มีอัตราส่วนเอเอสเอร้อยละ 50 โดยน้ำหนักจะมีค่าอุณหภูมิโก่งตัวด้วยความร้อนเท่ากับ 70 องศาเซลเซียสและมีค่าอุณหภูมิอ่อนตัวไวแคตเท่ากับ 83 องศาเซลเซียส นอกจากนี้ยังพบว่าพอลิเมอร์ผสมที่มีอัตราส่วนเอเอสเอร้อยละ 50 จะมีความทนทานต่อสภาวะอากาศ ได้ดีกว่าพีวีซีมาก จากนั้นจึงศึกษาวัสดุคอมพอสิตทดแทนไม้โดยใช้เมทริกซ์ที่เป็นพอลิเมอร์ผสมระหว่างพีวีซีและเอเอสเอที่อัตราส่วนของเอเอสเอเท่ากับร้อยละ 50 โดยน้ำหนัก โดยศึกษาผลของการเติมเส้นใยมะพร้าวในอัตราส่วนระหว่างร้อยละ 10-50 โดยน้ำหนัก พบว่าวัสดุคอมพอสิตแสดงสมบัติทางกลและทางความร้อนที่ดีขึ้นเมื่อปริมาณเส้นใยมะพร้าวเพิ่มสูงขึ้น และที่อัตราส่วนเส้นใยมะพร้าวร้อยละ 50 โดยน้ำหนักวัสดุคอมพอสิตจะมีค่าสตอเรจมอดูลัสที่อุณหภูมิห้องสูงถึง 5.06 จิกะปาสคาล และมีสมบัติทางความร้อนที่ดีที่สุด โดยจะมีค่าอุณหภูมิโก่งตัวด้วยความร้อน (เอชดีที) และอุณหภูมิอ่อนตัวไวแคตสูงถึง 82 องศาเซลเซียสและ 96 องศาเซลเซียส ตามลำดับ นอกจากนี้ยังพบว่าวัสดุคอมพอสิตทดแทนไม้ที่ใช้พอลิเมอร์เมทริกซ์ผสมระหว่างพีวีซีและเอเอสเอเสริมแรงด้วยเส้นใยมะพร้าว ยังมีค่าความแข็งแรงภายใต้การรับแรงกระแทกสูงกว่าระบบวัสดุคอมพอลิตทดแทนไม้ที่ใช้พอลิเมอร์เมทริกซ์พีวีซีเสริมแรงด้วยเส้นใยมะพร้าว และวัสดุคอมพอสิตทดแทนไม้ที่ใช้พอลิโอเลฟิน เช่น พอลิเอทิลีนและพอลิพรอพิลีนเป็นเมทริกซ์อีกด้วย

ABSTRACT

Impact Property Enhancement of PVC-Wood Composites Using Styrenic Copolymer

This is the cooperative research between Thailand Research Fund, Vinythai Public Company Limited, Bangkok, Thailand and Polymer Engineering Laboratory (PEL), Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand. The report consists of 2 parts: Part One, the research entitled *"Impact Property Enhancement of PVC-Wood Composites Using ABS as Impact Modifier,"* and Part Two, the research entitled *"Impact Property Enhancement of PVC-Wood Composites Using Acrylonitrile Styrene Acrylat*e*".*

Significant findings of part one can be summarized as follows:

The aim of this research is to develop of the high impact strength wood-substituted composites based on PVC with an incorporation of ABS. The characteristics of the PVC/ABS blend as a polymer matrix were firstly investigated by varying ABS content from 0-50 wt%, in PVC/ABS blends on mechanical, thermal and physical properties were investigated. The results showed that the PVC/ABS matrix at 50 wt% of ABS content provided the synergistic behavior on impact strength as high as 65 kJ/m^2, being higher than the impact strength of the PVC which was 6.5 kJ/m^2. In terms of mechanical properties, the modulus and strength under tensile and flexural test tended to increase with the increase of the PVC content in the blends. Additionally, thermal properties of the PVC/ABS blends, heat distortion temperature (HDT) and vicat softening temperature, systematically increased with increasing ABS content. HDT of the PVC/ABS blend was found to increase from 68°C for the neat PVC to 73°C for the PVC/ABS blend at 50/50 mass ratio and vicat softening temperature was found to increase from 77°C to 84°C. From those outstanding properties, PVC/ABS at a fixed mass ratio of 50/50 was selected to use as polymer matrix and then the effects of woodflour content varying from 10-50 wt% on the composites properties were studied. At 50 wt% of woodflour content, the composite provided the highest thermal stability with the service temperature as high as 87°C and 98°C for HDT and vicat softening temperature, respectively. Moreover, the storage modulus at room temperature of the PVC/ABS/wood composite at 50 wt% of woodflour content was high up to 5.44 GPa. Additionally, the impact strength value of the obtained

PVC/ABS/wood composites was also found to be higher than that of polyolefin composites such as HDPE/wood and PP/wood composites.

Significant findings of part two can be summarized as follows:

The aim of this research is to develop the high impact strength wood-substituted composites based on PVC and coconut fiber with an incorporation of ASA as impact modifier. The effect of ASA content ranging from 0-50 wt% on mechanical, thermal and physical properties of PVC/ASA matrix was firstly investigated. The results showed that the impact strength of the PVC/ASA matrix increased drastically at the ASA content of about 30-40 wt%. At the ASA content of 50 wt%, the greatest impact strength as high as 77 kJ/m^2 was obtained; this value was higher than the impact strength of the PVC which was only 6.8 kJ/m^2. The modulus and strength under tensile and flexural test tended to increase with the increase of the PVC content in the blends. In terms of thermal properties, heat distortion temperature (HDT) and vicat softening temperature of PVC/ASA blends systematically increased with increasing ASA content. HDT values of the PVC/ASA blend increased from 64°C (for the neat PVC) to 70°C (for the PVC/ASA blend at 50 wt% of ASA content). In addition, vicat softening temperature was found to increase from 77°C to 83°C. Moreover, PVC/ASA blends at a fixed mass ratio of 50/50 showed the superior weatherability than PVC. According to the results, PVC/ASA at a fixed mass ratio of 50/50 was used as polymer matrix for PVC/ASA/coconut fiber composites. The effects of coconut fiber content ranging from 10-50 wt% on the composites properties were studied. At 50 wt% of coconut fiber content, the composite provided the storage modulus at room temperature as high as 5.06 GPa, the highest service temperatures as high as 82°C, and 96°C for HDT and vicat softening temperature, respectively. Additionally, the impact strength of the obtained PVC/ASA/coconut fiber composites was also found to be higher than those of PVC/coconut fiber composite and other polyolefin composites (such as HDPE/wood fiber and PP/wood fiber composites).

EXECUTIVE SUMMARY

(31st August 2009 – 30th August 2011)

Objectives

1. To develop high impact and thermal stability PVC-based wood substituted materials by using styrenic copolymers as impact modifiers.
2. To examine the composition of ABS and ASA which provide the high impact strength for further used as wood composite matrices.
3. To explore the mechanical, thermal and physical properties of the resulting PVC-based wood composites.

Research Summary

In this research, high impact strength PVC/ABS/wood composite and PVC/ASA/coconut fiber composite at various wood contents were developed as a wood-substituted product.

In the 1st year of this research, the effects of type and content of ABS and woodflour contents on mechanical properties, i.e. tensile, flexural properties and impact strength, thermal properties, i.e. glass transition temperature, dynamic mechanical properties, vicat softening temperature, and heat distortion temperature as well as physical properties, i.e. density and water absorption of PVC/ABS(SP200)/wood composites were examined. Woodflour contents were added ranging from 0% to 50 wt% with the average particle sizes of woodflour of 280 μm. Three types of ABSs coded as SP100, SP200, SR101 showed the significant effect only on impact strength. ABS type SP100 and SP200, have a similar behavior on impact properties. PVC/ABS(SP200) blends, processed at temperature of 160°C, provided the highest impact strength. In addition, thermal properties of the PVC/ABS blends were only marginally changed with type of ABS. The effect of ABS(SP200) content in PVC/ABS(SP200) blends on several properties were investigated. When ABS(SP200) content increased, the mechanical properties, i.e. modulus and strength under tensile and flexural loading, of the PVC/ABS(SP200) blends decreased. However, the synergistic behavior in impact strength occurred at PVC/ABS mass ratio of 50/50 with ten times higher than the impact strength value of the PVC. From the DSC thermogram, the PVC/ABS(SP200) blends showed two distinct T_g's. T_g of the PVC rich phase was slightly shifted to higher, suggesting in partial miscible behavior in this blend.

Additionally, the ABS provided higher thermal stability to PVC such as HDT and vicat softening temperature.

Then, the PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 was chosen to be studied the effect of woodflour content on their properties. When the woodflour content increased, the tensile strength, elongation at break, flexural strength, and notched Izod impact strength of the obtained the PVC/ABS(SP200)/wood composites decreased, whereas the tensile modulus, and flexural modulus of the composites systematically increased. Moreover, as compared to PVC/wood composites, the presence of ABS(SP200) can enhance the impact strength value of the PVC/wood composite if the woodflour content is not exceed 40 wt%. When the woodflour content high up to 50 wt%, the ABS(SP200) showed no influence on impact properties of the wood composites. Furthermore, the impact properties of the PVC/ABS/wood composites were only marginally changed with type of ABS. In terms of thermal properties, HDT and vicat softening temperature of the PVC/ABS(SP200)/wood composite tended to increase with the increase of woodflour content. Finally, the water absorption of PVC/ABS(SP200)/wood composites increased with increasing woodflour content due to the hydrophilic by nature of wood structure.

In the 2nd year of this research, high impact strength polymer blends between PVC and ASA, as an impact modifier, with improved thermal properties and weathering durability were developed. The effects of the ASA content on mechanical, thermal, physical properties and outdoor weathering durability of the PVC/ASA blends may be summarized as follows. PVC/ASA blends exhibited highest impact strength, i.e. 77.6 kJ m^{-2}, when ASA content in the blend is about 50 wt%. Tensile and flexural properties of the blends were found to slightly decrease with the ASA content. Glass transition temperature and thermal stability of the blends could be enhanced by the presence of ASA in the blends. The shifting of the two glass transition temperatures of the PVC domain and ASA domain towards each other in the blend suggesting partially miscible nature of these polymers. Finally, outdoor weathering durability of the blends was substantially enhanced by the ASA addition as confirmed by a negligible color change of the blend samples after outdoor weathering up to 4 months.

In terms of PVC/ASA/coconut fiber composites, PVC/ASA blend at a fixed PVC/ASA mass ratio of 50/50 was chosen to be studied the effect of coconut fiber content on their properties. With increasing coconut fiber content in the composites, tensile modulus, flexural

modulus, and flexural strength of the PVC/ASA/coconut fiber composites systematically increased while tensile strength and notched Izod impact strength of the composites tended to decrease. In comparison with PVC/coconut fiber composites, PVC/ASA/coconut fiber composites was found to provide significantly higher impact strength value even at up to 50 wt% coconut fiber content. T_gs from DMA of PVC/ASA/coconut fiber composites systematically increase with the addition of coconut fiber in the composites and the result was consistent with the HDT and vicat softening temperature determination. Water absorption and swelling thickness of PVC/ASA/coconut fiber composites slightly increased with increasing coconut fiber content due to the hydrophilic nature of coconut fiber. Finally after natural weathering for 3 months, color fading of the composites was observed and tended to increase with increasing coconut fiber content due to more interfacial cracks observed between the fiber and the PVC/ASA matrix.

PART ONE

Impact Property Enhancement of PVC-Wood Composites Using ABS as Impact Modifier

(31st August 2009 – 30th August 2010)

This cooperative research between Thailand Research Fund, Vinythai Public Company Limited, Bangkok, Thailand and Polymer Engineering Laboratory (PEL), Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand, will take 24 months with a total budget of 1,500,000 baht from TRF and 500,000 baht in cash and 321,534 baht in kind from Vinythai PCL.

1. Introduction

1.1 General Introduction

Wood is one of the oldest building materials. It has a naturally beautiful texture and strength. The obvious drawbacks of natural wood products are high water uptake (24-100 wt%) [1], high flammability (Limiting Oxygen Index, LOI = 20-22) [2], termite irresistibility, liability to damage by fungi attack, and need some treatment and maintenance. The development of wood-substituted materials particularly based on Wood Plastic Composites (WPCs) is consequently of increasing interest in recent years since the problem from using wood above can be effectively solved or minimized by an incorporation of polymeric materials [1].

WPCs take advantage of both wood and plastic. The advantages of wood include low density, low equipment abrasiveness, relatively low cost, and biodegradability while plastic provides WPCs with better moisture resistance and decay resistance. Wood plastic composites materials are made by compounding plastic, called polymer matrix which functions as a binder, and natural fibers as fillers with other additives (lubricants, coupling agents, pigments, antioxidants, UV stabilizers, antimicrobial agents, etc.). Since the first WPC products were introduced in the 1980s, the market size has increased up to $1,565 million within 3 decades

[3]. Today more than 1.5 million tons of WPCs are produced worldwide, especially in North-America (about 1 million tons), Germany (70,000 tons), China (200,000 tons) and Japan (100,000 tons) [4]. That increase represents the potential of WPCs as a construction material. The initial market breakthrough for WPCs began in the US in the decking and railing market in 2000s [3]. These WPC home construction products were attractive to consumers because of their low maintenance cost even though WPCs prices were higher than the alternative competitor – pressure treated lumber. Nowadays, WPCs are widely used in decoration, building and construction. Their most widespread use is generally suffice to cover the greater range of current applications such as decking, railings, fencing, landscaping timbers, cladding and siding, park benches, molding and trim, window and door frames, and indoor and outdoor furnitures [1].

As WPC boards are competing in the market with common lumber, their price should be in the same level. In practical terms, their cost should be no more than 2-3 times higher than that of wooden boards, and that increase should be due to the advantages of WPCs such as good looks and the absence of knots, splinters, warping, and checking, acceptable mechanical properties, good durability, low maintenance, lack of microbial degradation, resistance to termites, and possibly even fire resistance. The boards can be made of any kind of plastic. However, the most widely used thermoplastics are commodity resins. The majority of WPC boards, manufactured and sold today, are based on polyethylene (PE), polypropylene (PP) or polyvinyl chloride (PVC) which can fit into the respective pricing category and at the same time having properties necessary for the WPC materials to pass the building standard [5].

PVC is one of the most versatile polymers and the following forms have important applications: rigid (unplasticized) grades, plasticized compounds, copolymers and blends [6]. Many properties of PVC are better than HDPE and PP such as stiffness, strength, weather resistance and inherent flame retardance property. It can be also modified easily by an incorporation of additives to obtain desired properties. It can be also blended with various polymers such as ABS (acrylonitrile-butadiene-styrene), PMMA (poly(methyl methacrylate)), EVA (ethylene vinyl acetate), CPE (chlorinated polyethylene), EPDM (ethylene propylene diene monomer, MBS (methyl methacrylate-butadiene-styrene), nitrile rubber, etc. [7]

In terms of Wood Plastic Composites, natural fiber is a good reinforcing filler. Wood fiber offers a number of advantages over the reinforcing inorganic fibers that are currently used, in terms of cost on a unit-volume basis, low density, high stiffness and flexibility during processing. In fact, the two major factors of the existence of WPC materials are: (a) to make the composite material less expensive and (b) to obtain material with overall better properties compared to both neat plastic and wood [5]. Furthermore, the addition of wood fiber keeps WPC having functions and appearance resemble to wood [8].

However, the use of wood fibers in a PVC matrix produces composites that are more brittle than neat PVC [9]. This is because wood fiber is not compatible with the polymer due to their hydrophilic character which results in poor stress transfer between the matrix and the fillers and, thus, unsatisfactory properties of the final products. Since impact strength is a vital property for many rigid PVC applications, rigid PVC/wood-fiber composites must be toughened for successful applications [9].

The addition of impact modifier is a conventional approach to toughen PVC/wood-fiber composites while the rubber toughening is the most often used method of improving the impact resistance of polymers [9]. ABSs are engineering thermoplastics exhibiting good processibility, excellent toughness, and sufficient thermal stability. The dominant property of ABS plastics is the very high impact strength. They also retain the excellent injection moulding behavior of styrene plastics, particularly good melt flow, low mould shrinkage and excellent surface finish [10]. More specifically, it has been reported that copolymers of SAN containing acrylonitrile between 11.5 to 26% by weight are miscible with PVC [11].

In summary, the reasons why ABS is recommended for PVC/wood composites as impact modifier are :

- compatible with PVC
- enhancing impact resistance
- good flow behavior
- good thermal stability
- low cost compared to the obtained properties

1.2 Composite Materials

Composite materials can be defined as a macroscopic combination of two or more distinct materials, having a recognizable interface between them [1]. However, composites that are usually used in building and construction applications, the definition can be restricted to include only those materials that contain reinforcement (such as fibers or particles) supported by a binder (matrix) material. The constituents can be organic, inorganic or metallic (synthetic and naturally occurring) in the form of particles, rods, fibers, plates, foams, etc. As compared to pure materials, these additional fillers often provide greater enhancement on such physically parameters as strength, density, electrical properties, and cost for a given application.

1.3 Wood Plastic Composites

WPCs are made by a combination of polymer matrix and natural fiber. Wood fiber gives good look and stiffness and reduces operating cost, while the role of a polymer matrix in a fiber-reinforced composite is to transfer stresses between the fibers, to provide a barrier against an adverse environment, and to protect the surface of the fibers from mechanical abrasion. The combination of wood and plastic leads to the high performance WPC materials, which take advantages of wood, including low density, low equipment abrasiveness, relatively low cost, and biodegradability, and plastic provides better mechanical properties, moisture resistance and decay resistance. The problem from using wood lumber can effectively be solved or minimized by an incorporation of polymeric materials to form wood plastic composites as summarized in Table 1.1.

Table 1.1 Properties comparison between wood, WPCs and polymers [12].

Property	Wood	WPCs	Polymers
Humidity resistance	--	+	++
Maintenance free	--	++	++
Elaborate design	--	++	++
Rigidity	++	++	-
Impact resistance	++	--	+
Aging	--	-	++
Fire properties	-	+	++ (PVC)
Cost	+	+	-

* (++) excellent, (+) good, (-) poor, (--) bad

The history of WPCs first appeared as thermosetting molding compounds Bakelite invented thermosetting polymer in the beginning of 1900s and used wood flour in 1920s. Thermoset wood composites created a base for the appearance of WPCs [1]. Nowadays, due to ease of processing and recyclability, the development of wood-substituted materials based on thermoplastic composites has high growth rate especially in construction sector [4]. Typically, useful properties of conventional thermoplastic wood composites compared to thermosetting wood composites include high cost-competitiveness, ease of processing, and recyclability. However, the most widely used thermoplastics are commodity plastics. The majority of WPC boards, manufactured and sold today, are based on polyethylene (PE), polypropylene (PP) or polyvinyl chloride (PVC) which can fit into the respective pricing category and at the same time having properties necessary for the WPC materials to pass the building standard [1].

1.4 Natural Fiber

All natural fibers, whether wood or nonwood types, are cellulosic in nature. They are complex lignocellulosic materials made up of several major and minor chemical compounds. Major compounds include cellulose, lignin, and hemicellulose. The amount of cellulose, in lignocellulosic system, can vary depending on the species and age of the plant [13].

Cellulose

Cellulose is the main component making up about 50% of the dry weight of wood. Lignin makes up approximately 15-30%, whereas hemicellulose accounts for 15-25% of the wood. Extractives (1-10%) and ash (0-0.5%) are the minor constituents of wood. The chemical composition of wood varies between species, which accounts for the range of values.

The cellulosic molecule is largely linear and its molecular weight varies depending on the origin of the sample. The hydroxyl groups on cellulose are also largely responsible for its reactive nature. The cellulose chains have many polar hydroxyl groups as shown in Figure 1.1. These groups form many hydrogen bonds with the hydroxyl groups on adjacent chains (i.e., between cellulose hydroxyl groups or each other), holding and bundling the chains firmly together to form hard, stable crystalline regions that give the bundled chains more stability and strength. Cellulose is a hygroscopic, polar molecule and easily undergoes hydrogen bonding, which accounts for the tendency of wood to absorb moisture from the environment. A high proportion of cellulose is crystalline. The absorption of water by cellulose depends on the number of free hydroxyl groups, not those linked with each other. Therefore, water cannot enter crystallines. Only amorphous regions are accessible by water. In addition, only hydroxyl groups present in amorphous cellulose are available for reaction with chemicals and function as the binding site within wood for adhesion [14].

Table 1.2 Composition of natural fibers [13].

Component	Composition (wt%)	Polymeric Nature	Water Affinity	Role
Cellulose	44%-50%	Linear, crystalline	Hydrophilic	Strength
Hemicellulose	20%-25%	Branched, amorphous	Hydrophilic	Bind microfibrils, structural reinforcement
Lignin	20%-30%	Amorphous	Hydrophobic	Stiffness

Extractives	0%-10%	Polymeric	Hydrophobic	Encrusting

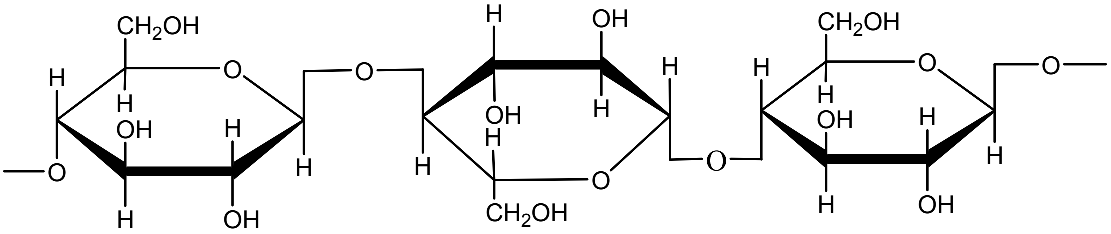


Figure 1.1: Structure of cellulose [13].

Hemicellulose

Hemicellulose is a polysaccharide and different from cellulose in that it consists of several sugar molecules. The structure of hemicellulose is shown in Figure 1.2. Its molecular chain is short, mostly branched and has lower molecular weight with a degree of polymerization of 50-200. Hemicellulose is primarily responsible for both the hygroscopic nature of wood and its lower thermal degradation. Generally, it occurs in higher concentration in hardwoods than in softwoods.

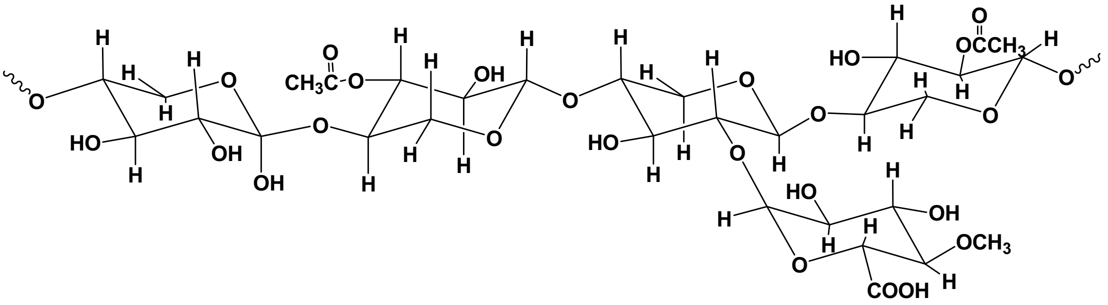


Figure 1.2: Structure of hemicellulose [13].

Lignin

The main difficulty in lignin chemistry is that no method has been established by which it is possible to isolate the lignin in its native state from the fiber. The chemical nature of lignin in lignocellulosic materials has been an important subject of study. Although the exact structural formula of lignin has not yet been established, most of the functional groups and units, which make up the molecule, have been identified. The high carbon and low hydrogen content of lignin suggest that it is highly unsaturated or aromatic in nature. The model of lignin structure is shown in Figure 1.3. Lignin is characterized by its associated hydroxyl and methoxy groups. The topology of lignin from different sources may be different but it has the same basic composition. Although the exact mode of linkages of lignin with cellulose in lignocellulosic natural fiber is not well known, lignin is believed to be linked with the carbohydrate moiety through two types of linkages, one alkali sensitive and the other alkali resistant. The alkali-sensitive linkage forms an ester-type combination between lignin hydroxyls and carboxyls of hemicelluose uronic acid. The ether-type linkage occurs through the lignin hydroxyls combining with the hydroxyls of cellulose. The lignin, being polyfunctional, exists in combination with more than one neighboring chain molecule of cellulose and/or hemicellulose, making a cross-linked structure [13].

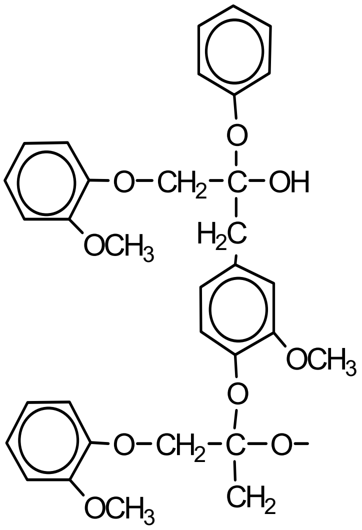


Figure 1.3: Model of lignin structure [13].

1.5 Polyvinyl chloride (PVC)

1.5.1 What is PVC?

PVC is a thermoplastic which is polymerized commercially by the free-radical polymerization by several techniques such as suspension, emulsion and microsuspension. The basic raw materials for PVC are derived from salt and oil. Chlorine is manufactured by the electrolysis of sodium chloride salt. The electrolysis of sea water produces chlorine. The chlorine is then combined with ethylene (C_2H_4), obtained from oil, and is converted at very high temperature to vinyl chloride monomer (VCM). The VCM is then polymerized to form PVC as shown in Figure 1.4. The molecular weights of PVC are in a range of 40,000 – 480,000 based on the weight average molecular weight (M_w) and 20,000 – 92,000 based on the number average molecular weight (M_n) whereas molecular weight distributions (M_w/M_n) of commercial PVC are between 1.9 and 5.2. PVC is produced to be in the form of white powder, called PVC resin, as shown in Figure 1.5. The particle size is ranging from 5-400 microns with the apparent bulk densities of 0.5-0.8 g/cm^3 [15].

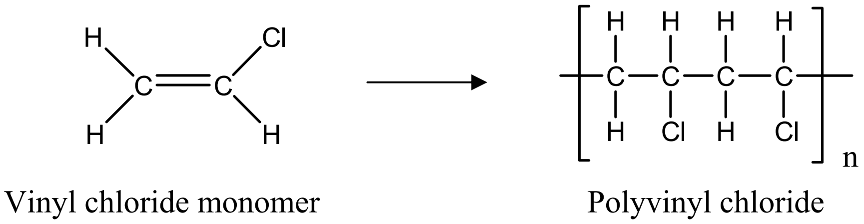


Figure 1.4: Vinyl chloride monomer and Polyvinyl chloride.

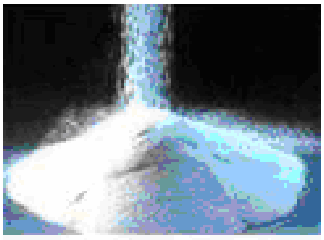


Figure 1.5: PVC resin [16].

1.5.2 Advantages of PVC

The low price of PVC renders its use desirable in many applications. Besides, this material is popular with its inherent flame retardancy and UV stability. PVC also has good mechanical properties, fungi, water and alcohols, and good resistance to acid, alkalies, fats and petroleum hydrocarbons. PVC is one of the world’s versatile polymers. It is extremely cost effective as compared to other plastics with a high degree of processing possibilities such as extrusion, injection, foaming, etc. It can be also processed in various forms such as rigid (unplasticized) grades, plasticized compounds, copolymers and blends. It is easy to modify with a wide range of additives and can be blended with various polymers. It is durable, easily maintained, and can be produced in an extensive range of applications with a large range of colours and transparency as shown in Figure 1.6.

Figure 1.6: Variety of PVC products [17,18].

1.5.3 Polyvinyl chloride as Wood Composite Matrix

The utilization of polyvinyl chloride as a wood composite matrix has been recently reported to experience a dramatical increase [13]. Typically the composites are used to produce window/door profiles, decking, railing, and siding as shown in Figure 1.7. The PVC wood composite compounding based on conical counterrotating intermeshing twin-screw extruder is demonstrated to be one effective way to get well dispersed wood composite products [19]. To obtain the enhanced PVC wood performance, heat stabilizers, processing aids, impact modifiers, lubricants, and pigments are also incorporated in the materials. The use of natural fiber with mica or glass fiber to form hybrid reinforcements is proved to enhance the mechanical properties of the final products. Furthermore, PVC wood has been proven to exhibit superior ultraviolet light and weathering resistance, and dimensional stabilities to those of natural wood. Besides, its inherent fire-resistant characteristics with a limiting oxygen index (LOI) as high as 50 (LOI > 26 is classified as self-extinguishable) [20].

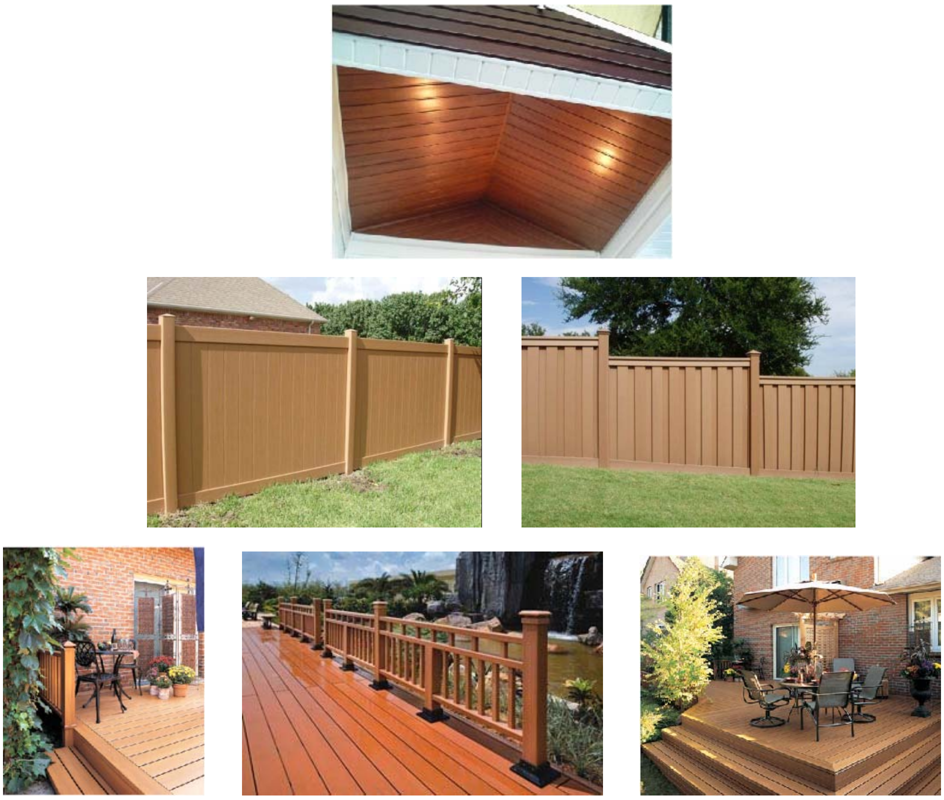


Figure 1.7: Applications of wood plastic composites [21].

1.5.4 Suspension PVC Resins

Suspension PVC resins are PVC homo-polymer resins which can be used in various techniques such as extrusion, calendering and injection. PVC resins are chosen from various molecular weights, presented by the different K-value which are related to mechanical properties. As an example, some properties of the Siamvic 258 RB, which is a PVC suspension type produced by VINYTHAI Public Company Limited and used in this study, are listed in Table 1.3. Moreover, Siamvic 258RB is a low K-value resin that is suitable for rigid PVC production processes such as good thermal stability, good initial color, no tendency to stick on hot metal surface, and very low level of fish-eyes. Moreover, it has very low dust during transportation and pneumatic filling of silos, regular feed of extruders as dry blend and it is easy to process even at low temperature [22].

Table 1.3 Characteristics of suspension PVC resin (Siamvic 258 RB) [22].

Characteristics	Units	Values (*)	Standards
Viscosity index	ml/g	82	ISO 1628-2
K-value (cyclohexanone)	-	58	DIN 53726
Polymerization degree	-	680	JIS K6721
Bulk density-compaction	kg/l	0.56	ISO 1068
Volatile matter	%	$\leq$ 0.3	ISO 1269
Particle size (sieve analysis)	micron	120-150	ISO 1624

(*) In the case of certain characteristics the values given in this table are means based on a large number of individual measurements distributed around the means in a range corresponding to the normal manufacture and measurement tolerances. These values should not be considered as specifications.

1.5.5 PVC Additives

Normally, the nature of PVC is hard, brittle and difficult to process. Many additives are incorporated into PVC to improve PVC formulation to be appropriate for particular application such as highly filled wood composite matrix.

1. Processing aids

Processing aids are chemicals which assist the melt processing of PVC. Processing aids do not reduce melt viscosity but they improve the elastic behavior of the melt. The high level addition of processing aids were found to render better PVC melt homogeneity, improve its mechanical properties (more elasticity, higher strength to prevent tearing) and in some cases speed up the PVC gelation times. Due to their high compatibility with PVC and high molecular weight, standard processing aids have the possibility to entangle short PVC chains, transfer the shear generated by the processing devices and promote fusion [23]. Examples of processing aids are methacrylate/acrylate copolymer, poly 2-methyl styrene, poly neopenthelene terephthalate, poly alkylene carbonate, etc. The level of usage can vary widely, depending on the PVC particle characteristics. The range is 0.8 to 20 phr, but most common range is 1-3 phr [24].

2. Lubricants

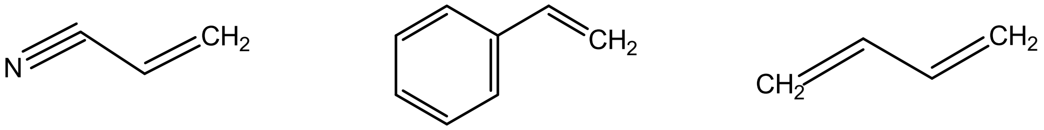
Lubricants are added to PVC compounds to facilitate processing and to permit control of processing rate. They prevent sticking and may also function as antistatic agents. Internal lubricants are chemical which lubricate the flow of PVC molecules within the melt whereas external lubricants prevent the plastic melt adhere to hot metal surfaces. In case of PVC, wax and its derivatives, glyceryl ester of fatty acids, long chain esters such as cetyl plamitate are most commonly used. Concentration depends on the number of lubricants used to get the desired balance of behavior. Total concentrations rarely exceed 4 phr. The normal concentration of internal/external lubricants is between 0.2-2.0 phr [24].

3. Heat stabilizers

Heat stabilizers are used to inhibit the degradation caused by heat and thermal unstability of PVC. It may also be degraded slowly by light. Typical examples of heat stabilizers are metallic soaps such as cadmium, barium, and zinc stearates which also act as lubricants. These chemicals simply react with HCl and are able to reduce further degradation. Calcium and zinc stabilizers are low in toxicity. Although increased calcium content leads to poorer initial color, long-term stability is improved. Higher zinc content improves initial color but reduces long-term stability. Stabilizers are added in the concentration range of <1 to 3 phr [24].

1.6 Acrylonitrile Butadiene Styrene (ABS)

ABS copolymers are a large family of thermoplastic materials, which consist of three monomers (acrylonitrile, butadiene and styrene). The chemical structures of those three monomers are shown in Figure 1.8. The proportions of the each component in ABS can vary from 15% to 35% by weight of acrylonitrile, 5% to 30% by weight of butadiene and 40% to 60% by weight of styrene.



Acrylonitrile Styrene 1,3-Butadiene

Figure 1.8: The chemical structure of three monomers of ABS.

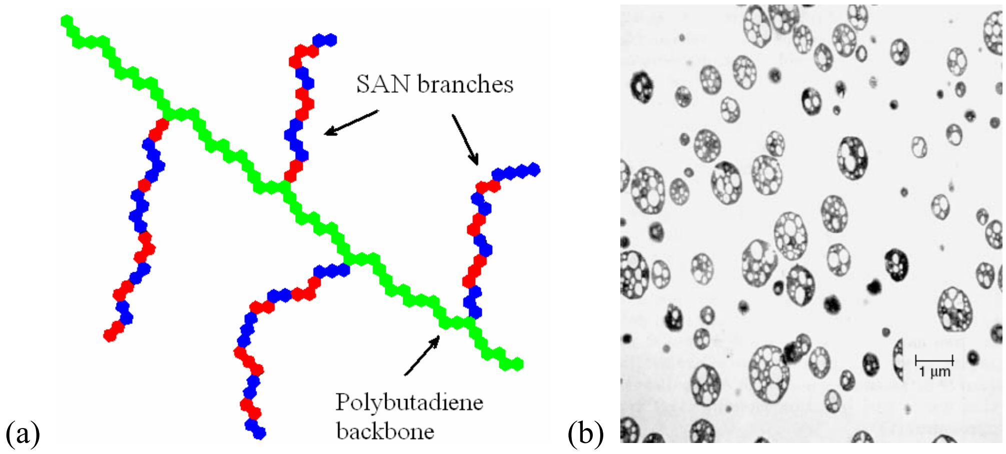


Figure 1.9: (a) The graft copolymer of SAN on polybutadiene.
(b) Transmission Electron Micrograph of ABS [25].

ABS polymer can be engineered by the manufacturer, depending on the ratio of the monomeric constituents and the molecular level connectivity. The acrylonitrile, being polar, attracts the other acrylonitrile on the other chains and binds the chains together, making ABS stronger than pure polystyrene and it also contributes strength, heat resistance, and chemical resistance. The butadiene, a rubbery substance, provides resilience even at temperature as low as −25°C. The butadiene component also contributes impact resistance, toughness, and flexibility. The styrene gives ABS the outstanding processability, including good melt flow, low mold shrinkage and excellent surface finish. It also contributes rigidity and processability [6].

ABS can be manufactured by several procedures. Graft polymerization techniques are commonly used to manufacture various grades of this material. It consists of two phases, SAN (styrene-acrylonitrile) matrix and SAN-g-PB (styrene-graft-polybutadiene) as an elastomeric phase. The SAN-g-PB is made by polymerizing styrene and acrylonitrile in the presence of polybutadiene, resulting in a long chain of polybutadiene with shorter chains of poly(styrene-co-acrylonitrile) as shown in Figure 1.9 (a). This characteristic provides a good dispersion of rubber phase in the matrix as shown in Figure 1.9 (b). ABS can process by two method, mechanical blending of SAN with a SAN-co-PB copolymer in common mixing equipment and polymerization processes which include the emulsion polymerization, suspension polymerization, and bulk polymerization [25]. All of these methods of preparation yield a large ABS family of great flexibility, not only depending on composition, but also depending on MW, degree of grafting, rubber particle size, and morphology, allowing the tailoring of properties with a wide range of features and applications. Some properties of ABS compared with PVC are listed in Table 1.4.

ABS materials can be readily processed on all thermoplastic processing equipment, including blow molding and thermoforming types. In addition, the blends with other polymers such as polystyrene, polyvinyl chloride, polycarbonates and polysulfones have been developed for used in many applications such as appliances, building and construction, electronics, and automotive industries [25]. ABS, which is an engineering plastic, is also used as an example of rather nonconventional wood plastic composite [1].

Figure 1.10: Three types of ABS used in this work are SP100, SP200 and SR101.

Table 1.4 The properties of PVC and ABS [26,27].

Properties	ASTM Test Method	PVC	ABS
1.Melt flow(g/10 min.)	D1238	1.4-54	1.1-1.8
2.Glass transition temperature, °C		75-105	91-110
3.Processing temperature, °C (C=Compression, I=Injection, E=Extrusion)		C: 141- 204 I: 149-213	C: 163-177 I: 193-274
4.Molding pressure range, MPa		68.95-275.80	55.16-172.37
5.Compression ratio		2.0-2.3	1.1-2.0
6.Mold shrinkage, in./in.	D995	0.002-0.006	0.004-0.009
7.Tensile strength at break, MPa	D638	40.68-51.71	30.34-43.44
8.Elongation at break, %	D638	40-80	3.5-75
9.Tensile yield strength, MPa	D638	40.68-44.81	19.30-43.43
10.Compressive strength, MPa	D695	55.16-89.63	31.02-55.16
11.Flexural strength, MPa	D790	68.95-110.32	37.23-75.84
12.Tensile modulus, MPa	D638	2413-4137	1034-2413
13.Compressive strength, MPa	D695	74.6	46.5
14.Flexural modulus, MPa	D790	2068-3447	1234-2585
15.Notch Izod impact, J/m (3.2 mm thickness)*	D256A	4.46-245.0	66.84-116.97
16.Hardness	D2240	Shore D65-85	R85-106
17.Coefficient of linear thermal expansion, 10^{-6}in./in./°C	D696	50-100	95-100
18.Deflection temperature under flexural load, °C	D648	60-76	96-102
19.Specific gravity	D792	1.30-1.58	1.01-1.05
20.Water absorption % (24 hr.)	D570	0.04-0.4	0.20-0.45

*The unit of impact strength value can be reported in J/m [ft·lbf/in.] or kJ/m^2 [ft·lbf/in.^{2}].

In this work three types of ABS were being used, SP100, SP200, SR101 shown in Figure 1.10, which are the three highest impact strength among commercial ABSs available in Thailand. The properties of ABS are listed in Table 1.5.

Table 1.5 The properties of three types of ABS used in this work [28,29,30].

Properties	**SP100**	**SP200**	**SR101**
Melt flow index (g/10min) at 220°C/10 kg	18	17	7
Notched Izod Impact Strength (kJ/m^2) at 6 mm thickness at 23°C	33	35	29
HDT (6 mm thickness at 0.45 MPa)	90	90	92
Flexural Strength (MPa)	64	56	59
Tensile Strength (MPa)	44	41	43
Flexural Modulus (GPa)	2.16	2.01	2.01

1.7 PVC/ABS Blends

The low price of PVC renders its use desirable in many applications. When blended with ABS, this material will provide high impact strength, toughness and flame retardance. PVC provides the inherent flame retardance with UV stability, whereas ABS provides the impact strength and processability. Although PVC is immiscible with ABS, the interfacial tension between the SAN phase and PVC is low enough to allow enough compatibility. The compatibility of this polymer system occurres due to the similarity of the solubility parameters of the SAN matrix of ABS and PVC. The effect of this compatibilization is the improvement in the impact strength of the PVC/ABS blends [25] due to well dispersed rubber particles in the matrix easier. This is responsible for the enhancement of toughness.

Not only improving the impact strength, the addition of ABS into PVC also provides good processability and hot tear strength [25]. High rubber, low modulus grades of ABS made by emulsion polymerization are often used for the impact modification of PVC. Because of the thermal degradation problem of PVC, blending is done typically in Banbury type mixers. The blend exhibits significantly improved notched Izod impact strength (≥1000 J/m) over PVC [25]. The primary application of this type of PVC/ABS blend, particularly in Western Europe, is in the manufacture of vacuum thermoforming automotive and mass-transit interiors. The inherent flame retardance of PVC makes it suitable for applications where the more expensive Flame Retardant-ABS could be employed [31]. Pre-compounded blends of ABS and PVC have also been commercially available for molding and extrusion applications as low cost alternatives to flame retarded grades of ABS and PPE (Polyphenylene oxide)/HIPS (High impact polystyrene) blends. Such PVC/ABS blends have been used in appliance and business machine housings, TV cabinets, electrical and electronic component manufacture [25]. Some properties of commercial PVC/ABS are also shown in Table 1.6.

Table 1.6 Properties of PVC/ABS blends [25].

Property	ASTM Test Method	Units	PVC/ABS Cycovin KAF B.F.Goodrich	PVC/ABS Kaneka ENPLEX Kanegafuchi
PHYSICAL				
Density	D792	kg/m^3	1200	1200
Mold Shrinkage	D955	%	0.4	0.4
Water Absorption (24 hrs.)	D570	%	0.09	0.09
MECHANICAL				
Flexural Modulus	D790	MPa	2310	2740
		kpsi	330	390
Flexural Strength	D790	MPa	67	61
		kpsi	9.6	8.7
Tensile Strength at Yield	D638	MPa	40	44
		kpsi	5.8	6.3
Elongation at Break	D638	%	20	20
Rockwell Hardness	D785		R100	R105
IMPACT				
Notched Izod Impact	D256	J/m	570	201
at 23°C		ft-lb/in.	10	3.7
THERMAL				
Heat Deflection Temp	D648			
at 0.45 MPa		°C	-	80
at 1.82 MPa		°C	79	71
Flammability Rating	UL94		V-0	V-0

1.8 Toughening Mechanisms

Toughening mechanisms of polymer blend, which depends on the dispersion of rubber particle in matrix, include energy absorption by rubber particle, debonding at the rubber-matrix interface, matrix crazing, shear yielding or combination of shear yielding and crazing as shown in Figure 1.11 [32].

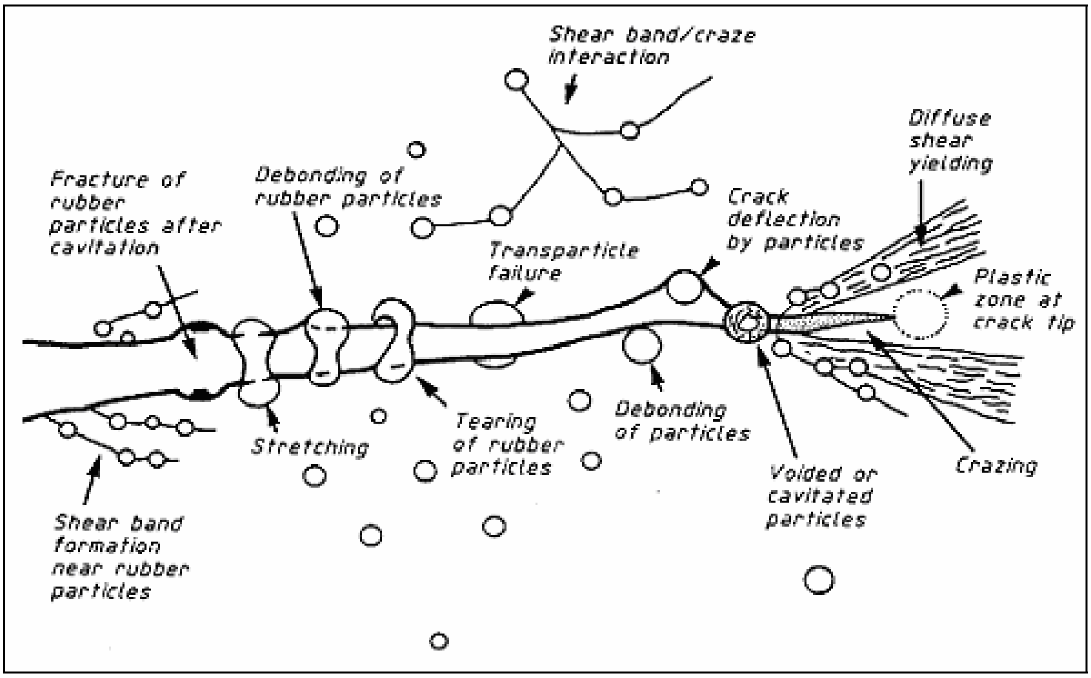


Figure 1.11: Toughening mechanisms in rubber filled modified polymers [32].

1.8.1 Matrix Crazing

Crazing can be defined as fine, thin, tiny type cracks that may extend in an plastic network [33]. The formation of crazes is like cracks in that they are wedge shaped and formed perpendicular to the applied stress. They differ from cracks that a crack is an open fissure in the material. However, a craze constitutes a relatively stable structure, by containing plastic that is stretched and highly oriented fibrillar and microfibrillar structures [25]. These phenomena are modeled in Figure 1.12. Another major distinguishing feature is that unlike cracks, crazes are able to support stress [33]. A craze can be also described as a layer of polymer a nanometer to a few micrometers thick, which has undergone plastic deformation approximately in the direction normal to the craze plane as a response to tension applied [25].

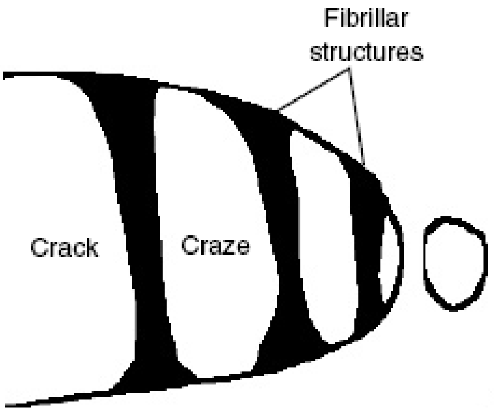


Figure 1.12: Illustration of structures found in crazing [34].

Crazing is an important source of toughness in rubber-modified thermoplastics. Under tensile stress, crazing is initiated at the maximum strain point (maximum tri-axial stress concentration) near the center of rubber particles. Craze growth is terminated by encountering with other rubber particles. The rubber domains may cavitate, forming internal voids, thus relieving triaxial stresses inside the plastic. This mechanism can prevent craze growth and crack formation. The dense crazing influences high energy absorption because, when the craze appears, fibril network will from at the craze tip. This fibril network is high orientated, and contributes to high load bearing of craze. However, crack can form by breaking down the craze fibril and forms void. This void expands slowly by rupture of surrounding craze fibril until void becomes crack.

Stress Whitening

It is the appearance of white regions in a thermoplastic when it is stressed. A stress-whitening zone may be a sign of the formation of many microcracks and fine crazes in the specimen [6]. Stress whitening occurs fairly late in the rupture stage, just prior to yielding [33]. The whitish surface appearance is a result of the mismatch in refractive index in the area of stress concentration.

1.8.2 Shear Yielding

Yielding is a mechanism, in which a thin layer of polymer deforms in shear at constant volume. It is characterized by regions of sheared polymer oriented approximately at 45°C to the tensile or compression stress. Unlike crazing, shear flow is essentially a process continuous in space, i.e., one that may spread through a much greater volume fraction [25]. Shear yielding involves shear band formation, where the chains slip, becoming highly oriented at approximately 45° to the stress direction. Formation of shear bands involves a limited slip or yielding of one portion of the polymer relative to another, leaving a highly oriented band of material connecting the two portions. Ideally shear band formation should precede crazing, forcing the crazes to propagate through the shear bands. This consumes extra energy, providing an additional toughening mechanism .

Shear yielding in the matrix phase plays a major role in the rubber toughening mechanisms. Shear bands (in Figure 1.13) are the barrier to propagations of craze, which delays material failure. Since molecular orientation in shear band is perpendicular to the crack growth direction, shear band is able to limit the craze growth.

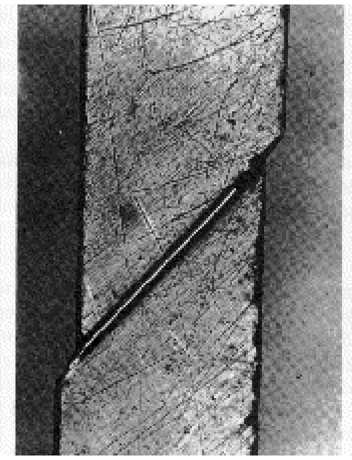


Figure 1.13: Shear banding deformation [35].

Another shear-type response (e.g., cold drawing in Figure 1.14) predominates in rubber-modified PVC. Cold drawing manifests itself as a necking of the polymer during stretching. Necking starts at a localized point in the specimen, and the cross section becomes much less than that of the remaining portion of the specimen while the force remains nearly constant during stretching. Cold-drawing after the yield point means that there must be a strain-hardening process; otherwise, the material would break without drawing at the reduced cross section where necking took place. The strain hardening generally results from molecular orientation, which increases the modulus and tensile strength [36].

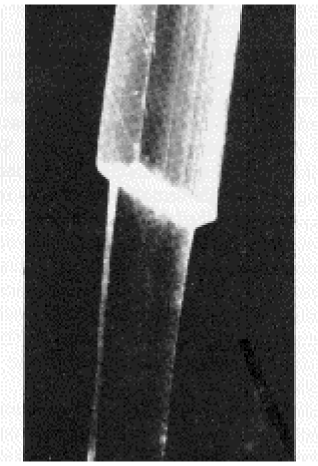


Figure 1.14: Necking in cold drawing deformation [35].

1.8.3 Energy Absorption by Rubber Particles

Collyer [32] suggested that on stressing or during crack formation, the rubber particles will dissipate the bulk strain energy by the cavitation, which leads to reduction in the yield stress of the materials. With this reason, shear yielding is easily formed and enhanced by the void in the matrix caused by the cavitated rubber particles [32]. The fibrils of rubber particle will bridge across the fracture surface and inhibit crack growth. The total fracture energy is the sum of energy to break the glassy matrix and to break the rubber particle [37].

The most common mechanism of toughening by a discrete rubbery phase is based on the ability of stress concentrations at the interface to induce a combination of crazing and shear yielding in the matrix. In this way, strain energy that could otherwise drive a macroscopic crack is dissipated throughout a large volume of material; also in some cases, shear banding may hinder the development of cracks. Cavitation at the interface, as in a polyethylene/PVC blend and in rubber-toughened epoxies, or within the rubber particles, as in MBS (Methymethacrylate-Butadiene-Styrene)-toughened PVC, provides another mode of energy dissipation. In the latter, the rubber effectively shifts the ductile-brittle transition for notched PVC to below room temperature [6].

For example, most of the creep in a 95/5 mass ratio of PVC/ABS blend involves changes in extension (due to shear) rather than changes in volume (due to cavitation during crazing of the matrix). With this blend, only about 10% of the creep was associated with crazing, in comparison with 95% for high-impact polystyrene tested under similar loads. It was suggested that shear bands generated in the PVC could control the growth of any crazes that might develop. Interestingly, multiple crazes around rubber particles have been observed in deformed but broken rubber-modified PVC, but apparently not often in fractured PVC blends. The stress whitening observed in highly deformed PVC blends must therefore be attributed to another cause such as mismatches in refractive index between the matrix and rubber that could arise due to drawing of the PVC or cavitation in the rubber .

The degree of toughening depends on the concentration of the rubbery phase, other parameters being equivalent. Normally, a minimum proportion of modifier is needed to achieve an increased impact strength. Although most reports are restricted to concentrations of modifier < 50 wt%, results of a few studies over the whole concentration range from 0 to 100 wt% of PVC provide excellent examples of synergism in blends. In such cases, peaks are observed in impact strength at an intermediate concentration; the corresponding blend is tougher than either constituent (Figure 1.15). Similar behavior has been reported for a series of acrylic modifiers in PVC; with both ABS and acrylic modifiers, the position of the curves depends on the grade, but the shape is similar. As modifier is added to the notch-sensitive PVC, the yield stress is lowered with respect to the fracture stress, and the impact strength rises to very high values in the case of a ductile polymer such as PVC. However, beyond a certain modifier content, the role of the PVC is progressively diminished as the composition approaches that of the rubber, which is inherently not as tough as PVC at its best. Thus, there is competition between strengthening of the rubber by PVC and weakening of the blend at high concentrations of rubber (which probably corresponds to a continuous rubber phase).

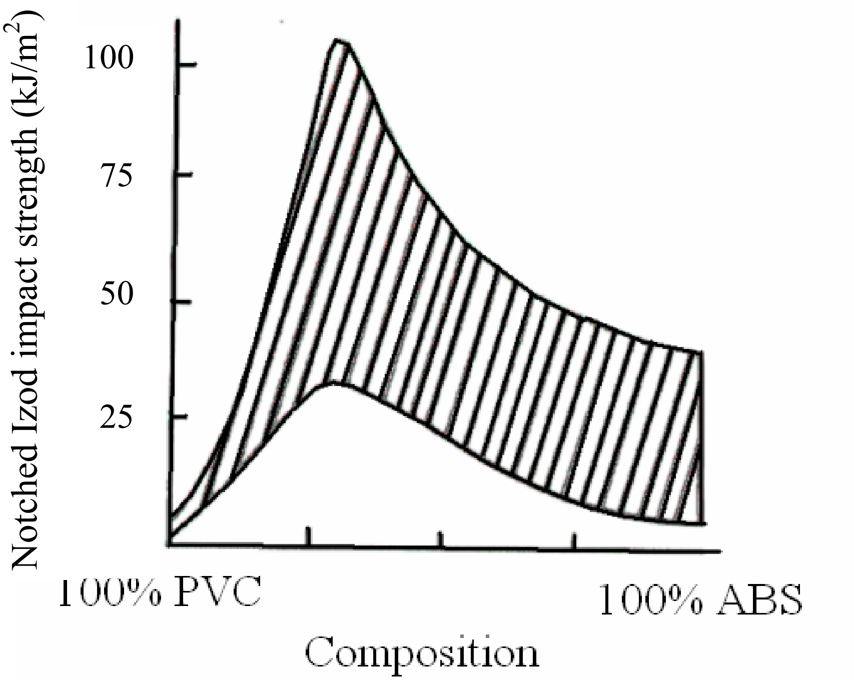


Figure 1.15: The range of synergism on impact strength of PVC/ABS blends [6].

2. Literature reviews

Chonsaranon [38] studied PVC/wood composites. It was found that the mechanical properties of the composites, including impact strength, decreased with increasing woodflour content as shown in Figure 2.1. This was possibly due to its hydrophilic character which resulted in poor stress transfer or poor interaction between the matrix and the filler and, thus, leading to the unsatisfactory properties of the final products [38].

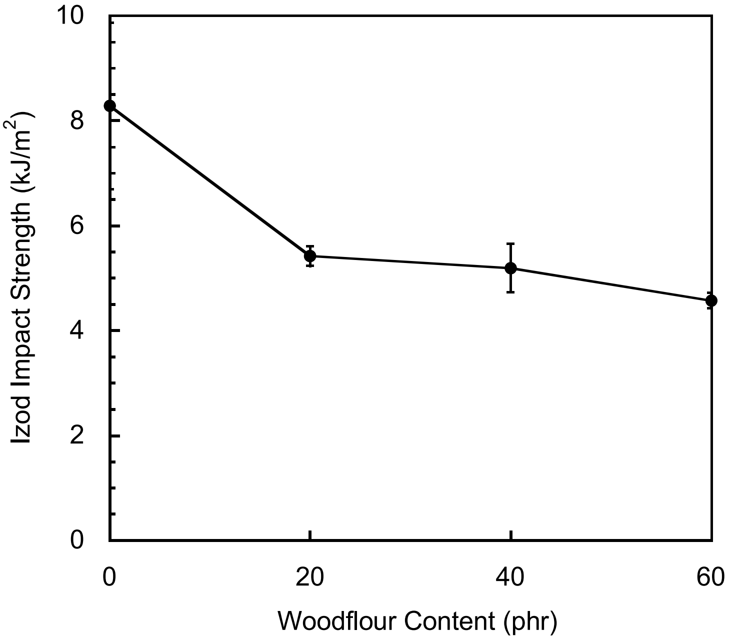


Figure 2.1: Impact strength of PVC wood composites at various woodflour contents [38].

Sombatsompop and Chaochanchaikul [39] studied the effect of woodflour content on rheological and structural changes and thermo-mechanical properties including impact property of PVC/wood composites. The untreated woodflour was used as filler. They also found the decrease in mechanical properties. The results in Figure 2.2 revealed that the composites having woodflour higher than 16.7 wt% showed a benefit of cost savings but the mechanical properties, including impact strength of the PVC/wood composites, considerably decreased with the increase of woodflour content. The decreases in the mechanical properties of PVC with woodflour were explained in association with the presence of moisture, interfacial defects between fiber and polymer, and fiber dispersions in the PVC matrix [39].

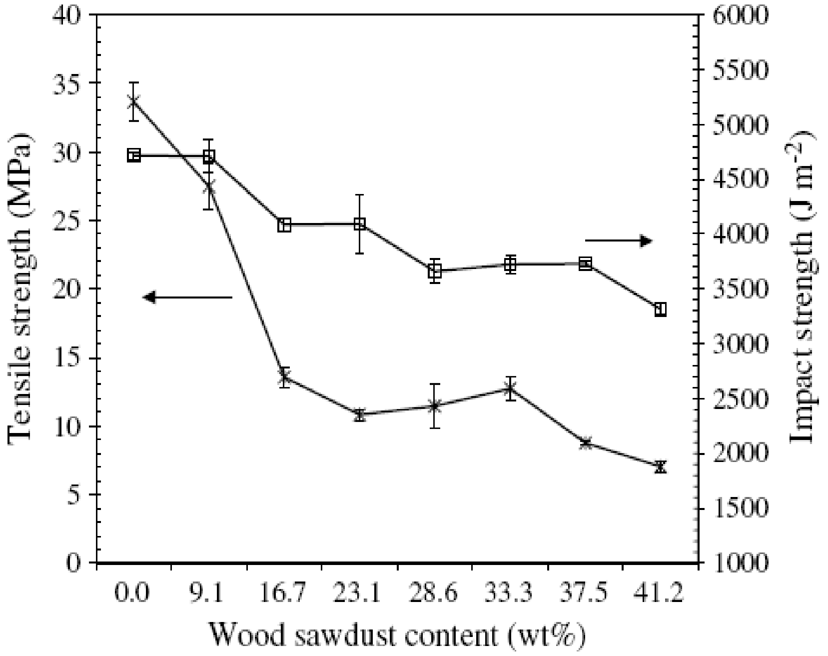


Figure 2.2: Tensile and impact strength as a function of woodflour content [39].

There are several methods to modify PVC/wood composite to improve impact strength and other mechanical properties such as treating fiber with other chemicals, reinforcing with other fibers to obtain hybrid wood composites, impregnation of monomer to penetrate into pore of wood fiber , and using rubber containing modifiers.

Sombatsompop and Chaochanchaikul [40] also studied PVC/wood composites with various types and concentrations of silane coupling agents. Three types of silane were used in that paper which are

- N-2(aminoethyl)3-aminopropylmethyl dimethoxysilane (KBM602)
- N-2(aminoethyl)3-aminopropyl trimethoxysilane (KBM603)
- N-2(aminoethyl)3-aminopropyl triethoxysilane (KBE603)

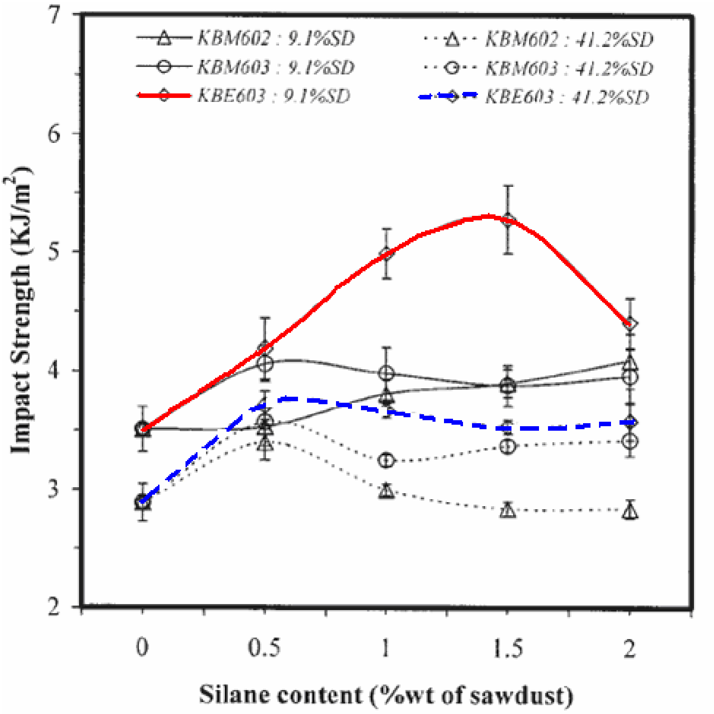


Figure 2.3: Effect of silane coupling agent on impact strength of PVC/wood composites: (—) 9.1 wt% and (- - -) 41.2 wt% of woodflour content [40].

Figure 2.3 showed that the impact strength of PVC/untreated-woodflour composites decreased with the increase of woodflour content. The silane coupling agents influenced the impact strength of the composites with low woodflour content much more than those with high woodflour content.

An incorporation of coupling agent type KBE603 could improve the impact strength maximum about 1.8 kJ/m^2 for composites with low woodflour content at 9.1 wt% and 0.8 kJ/m^2 for composites with high woodflour content at 41.2 wt%. the improving impact strength is preferable, however; the addition of silane content decreased the tensile strength and modulus significantly as shown in Figures 2.4 and 2.5.

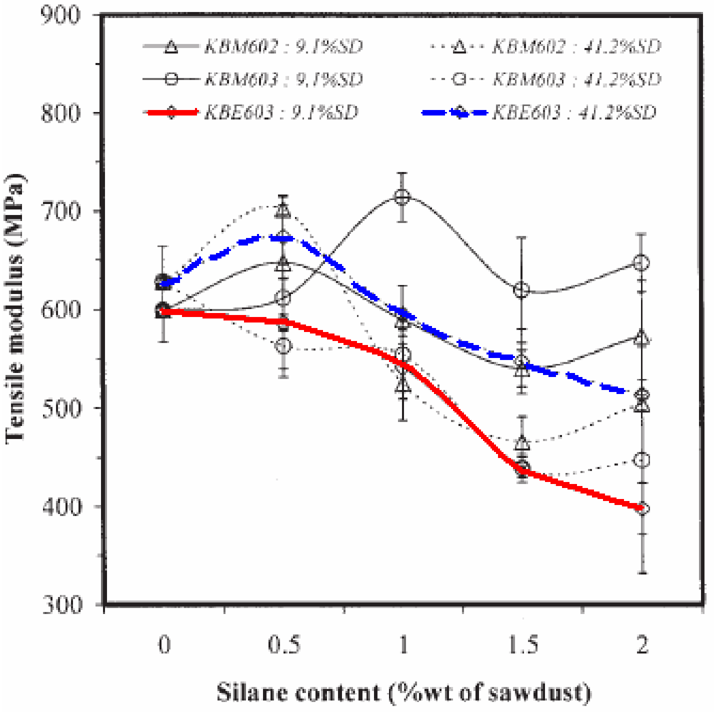


Figure 2.4: Effect of silane coupling agent on the tensile modulus of PVC/wood composites: (—) 9.1 wt% and (- - -) 41.2 wt% of woodflour content [40].

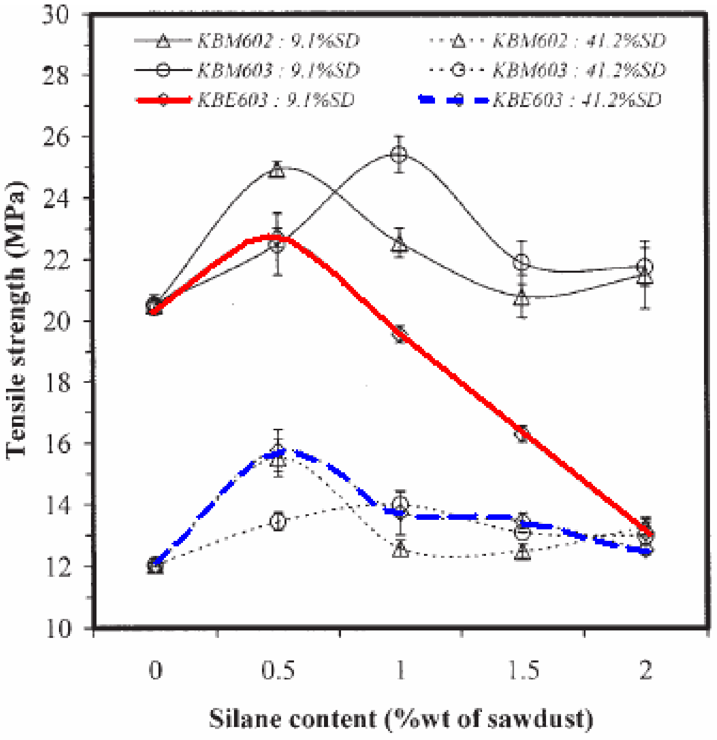


Figure 2.5: Effect of silane coupling agent on the tensile strength of PVC/wood composites:(—) 9.1 wt% and (- - -) 41.2 wt% of woodflour content [40].

Nowadays, WPC researches are focused on the composites at high woodflour loading to get the benefit of cost savings. It is found that rubber toughening is the most often used method of improving the impact resistance of polymers [9]. The use of impact modifier, containing an elastomer, is another solution in toughening of materials. It is usually blended with rigid matrix polymer.

Mengeloglu, Matuana and King [9] examined the effects of impact modifier types and addition levels on the mechanical properties of rigid PVC/wood-fiber composites. Three types of impact modifiers were used, CPE (Chlorinated polyethylene), MBS (Methymethacrylate-Butadiene-Styrene), and ACR (Acrylic impact modifier). The content of wood fiber was constant for all composites at 50 phr [9].

In Figure 2.6, it was found that the impact strengths of PVC/wood composite at 16.7 wt% content of impact modifier were improved from 2 kJ/m^2 to 4 kJ/m^2 or an increase of 2 kJ/m^2 increased for CPE and by 5 kJ/m^2 when modified with MBS or ACR. The use of impact modifier was found to effectively improve the impact strength of wood composites [9].

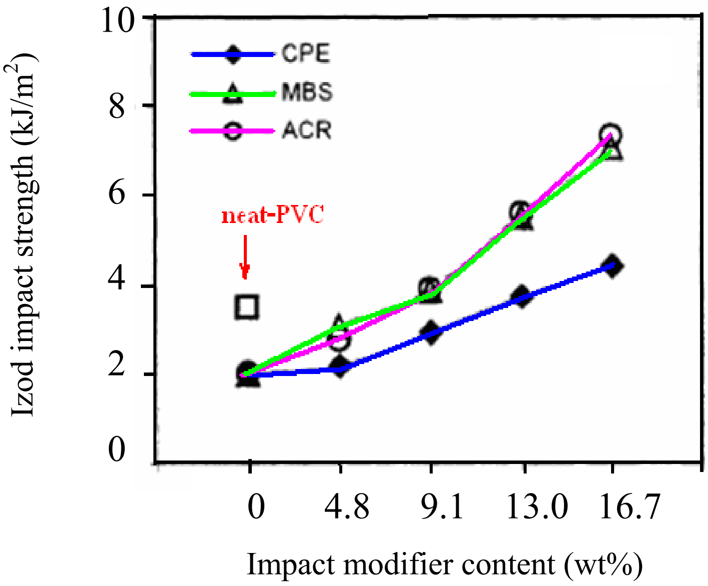


Figure 2.6: Effects of various impact modifiers on impact strength of PVC/wood composites at 33.3 % by weight of woodflour content [9].

When the glass transition temperatures of all impact modifiers were considered, the glass transition temperatures were -70°C, -16°C, and -60°C to -45°C for MBS, CPE, and ACR, respectively [19]. Consequently, the thermal stability of PVC wood composites based on these impact modifiers will be sacrificed and will significantly limited their use especially in the tropical region such as Thailand. To obtain both impact property enhancement as well as good thermal stability, high glass transition temperature impact modifiers including ABS (T_g = 100°C) was used in this work. ABS is also one of the impact modifier used in a variety of resins with PVC. PVC/ABS blend provides the inherent flame retardance with stiffness of PVC and thermal stability, impact strength and processability of ABS. The commercial grade of PVC/ABS blends are available such as Boltaron 6500 by Boltaron Performance Products or Royalstat R63 and Royalex by Spartech Plastics [27].

Jin *et al*. [41] had studied the effect of AN (Acrylonitrile) content in SAN (copolymer of styrene-acrylonitrile) on impact strength, compatibility and morphology of PVC/ABS blends. When some amount of matrix SAN35 (SAN contain 35 wt% of acrylonitrile) was replaced by SAN25 (SAN contain 25 wt% of acrylonitrile) in a PVC/ABS blend at a mass ratio of 50/50, about a twofold increase of impact strength was observed. This supported that the mixed phase of SAN and PVC at the interface was thickened. This attributed to the partial miscibility of these polymer system. The use of SAN25 can alleviate the difference in the intermolecular interactions of SAN35 and PVC, because the solubility parameter value of SAN25 lies between those of SAN35 and PVC.

Sharma, Anand, and Kulshreshtha [42] studied the addition of ABS between 10 to 50% by weight into PVC/ABS blend and found that ABS could effectively improve the impact strength of the blend. The greatest enhancement occurred at 50% by weight of ABS content as shown in Figure 2.7. Good properties of these systems originated from the miscibility between PVC and SAN-part of ABS.

At low concentrations of ABS, a small number of rubber particles (i.e., the butadiene particles in ABS) is insufficient to significantly improve the impact strength. The increase of ABS content up to 50 wt% increased impact strength. The maximum impact strength obtained at the optimum blend composition is considerably higher than that of neat ABS itself or the synergism on impact strength occurred [42]. Since the particle size of the dispersed polybutadiene phase of ABS is unlikely to change with blend composition it is evident that there exists a critical volume fraction of rubber phase necessary for the maximum improvement in impact strength. When this critical concentration of rubber (or ABS) is exceeded, impact strength drops. The synergistic characteristic in impact properties observed in PVC/ABS blend thus makes this system highly attractive for several applications. In this work, it was investigated as a potential matrix for making wood composites with improved impact properties which is one crucial requirement in the industry.

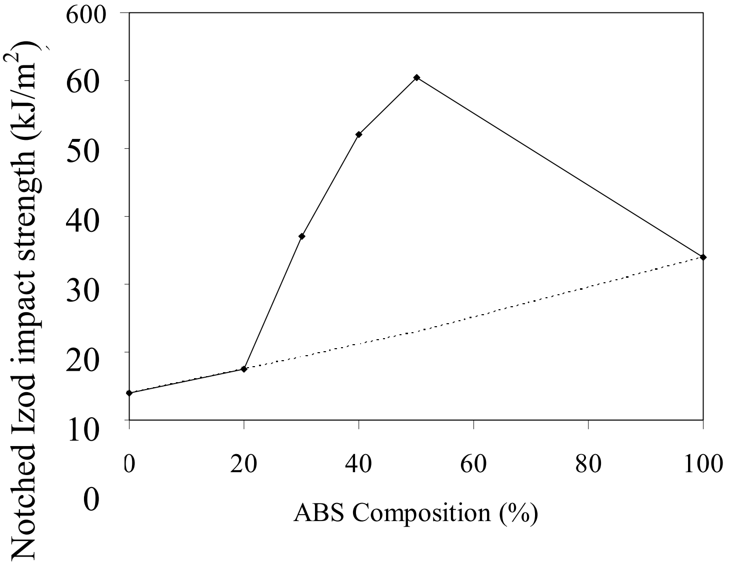


Figure 2.7: PVC/ABS blends showed synergism on impact strength [25].

Sharma et al. [42] discussed about the development and nature of property relationships generated by blending a low cost homopolymer (PVC) with ABS terpolymer. The blend properties are strongly influenced by the phase behaviour of the constituents which is due to interactions among them. PVC/ABS blends are microheterogeneous: they have a rigid matrix with soft dispersed phase but are mechanically compatible. Because of this partial compatibility, additive responses are observed (as a function of blend ratio) in tensile strength and modulus, flexural strength and modulus, and viscosities. The mutual interaction also accounts for positive deviations of experimental specific gravities from empirically calculated ones, using the values for PVC & ABS alone. The pay-off for blending comes from “synergistic” improvements in the impact strength of PVC/ABS blends, which undoubtedly comes from the presence of discrete elastomeric phase. The synergism of the PVC/ABS blend system may provide the enhancement on the impact strength of PVC wood by using PVC/ABS blend as a wood composite matrix. PVC/ABS blends are attractive not only due to their high impact but offer built-in flame retardance, moderate cost, good processability, high gloss, etc.

3. Objectives of this research

The overall objective of this cooperative research aimed to generate the technical knowledge and formulations for producing the PVC wood composites as an alternative for natural wood with appropriate physical, mechanical and thermal properties by combining PVC resin produced by Vinythai PCL and woodflour available locally. ABS, one of the styrenic-based copolymer, is added in order to improve the impact properties of PVC wood composites without the sacrifice of thermal properties of the PVC matrix. The main objectives are:

1. To develop high impact PVC-based wood substituted composites by using styrenic copolymers as impact modifiers.
2. To examine the effects of type and content of ABS on the other essential properties of both PVC/ABS blends as wood composite matrices.
3. To explore the effects of woodflour content on the mechanical, thermal and physical properties of the resulting PVC/ABS wood composites.

4. Scope of the 1st year research

1. Studying the material preparations for PVC dryblend and woodflour (*Xylia xylocarpa*).
2. Treatment of woodflour, i.e. drying, grinding, sieving etc.
3. Processing PVC/ABS blends with 3 types of ABS, namely SP100, SP200 and SR101 at a mass ratio of 50/50 by two-roll mills at the temperatures of 150, 160, 170, 180°C.
4. Evaluating the optimal processing condition and type of ABS that provide the highest impact strength to PVC/ABS blends.
5. Preparing PVC/ABS blends at various contents of ABS ranging from 0, 10, 20, 30, 40 and 50% by weight by two-roll mills.
6. Investigating the mechanical, thermal, and physical properties of the PVC/ABS blends on following properties: mechanical properties (tensile, flexural and impact strengths), thermal properties (glass transition temperature (T_g), heat distortion temperature (HDT), and vicat softening temperature), and physical properties (density, moisture and water absorption, melt rheology). Moreover, weatherability properties were also observed such as color change measurement and surface characterization by optical microscope and SEM.

7. Preparing PVC/ABS woodflour composites at contents of 0, 10, 20, 30, 40 and 50 wt% using woodflour with the average particle size of 280 µm.
8. Investigating the mechanical, thermal and physical properties of the PVC/ABS wood composites.
9. Evaluating the maximum loading of woodflour to be incorporated into PVC/ABS wood composites to be used as wood-substituted material.

5. Experimental

5.1 Materials

Polymeric matrix used in this study is polyvinyl chloride grade 258RB obtained from Vinythai Public Company Limited., Thailand. It had K value of 58 and bulk density-compaction of 0.56 kg/l. There were four additives used in this research, consisted of Kane Ace PA 20 (Processing aids), SAK-WP-08-NP (Heat stabilisers), Loxiol P1141 (Internal lubricants), and Calcium stearate (External lubricants). The additives, Kane Ace PA 20 (Processing aids), SAK-WP-08-NP (Heat stabilisers), and Calcium stearate (External lubricants) were provided by Vinythai Public Company Limited., Thailand whereas Loxiol P1141 (Internal lubricants) was supported by the Siam Chemical Solutions Co., Ltd. Thailand. The natural fiber used was redwood (*Xylia xylocarpa*) with an average particle size of 280 µm. It was a waste material from a saw-mill factory in Thailand. Three types of ABS (SP100, SP200, SR101) were used as impact modifiers and were supplied by IRPC Public Co., Ltd. Thailand.

5.2 Methodology

5.2.1 Matrix Preparation

5.2.1.1 Preparation of PVC Dryblend

PVC powder used in this work was blended in high speed mixer with the four additives to obtain an appropriate PVC compound for a wood composite matrix. The additives used in this research are Kane Ace PA 20 (processing aids) which was found to render better PVC melt homogeneity, improve its mechanical properties and speed up the PVC gelation times. SAK-WP-08-NP (heat stabilizers) was used to retard or prevent the dehydrochlorination reaction of PVC. Loxiol P1141 (internal lubricants) which lubricated between PVC molecules influenced directly on melt rheology, and finally, Calcium stearate (external lubricants) used to prevent the plastic melt to adhere to hot metal surfaces. All additives were blended following PVC formulation shown in Table 5.1.

Table 5.1: PVC dryblend formulation.

Ingredient	Composition (phr*)	Composition (wt%)
PVC (Siamvic 258 RB)	100.0	88.9
Stabilizer (SAK-WP-08-NP)	4.0	3.6
Processing aid (Kane Ace PA 20)	6.0	5.3
Internal lubricant (Loxiol P1141)	2.0	1.8
External lubricant (Calcium stearate)	0.5	0.4
Total	112.5	100.0

(* phr = part per hundred,parts of virgin PVC)

PVC powder was blended with the four additives in a high speed mixer model Plasmec Turbomixer (made in Italy) 100L with a cooler as seen in Figure 5.1. The apparatus consisted of two mixing tanks, operating with 2 steps of hot and cold mixers as following details:

Figure 5.1: High speed mixer: Plasmec Turbomixer 100 litres with a cooler for PVC dryblend prepartion.

Hot Mixing Step

- Adding PVC resin and solid additives into the mixer.
- Stirring at low speed (400 rpm), the temperature of the mixture increased due to frictional heat generation between PVC particles.

- Mixing at high speed (1200 rpm) until the temperature reached 70°C.
- Adding liquid additive i.e. Loxiol P1141, stirring until the temperature was 120°C.
- Discharging to a cold mixer.

Cold Mixing Step

- The hot dryblend was cooled by cooling water at temperature of 15-20°C.
- Mixing until the temperature of the dryblend decreased to 35°C.
- Discharging the dryblend to a container.

5.2.1.2 Preparation of PVC/ABS Blends

The obtained PVC compound was blended with ABS pellet by two-roll mills shown in Figure 5.2. The total amount of material loading on the two-roll mills should not exceed 300 g. Table 5.2 showed the amount of both PVC dryblend and ABS at various compositions of PVC/ABS blend ranging from 10-50 wt% of ABS. The PVC dryblend and ABS pellet were mixed by two-roll mills using 0.125 mm gap at various temperatures of 150, 160, 170 and 180°C for 6 minutes each. The obtained compound was then preheated for 3 minutes and compression-molded at temperature of 170°C and pressure of 150 bar for 4 minutes. The cooling time used was 4 minutes. The compression molded sheets were then cut into test pieces for further property characterizations.

Table 5.2: Amount of PVC and ABS for each blend formulation prepared by two-roll mills.

PVC/ABS blends (wt%)	PVC dryblend (g)	ABS (g)
10	270	30
20	240	60
30	210	90
40	180	120
50	150	150

Figure 5.2: Two-roll mills for PVC/ABS blends preparation (Lab Tech).

5.2.2 Composite Preparation

5.2.2.1 Preparation of Woodflour

Woodflour used in this research was redwood (*Xylia xylocarpa)*. The woodflour was cut by Fritsch 15 pulverisette cutting mill depicted in Figure 5.3 to reduce the particle size to 106-425 µm. The sieved woodflour was dried in an oven at 105°C for 24 hours before use. The data from sieve analysis was shown in Table 5.3.

Figure 5.3: Fritsch pulverisette 15 cutting mill with 4 fixed knives [43].

Table 5.3: Particle size distribution of woodflour used in this work.

Particle size (µm)	Content (wt%)
300-425	40-45
250-300	20-25
180-250	15-20
106-180	10-15
Balance pan	0-5

Weight average particle size of woodflour can be obtained by determining the midpoint of each class interval of particle size distribution and multiplying by each content as a class frequency and then dividing by total frequency. In this work, the average particle size was 280 µm.

5.2.2.2 Preparation of PVC/ABS/Wood Composites

The type and content of ABS, which its blend showed the greatest impact strength, was selected to blend with PVC and then used as a wood composite matrix. For PVC/ABS blend at a mass ratio of 50:50, the amount of PVC and ABS required for wood composite preparation at various woodflour contents is summarized in Table 5.4. The obtained mixtures were then mixed by two-roll mills using 0.3 mm gap at the same temperature that used to process the PVC/ABS matrix. The obtained compound was then preheated for 3 minutes and compression-molded at the temperature of 170°C and at the pressure of 150 bar for 4 minutes. The compression molded sheets were then cut into test pieces for further property characterizations.

Table 5.4: Amount of PVC dryblend and ABS required at various woodflour contents.

Woodflour content (wt%)	PVC dryblend (g)	ABS (g)	Woodflour (g)
10	135	135	30
20	120	120	60
30	105	105	90
40	90	90	120
50	75	75	150

5.3 Polymer Blends and Wood Composites Characterizations

5.3.1 Mechanical Property Characterizations

5.3.1.1 Tensile Property Measurement

Tensile properties were obtained by a universal testing machine (Instron Instrument, model 5567) according to ASTM D638. The test specimens were a dumbbell shape with a uniform thickness. They were tested using a crosshead speed of 5 mm/min. The tensile modulus defined as the ratio of stress to strain which was determined from the initial slope of the stress-strain curve whereas the tensile strength was the ultimate stress. Five specimens from each blend and composite were tested and the average values were reported.

5.3.1.2 Flexural Property Measurement

Flexural modulus and flexural strength of the composite specimens were measured by a universal testing machine (Instron Instrument, model 5567) according to ASTM D790]. Three-point bending test was carried out at room temperature at the crosshead speed of 1.2 mm/min with a support span of 48 mm. The dimension of the specimen was $12.7\times64\times3.2$ mm^3. Five specimens from each blend and composite were examined and the average values were reported.

5.3.1.3 Notched Izod Impact Property Measurement

An impact test is a high-speed fracture test that measures energy to break a specimen. The energy required to break the specimen is determined from the loss in kinetic energy of the pendulum weight. Izod impact strength of the specimens was obtained by an impact tester (Yasuda) according to ASTM D256. Notched Izod impact was a single point test from a swinging pendulum. The sample was clamped into the pendulum impact test fixture with the notched side facing the striking edge of the pendulum. The pendulum was released and allowed to strike through the specimen. ASTM impact energy was expressed in kJ/m^2. The test result was obtained from the average of 10 specimens. The dimension of the test specimen was $12.7\times60\times3.2\ mm^3$ while the depth under notch of the specimen was 10 mm.

5.3.2 Thermal Characterizations

5.3.2.1 Dynamic Mechanical Analysis (DMA)

Thermal characteristics of the blend and composite specimens were examined by a dynamic mechanical analyzer (NETZSCH, DMA242). The shape of the test specimen was rectangular with 50 mm in length, 10 mm in width, and 2 mm in thickness. The three point bending mode of deformation was used under a test temperature range from 30°C to 150°C with a heating rate of 2 K/min. The test amplitude and frequency were 30μm and 1Hz, respectively. The glass transition temperature was obtained both from the peak of the loss modulus and the loss tangent.

5.3.2.2 Differential Scanning Calorimetry (DSC)

DSC measurements were carried out with the TA instruments, model DSC 2910. The sample weight was approximately 7-8 mg. The temperature was equilibrated at 30°C and the samples were heated from 30 to 150°C with the heating rate of 10°C/min. Nitrogen purge gas flow rate was maintained to be 50 ml/min.

5.3.2.3 Vicat Softening Temperature

Vicat softening temperature was the temperature at which a flat-ended needle penetrates a specimen to the depth of 1 mm under a specific load. The temperature reflects a softening point to be expected when a material is used at elevated temperature. A test specimen was placed in a testing apparatus so that the penetrating needle rested on its surface at least 1 mm from the edge. A load of 50 N was applied to the specimen. The specimen was then lowered into a silicone oil bath at 30°C. The bath was heated at a rate of 50°C/h until the needle penetrated 1 mm following ASTM D1525 procedure. The temperature at which the needle had penetrated to a depth of 1 ± 0.01 mm was recorded as a vicat softening temperature.

5.3.2.4 Heat Distortion Temperature (HDT)

Heat distortion temperature was defined as the temperature at which a standard test bar deflected to a specified distance under a load applied at its center to give a maximum stress. It was used to determine short-term heat resistance. It distinguished between materials that were able to sustain light loads at high temperatures and those that lose their rigidity over a narrow temperature range. The specimen was placed under a deflection measuring device under 1 kg load. The specimen was then immersed in silicone oil with a mean of raising temperature at 120°C/h or 2 ± 0.2°C/min until it deflected 0.25 mm following ASTM D648. This temperature was recorded as the heat distortion temperature under flexural load of the test specimen.

5.3.3 Physical Properties

5.3.3.1 Density Measurement

The density of the woodflour-polymer composites was measured by a water displacement method described in ASTM D792. The dimension of the specimen was $20 \times 20 \times 4$ mm^3. All specimens were weighed both in air and in water. Then, the density was calculated from the following equation:

$$\rho = \left(\frac{A}{A - B} \right) \times \rho_0$$

where ρ is the density of the specimen (g/cm^3), A and B are weights of the specimen in air and in the auxiliary liquid (g) (de-mineralized water was used in this study), ρ_0 is the density of the auxiliary liquid at the given temperature (g/cm^3).

5.3.3.2 Water Absorption Measurement

Water absorption measurement was conducted following ASTM D570, using a specimen in the form of a disk 50.8 mm (2 in.) in diameter and 3.2 mm (1/8 in.) in thickness. Three specimens were conditioned in an oven at 50°C for 24h, cooled in a desiccator, and then weighed. The specimens were then immediately immersed in distilled water and were weighed periodically. Based on the initial mass of each specimen, the amount of water absorbed was calculated from the following equation:

$$WA(\%) = \left(\frac{M_e - M_o}{M_o} \right) \times 100$$

Where M_e and M_o are the mass of the specimen after and before immersion, respectively.

5.3.3.3 Melt Rheology

Rheological properties of each blend ratio were examined by a plastometer (Model R33, A.Macklow Smith Company Limited, UK) equipped with extrusion chamber comprises of a cylinder, a piston and a die. The sample to be tested was placed in a cylinder, and a piston. The cylinder was then placed in pockets of the soaking oven to be preheated up to the required test temperature. The cross sectional area of the cylinder was 3.226 cm^2 ($0.5''^2$). The sample weight was 12.7 g. The extrusion was performed at 190°C with a piston rate at 30 mm/min pass a 4 mm in diameter die.

5.3.4 Natural Weathering Test

5.3.4.1 Color Change Measurement

This test method originally resulted from the consolidation of separately published methods for instrumental evaluation of color differences. The total difference, ΔE_{ab}^*, between two colors each given in terms of lightness (L*) and chromaticity coordinate (a* and b*) is calculated following ASTM D 2244 by Ultrascan Pro (Hunter Lab, USA) which measures both reflected and transmitted color and meets CIE (International Commission on Illumination):

$$\Delta E_{ab}^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

The magnitude, ΔE_{ab}^*, gives no indication of the character of the difference since it does not indicate the relative quantity and direction of hue, saturation, and lightness differences. The direction of the color difference is described by the magnitude and algebraic signs of the component ΔL^*, Δa^* and Δb^*.

$$\Delta L^* = L_1^* - L_0^*, \Delta a^* = a_1^* - a_0^*, \Delta b^* = b_1^* - b_0^*$$

Where L_0^*, a_0^* and b_0^* refer to the initial values, and L_1^*, a_1^* and b_1^* refer to the final values of a specimen. The signs of the components ΔL^*, Δa^* and Δb^* have the following approximate meanings:

$+\Delta L^*$= lighter, $-\Delta L^*$ = darker
$+\Delta a^*$ = redder (less green), $-\Delta a^*$ = greener (less red)
$+\Delta b^*$ = yellow (less blue), $-\Delta b^*$ = bluer (less yellow)

5.3.4.2 Scanning Electron Microscope

Surface texture of weathering specimen and the interfacial interaction or the adhesion or between woodflour filler and polymer matrix were examined using SEM micrographs. The micrographs were obtained using SEM (Model JSM-5800LV, Jeol), at an acceleration voltage of 15 kV. The surface of each specimen was coated with thin gold film, of which the thickness was between 10 to 20 nm, prior to obtaining the micrograph.

6. Results and discussion

To study the effect of ABS as impact modifier in PVC/wood composites, the characteristics of the PVC/ABS blend as a polymer composite matrix were firstly investigated by varying ABS content and the effects of type of ABS on the properties of the blends were also examined. Furthermore, the effects of woodflour contents on the some essential properties of PVC/ABS/wood composites were determined.

6.1 Effects of Type of ABS on Properties of PVC/ABS Blends

6.1.1 Effects of Type of ABS and Processing Temperature on Impact Properties of PVC/ABS Blends

In Figure 6.1, impact properties of PVC/ABS blends from three different types of ABS namely SP100, SP200, and SR101, at a fixed mass ratio of 50/50, and various processing temperatures from 150^{o}C to 180°C were evaluated. From the figure, we can see that SP100 and SP200 showed a similar effect on impact properties, i.e. they provided the highest impact strength of PVC/ABS blends at processing temperature of about 160°C. The highest impact strength of PVC/SR101, however, was observed at 150°C. Another interesting feature in Figure 6.1 is that the impact strength of the blends does not follow the rule of mixture. According to the experimental results, the impact strength of the PVC was determined to be approximately 6-7 kJ/m^2 whereas that of ABS was around 35-45 kJ/m^2. The impact properties of the blends greatly increased compared to that of PVC. The synergistic behavior in impact strength i.e. the impact strength was higher than that of each individual polymer, was observed with an incorporation of those three types of ABS in the PVC. From these results, the PVC/ABS blends using ABS(SP200) provided the impact strength value as high as 65 kJ/m^2 and the obtained value was about ten times greater than the impact strength of the neat PVC. In addition, SP100 was also found to provide similar enhancement on impact strength as that of SP200 because of the similarity in their impact property.

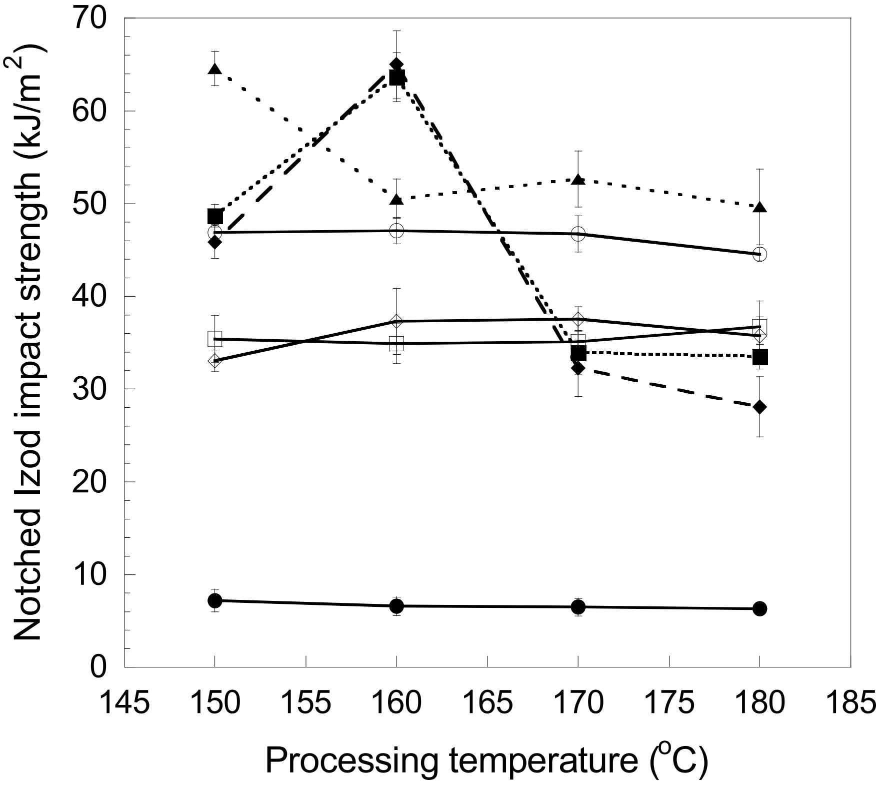


Figure 6.1: Effects of ABS type and processing temperature under two-roll mills on notched Izod impact strength of PVC/ABS blends at a fixed mass ratio of 50/50: (●) PVC (■) PVC/SP100 (◆) PVC/SP200 (▲) PVC/SR101 (○) SP100 (□) SP200 (◇) SR101.

6.1.2 Effects of Type of ABS on Glass Transition Temperature of PVC/ABS Blends

Useful information about phase equilibrium of multiphase polymer systems can be obtained from thermal properties, such as glass transition temperature (T_g). DSC thermograms of PVC, ABS and PVC/ABS blends at a fixed mass ratio of 50/50 using various type of ABS are plotted in Figure 6.2. The glass transition temperatures were determined from the midpoint of the step change of DSC thermograms and the values were summarized in Table 6.1. T_g of PVC was determined to be 81°C and those of ABS were found to be 103°C, 102°C, 105°C for SP100, SP200, and SR101, respectively. For PVC/ABS blends, the addition of ABS into PVC at a fixed content of 50 wt% namely PVC/SP100, PVC/SP200, and PVC/SR101 showed two distinct T_g's. The lower T_g was attributed to that of PVC-rich domain (T_{g1}) whereas the higher

T_g was that of ABS-rich domain (T_{g2}). All T_g's of the PVC domain in the blends were determined to be 83°C which was approximately 2°C higher than that of the neat PVC while T_g's of ABS domain in the blends showed the same values as those of the neat ABS i.e. 103°C, 102°C, 105°C for PVC/SP100, PVC/SP200, and PVC/SR101, respectively.

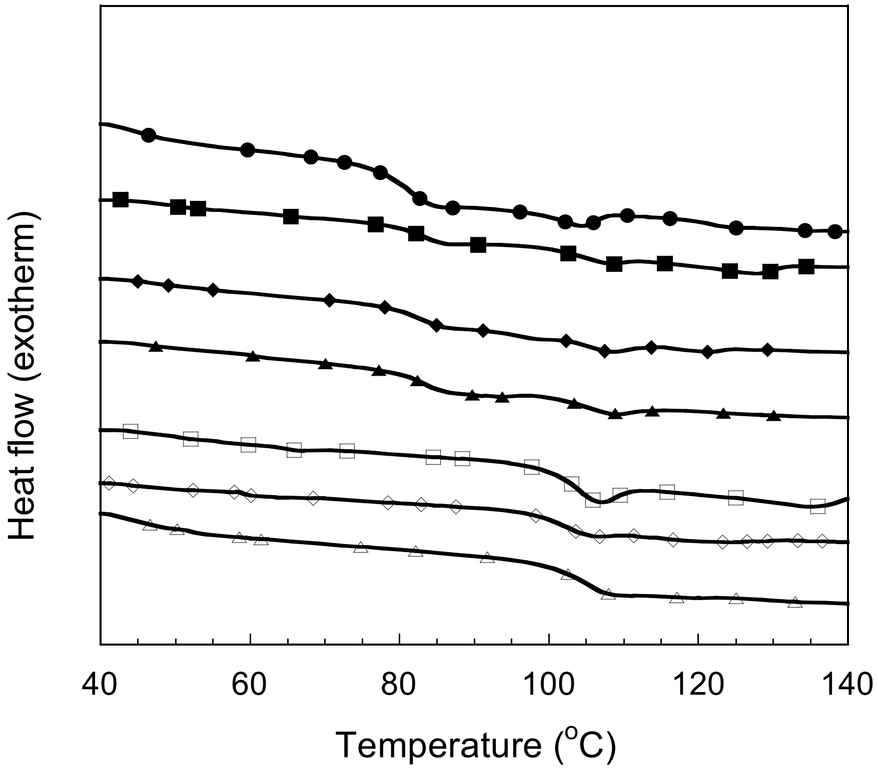


Figure 6.2: DSC thermograms of PVC/ABS blends: (●) PVC (■) PVC/SP100 (◆) PVC/SP200 (▲) PVC/SR101 (○) SP100 (□) SP200 (◇) SR101.

It can be seen that T_g of the PVC domain in the blend was slightly affected by the presence of the ABS signifying the partially miscible nature of these blends. A similar behavior of the same blend was also observed by Bensemra *et al.* [44]. The slight enhancement in T_g, implied the diffusion of a higher T_g component, ABS, into the PVC phase as a consequence of their similar polarity and partially miscible nature of these blend pairs [44, 45]. Additionally, this behavior might imply that the presence of ABS in the PVC might obstruct the motion of molecular chains of the PVC, possibly due to impediment of SAN from ABS [44, 45]. In terms of various types of ABS used, the type of ABS was observed to show similar effect on the shifting of the T_g of PVC domain in the blends.

Table 6.1 Glass transition temperatures obtained from the midpoint of step change in DSC thermogram of PVC, ABS and PVC/ABS blends at a fixed mass ratio of 50/50.

Samples	**T_{g1} (°C)**	**T_{g2} (°C)**
PVC	81	-
PVC/SP100	83	103
PVC/SP200	83	102
PVC/SR101	83	105
SP100	-	103
SP200	-	102
SR101	-	105

6.1.3 Effects of Type of ABS on Thermomechanical Properties of PVC/ABS Blends

The glass transition temperature (T_g) of the neat PVC, the neat ABS and the blends of PVC with various types of ABS can be also determined by the loss modulus curve from dynamic mechanical analysis (DMA) as shown in Figure 6.3. The glass transition temperatures were determined from the peak of loss modulus in the DMA thermograms. T_g of the PVC was determined to be 83°C and T_g's of ABS were found to be 107°C, 106°C, 108°C for SP100, SP200, and SR101, respectively. For the PVC/ABS blends, the addition of ABS into PVC at a fixed mass ratio of 50 wt% of ABS exhibited a large peak of loss modulus between the T_g's of PVC and ABS. The peak was resulted from the merging of the peak of loss modulus of the PVC and the ABS (SP100, SP200, SR101). This important characteristic was also attributed to the partial miscibility of these blends. All PVC/ABS blends at 50/50 mass ratio showed maximum loss modulus at about the same temperature, which was determined to be 93^{o}C.

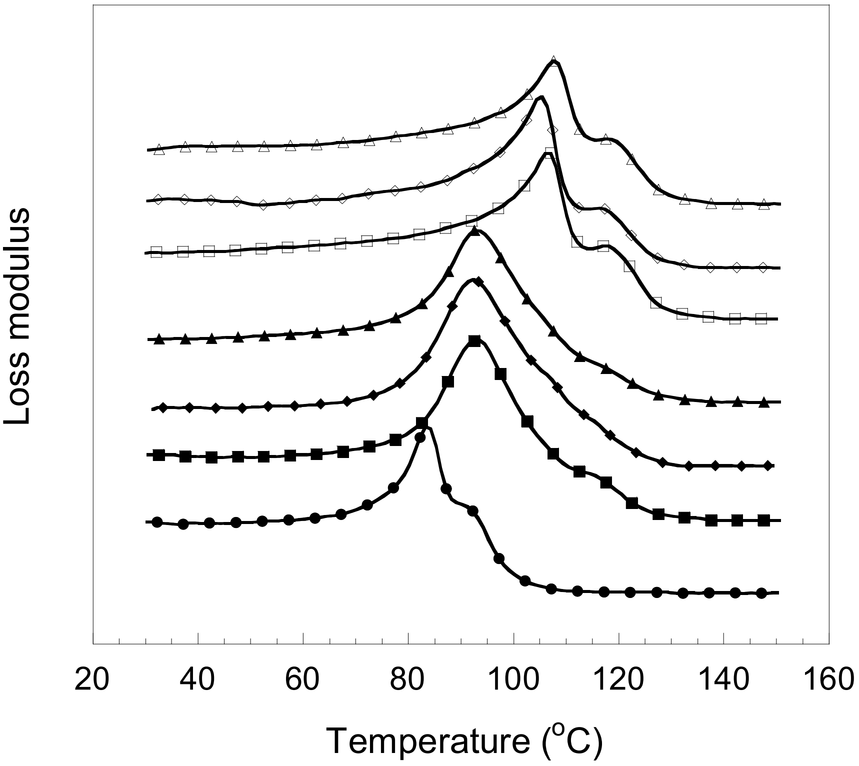


Figure 6.3: Loss moduli of PVC, ABS and PVC/ABS blends at a fixed mass ratio of 50/50: (●) PVC (■) PVC/SP100 (◆) PVC/SP200 (▲) PVC/SR101 (○) SP100 (□) SP200 (◇) SR101.

The glass transition temperatures could also be determined precisely from the peak of loss tangent as shown in Figure 6.4. The obtained T_g values were also summarized in Table 6.2. T_g of the PVC was determined to be 94°C and T_g's of ABS were found to be 122°C, 120°C, 122°C for SP100, SP200, and SR101, respectively. For the blends, T_g's of PVC domain in the blend (T_{g1}) were found to be 97°C, 96°C and 97°C for PVC/SP100, PVC/SP200 and PVC/SR101, respectively while T_g's of three types of ABS domains in the blends (T_{g2}) exhibited the values of 119°C, 116°C and 120°C for PVC/SP100, PVC/SP200 and PVC/SR101, respectively. In summary, the glass transition temperatures of PVC and ABS domains in the blends were found to slightly shift by 2-4°C. Each type of the ABS showed a similar shift of the T_g's of the PVC/ABS blends towards each other. This important characteristic was attributed to the partially miscible nature of these blend systems mentioned in the previous section.

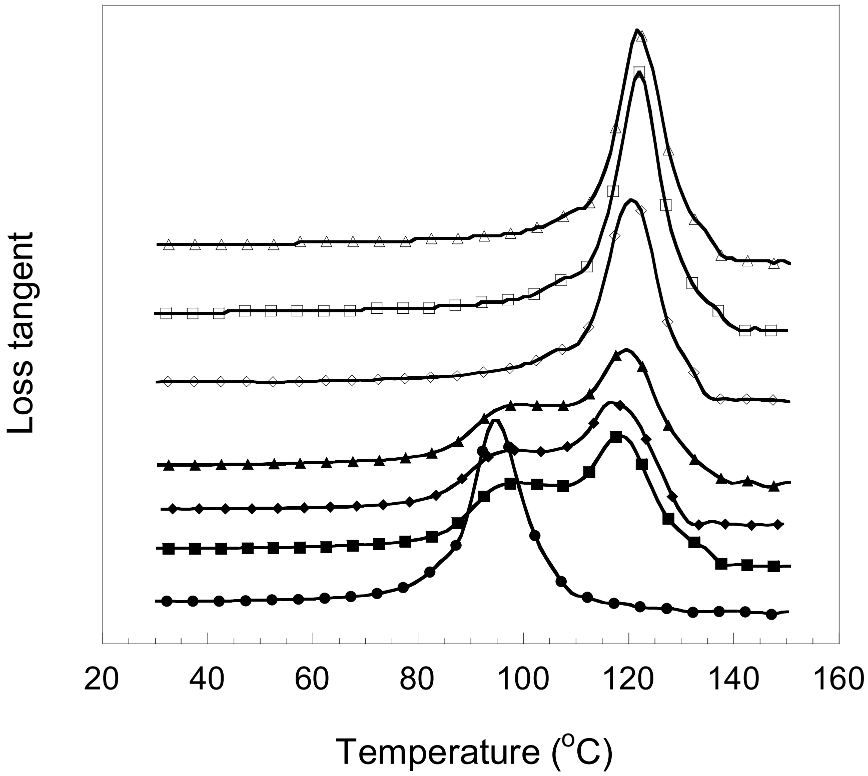


Figure 6.4: Loss tangents of PVC, ABS and PVC/ABS blends at a fixed mass ratio of 50/50: (●) PVC (■) PVC/SP100 (◆) PVC/SP200 (▲) PVC/SR101 (○) SP100 (□) SP200 (◇) SR101.

Table 6.2: Glass transition temperatures of PVC, ABS and PVC/ABS blends at a fixed mass ratio of 50/50 from loss tangent curves.

Samples	**T_{g1} (°C)**	**T_{g2} (°C)**
PVC	94	-
PVC/SP100	97	119
PVC/SP200	96	116
PVC/SR101	97	120
SP100	-	122
SP200	-	120
SR101	-	122

Besides the miscibility determination of polymer blends, DMA can also provide information on rigidity of the specimens. According to Figure 6.5, storage modulus at room temperature of PVC was approximately 3.0 GPa while the storage moduli for ABS coded as SP100, SP200, and SR101, were determined to be 2.38, 2.40 and 2.12 GPa, respectively. The higher storage modulus at room temperature of the neat PVC compared to those of the ABS was due to the fact that the PVC was more rigid than the ABS which contains significant amount of polybutadiene rubber. Furthermore, the change in slope of the modulus curve indicated thermal instability of the material. From the thermograms, PVC lost its rigidity at elevated temperature more readily than ABS. An incorporation of the ABS into PVC was found to improve thermal stability of the PVC. The room temperature storage modulus values of the blends were found to be 2.25, 2.48 and 2.23 GPa for PVC/SP100, PVC/SP200, and PVC/SR101, respectively. In summary, the type of ABS showed negligible effect on glass transition temperature as well as on storage modulus of the resulting PVC/ABS blends.

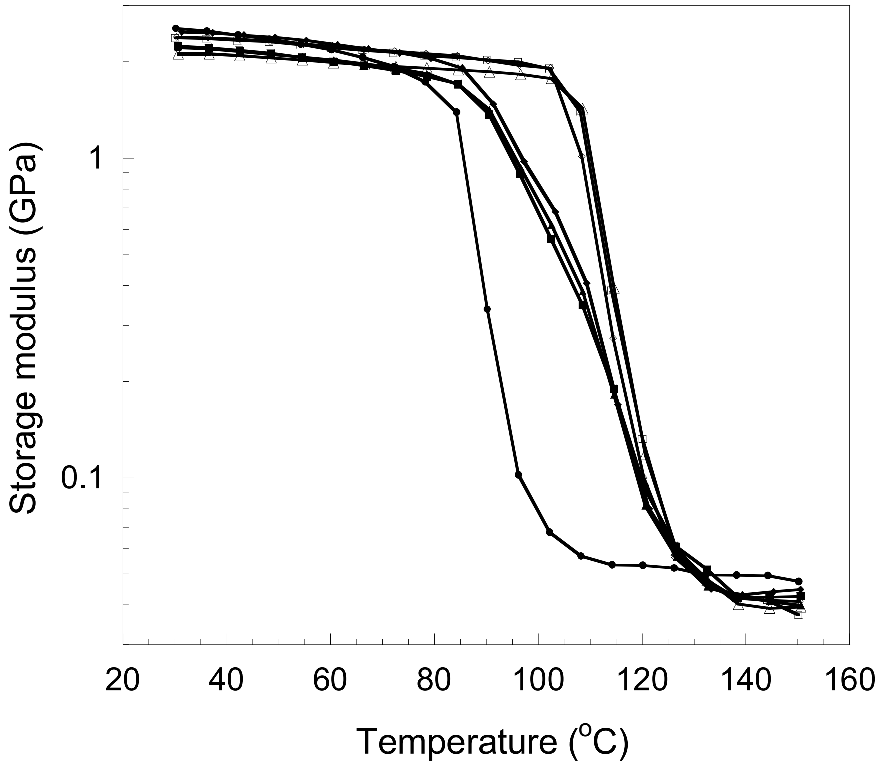


Figure 6.5: Storage moduli of PVC, ABS and PVC/ABS blends at a fixed mass ratio of 50/50: (●) PVC (■) PVC/SP100 (◆) PVC/SP200 (▲) PVC/SR101 (○) SP100 (□) SP200 (◇) SR101.

6.2 Effects of ABS Content on the Properties of PVC/ABS Blends

6.2.1 Effects of ABS Content on Mechanical Properties of PVC/ABS Blends

6.2.1.1 Tensile Properties

Since ABS(SP200) rendered the highest impact strength to the PVC/ABS blends compared to SP100 and SR101, this type of ABS was further used to evaluate the effect of its content on properties of the obtained PVC/ABS blends. Tensile properties of PVC/ABS blends were determined by a universal testing machine following the ASTM D638 of specimen Type I. Tensile properties of the PVC/ABS blends at 0 wt% to 50 wt% of the ABS were examined. The tensile properties of PVC/ABS(SP200) at various ABS(SP200) contents are shown in Figure 6.6 and the values are tabulated in Table 6.3. The tensile strength of the neat PVC was determined to be 51 MPa and that of ABS(SP200) was 36 MPa while the tensile strength of the PVC/ABS(SP200) blends was found to decrease with increasing ABS(SP200) content. From Table 6.3, the PVC/ABS(SP200) at a mass ratio 90/10 (10 wt% of ABS content) showed the tensile strength of 49 MPa and decreased to 43 MPa with the increase of ABS content to 50 wt%.

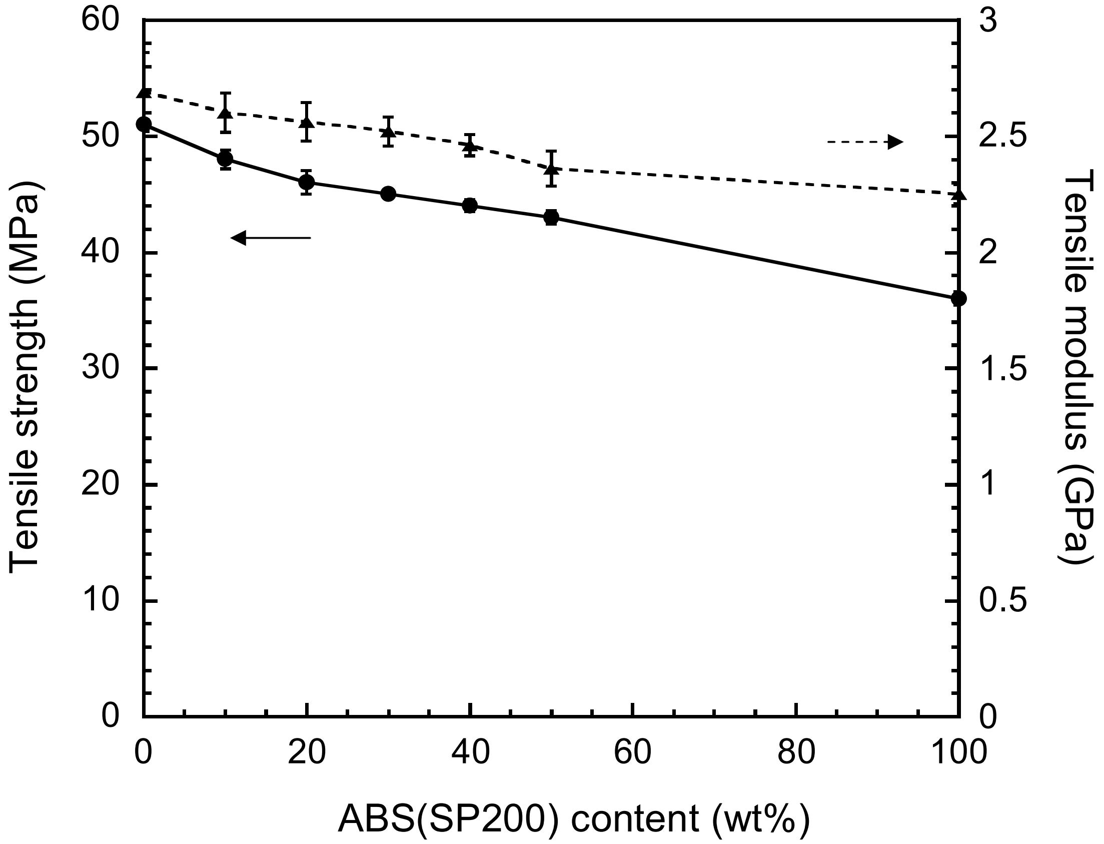


Figure 6.6: Tensile properties of PVC/ABS(SP200) blends at various mass blending ratios**:** (●) tensile strength (▲) tensile modulus.

Table 6.3: Tensile properties of PVC/ABS(SP200) blends at various mass ratios.

Samples	**Tensile modulus (GPa)**	**Tensile strength (MPa)**	**Elongation at break (%)**	**Energy at break (J)**
PVC	2.69 ± 0.17	51 ± 0.4	87.0 ± 46.7	141 ± 80
PVC/SP200 90/10	2.60 ± 0.08	49 ± 0.8	48.9 ± 30.8	74 ± 53
PVC/SP200 80/20	2.56 ± 0.08	46 ± 1.0	29.1 ± 23.4	60 ± 33
PVC/SP200 70/30	2.52 ± 0.06	45 ± 0.3	31.8 ± 21.5	49 ± 32
PVC/SP200 60/40	2.46 ± 0.05	44 ± 0.5	17.0 ± 16.3	32 ± 26
PVC/SP200 50/50	2.36 ± 0.08	43 ± 0.6	18.9 ± 7.2	28 ± 10
SP200	2.25 ± 0.04	36 ± 0.6	4.6 ± 3.8	6 ± 5

Tensile modulus of material was defined as initial slope of the stress-strain curve. From Table 6.3, tensile moduli of PVC and ABS were calculated to be 2.69 GPa and 2.25 GPa, respectively, suggesting that the PVC had slightly higher rigidity than the ABS. Tensile moduli of the PVC/ABS blends were expectedly found to increase with increasing PVC contents. On the other hand, the elongation at break of the blends tended to decrease with increasing ABS content. In Figure 6.7, the tensile elongation of the ABS(SP200) was clearly lower than that of PVC. Additionally stress whitening was observed in all deformed samples. This phenomenon is associated with the formation of many micro-cracking in the specimens. The whitening zone was resulted from the mismatch in refractive index in the area of stress concentration. The higher the PVC fraction, the greater the stress whitening phenomenon was observed in the specimens. The area under the tensile stress-strain curve was related to energy required to break the specimen. In Table 6.3, PVC was found to require the highest energy to break whereas the PVC/ABS blends tended to absorb more energy with an increasing amount of the PVC. The presence of processing aid and internal lubricant could substantially improve the mechanical properties of rigid PVC not only in the thermoplastic state but also in the thermoelastic state (tensile strength and elongation at break) [24]. That explained why the PVC sample exhibited a relatively high elongation at break than ABS.

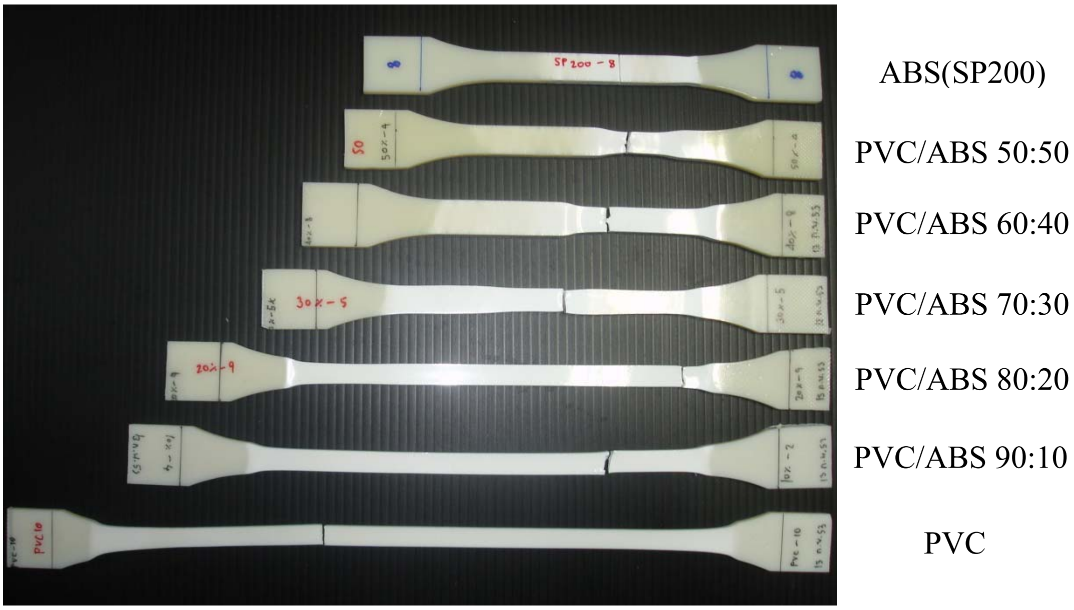


Figure 6.7: Elongation at break of PVC/ABS(SP200) blends at various mass blending ratios.

6.2.1.2 Flexural Properties

Flexural properties of the PVC/ABS blends were also studied following ASTM D790. The content of ABS(SP200) in PVC/ABS blends was varied from 0 wt% to 50 wt%. The obtained flexural modulus and flexural strength values were depicted in Figure 6.8 and also summarized in Table 6.4. The flexural strengths of the neat PVC and the neat ABS were determined to be 92 MPa and 65 MPa. In addition, the flexural strength value of the blend systems tended to decrease when the ABS(SP200) content increased. The PVC/ABS(SP200) blends at various blending ratios in a range of 0 wt% to 50 wt% of ABS(SP200) showed the flexural strength of 89 MPa at 10 wt% of ABS(SP200). This value decreased to 75 MPa for the blend containing 50 wt% of the ABS(SP200). The effect of the ABS content on PVC/ABS blends tended to follow the additivity rule with the systematic variation in their values as described above.

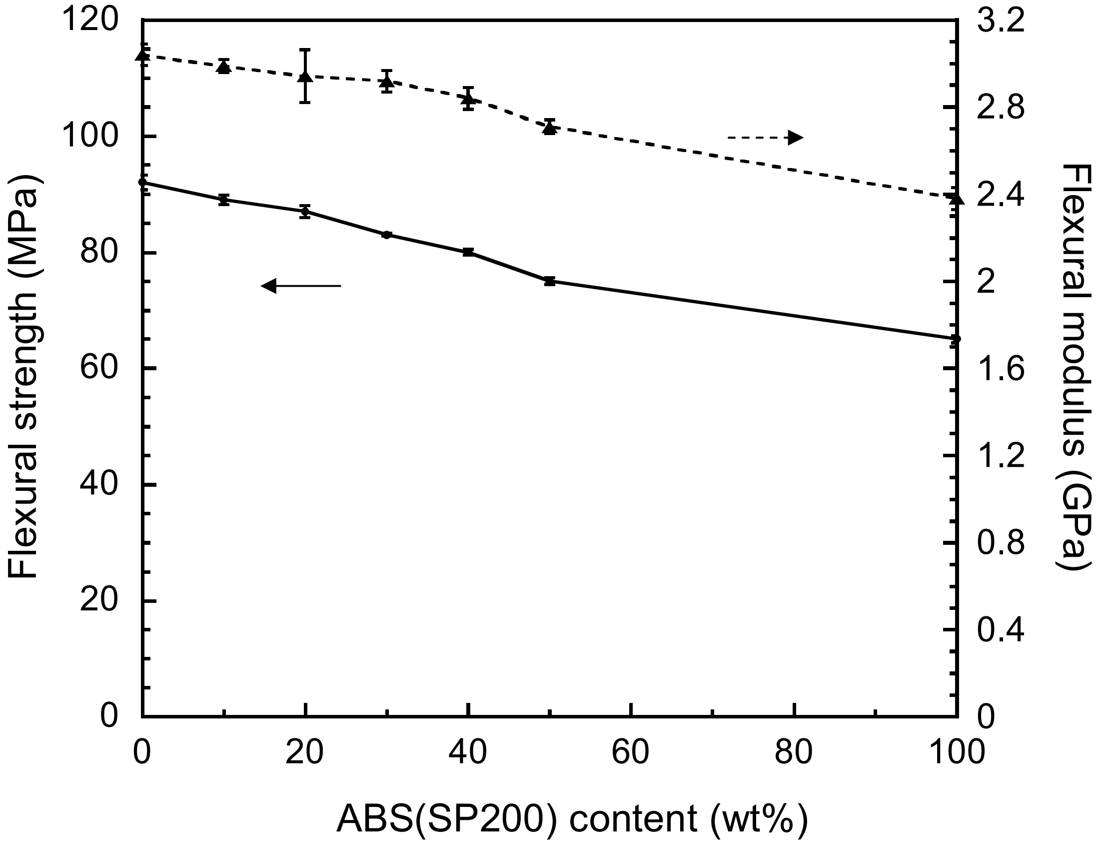


Figure 6.8: Flexural properties of PVC/ABS blends at various mass blending ratios: (●) flexural strength (▲) flexural modulus.

The flexural moduli of the neat PVC and ABS(SP200) were determined to be 3.04 GPa and 2.38 GPa, respectively. It corresponded to the modulus results from dynamic mechanical analysis discussed earlier. Due to the higher rigidity of PVC, flexural moduli of the PVC/ABS blends were expectedly found to increase with increasing PVC content. The flexural modulus of PVC/ABS(SP200) blends were determined to be 2.98 GPa at 10wt% of ABS(SP200) and this value decreased to 2.71 GPa for the blend at 50wt% of ABS(SP200).

Table 6.4: Flexural properties of PVC/ABS(SP200) blends at various mass ratios.

Samples	Flexural modulus (GPa)	Flexural strength (MPa)
PVC	3.04 ± 0.05	92 ± 1.3
PVC/SP200 90/10	2.98 ± 0.03	89 ± 0.8
PVC/SP200 80/20	2.94 ± 0.12	87 ± 1.0
PVC/SP200 70/30	2.91 ± 0.05	84 ± 0.3
PVC/SP200 60/40	2.84 ± 0.05	81 ± 0.5
PVC/SP200 50/50	2.71 ± 0.03	75 ± 0.6
SP200	2.38 ± 0.05	65 ± 0.6

6.2.1.3 Impact Properties

The effect of ABS(SP200) content ranging from 0 wt% to 50 wt% on notched Izod impact strength of the PVC/ABS blends was examined and the results were plotted in Figure 6.9. In Figure 6.9, the impact property was observed to deviate from the rule of mixture. That is the impact strength of PVC was found to be approximately 7 kJ/m^2 whereas that of ABS(SP200) was about 35 kJ/m^2. The synergistic behavior in impact strength was evidently observed with an incorporation of ABS(SP200) into PVC. An incorporation of the ABS(SP200) in the range of 10 wt% to 50 wt% resulted in an increase in the impact strength values from 9.1 kJ/m^2 to 65 kJ/m^2. Furthermore, the maximum observable enhancement in the impact strength of the PVC/ABS blend at 50 wt% of the ABS as high as 65 kJ/m^2 was substantially higher than those of the PVC and the ABS. This behavior was possibly due to the presence of rubber particle in ABS which effectively acted as an impact modifier of the PVC as well as the possibility of the formation of the blend morphology that favored the energy absorption upon impact loading. The impact fracture surface of the PVC/ABS blends were also observed as shown in Figure 6.10. The figure depicted the cross sectional area of impact specimen at 10-50 wt% of ABS content compared to the neat PVC and ABS(SP200). The fracture surface of the neat PVC revealed a more mirror-like surface of a brittle failure nature whereas that of ABS showed a rough surface with plastic deformation of ductile failure. The PVC/ABS blends exhibited a systematic variation in their fracture surface from a more brittle to a more ductile failure with increasing ABS content in the blends. Moreover, PVC/ABS(SP200) blends evidently provided stress whitening effect on their fracture surface in these specimens that contained ABS. The stress whitening could possibly form by drawing and cavitation of the rubber domains in the ABS phase [6].

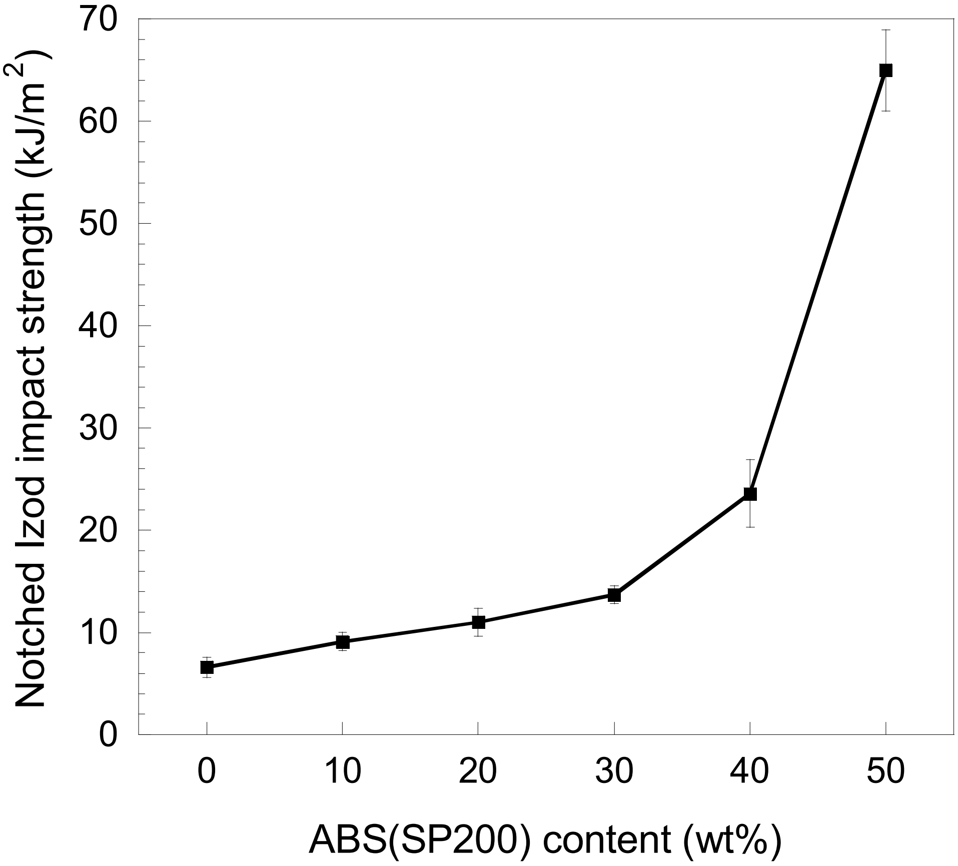


Figure 6.9: Impact properties of the PVC/ABS(SP200) blends at various mass ratios.

The impact properties observed here for the PVC/ABS blends were consistent to those reported by Sharma *et al.* [42]. Moreover, Belhaneche-Bensemra had studied effect of plasticizer on the notched Izod impact resistance between PVC/ABS blend with the presence and absence of plasticizer. The results suggested that PVC without plasticizer showed moderate impact strength of the obtained blend whereas the addition of ABS into PVC provided relatively high impact strength blend samples [44].

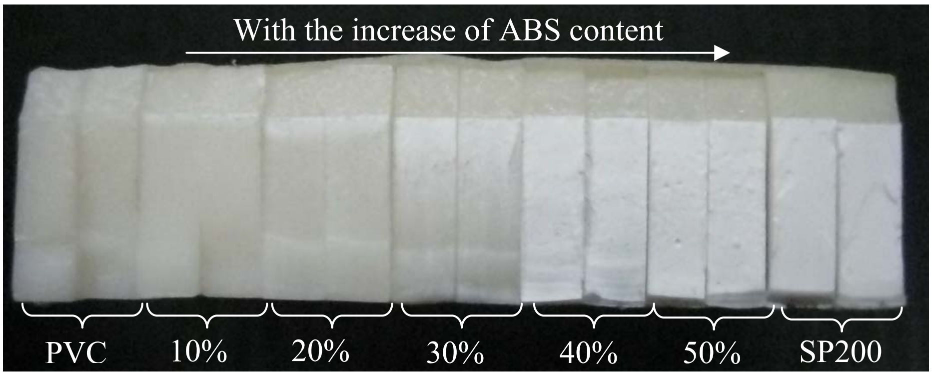


Figure 6.10: Fracture surface of notched Izod impact of PVC/ABS(SP200) specimens at various mass ratios.

6.2.2 Effects of ABS Content on Thermal Properties of PVC/ABS Blends

6.2.2.1 Effects of ABS Content on Glass Transition Temperature of PVC/ABS Blends

The effects of ABS(SP200) content on the glass transition temperature (T_g), determined by DSC, of the PVC/ABS(SP200) blends were depicted in Figure 6.11. The T_g's of PVC/ABS blends at ABS contents in a range of 0-50 wt% were determined. As shown in Figure 6.11, all PVC/ABS blends also showed two distinct T_g's of the PVC-richand ABS(SP200)-rich domains in the blend (T_{g1} and T_{g2}). The T_g's of the neat PVC and ABS(SP200) were found to be at 81°C and 102°C. For the PVC/ABS(SP200) blends, T_g's of PVC in the blends or T_{g1} wereobserved to increase with an increase of ABS content from 81°C for the neat PVC to about 83°C at 50 wt% of the ABS content. The T_g's of ABS in the blends or T_{g2} were more difficult to observe because there was overlapping transition possibly vitrification of PVC near the position of T_g of ABS in the blend.

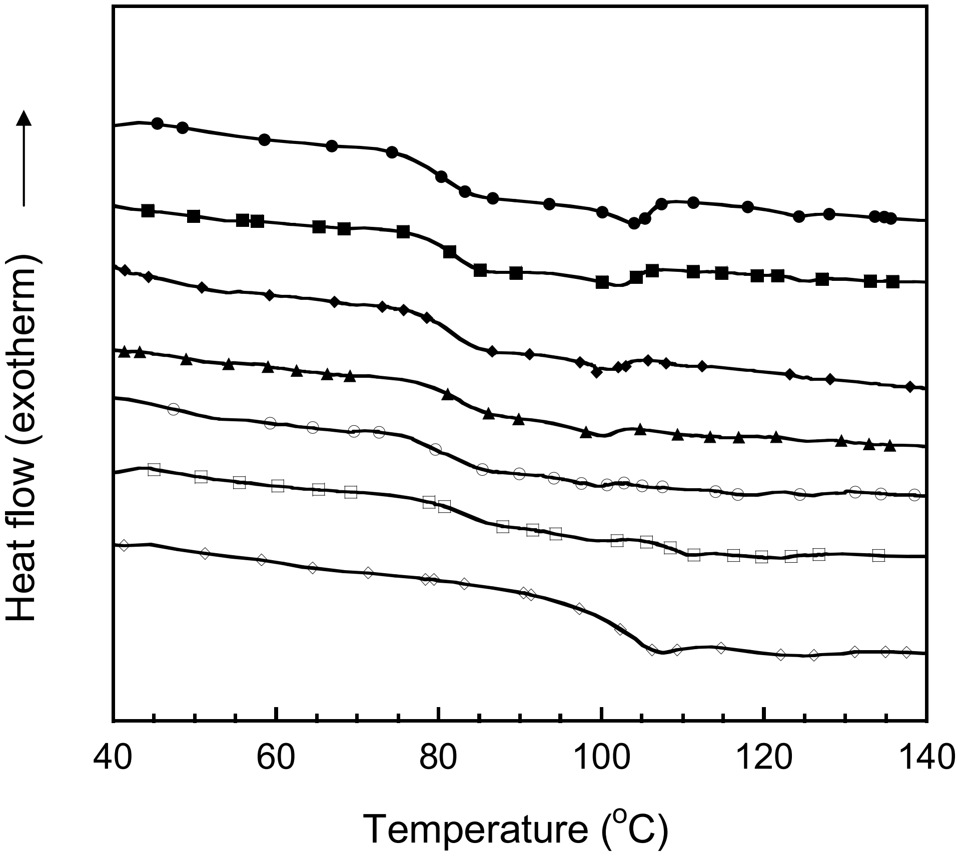


Figure 6.11: DSC thermograms of the PVC/ABS(SP200) blends at various mass ratios:

(●) PVC (■) PVC/SP200 90/10 (◆) PVC/SP200 80/20 (▲) PVC/SP200 70/30 (○) PVC/SP200 60/40 (□) PVC/SP200 50/50 (◇) SP200 (ABS).

6.2.2.2 Effects of ABS Content on Thermomechanical Properties of PVC/ABS Blends

From the previous section, the addition of ABS into PVC at a fixed mass ratio of 50 wt% of ABS exhibited a merging peak of loss modulus, located between the T_g's of PVC and ABS. In this section, loss moduli of PVC/ABS blends were also investigated with the ABS content in the blend ranging from 10-50 wt% as shown in Figure 6.12. According to the results, the loss modulus curves showed the merging peak at every blending mass ratio. As clearly seen, the peak of loss modulus of the blend gradually shifted to a higher value when the content of ABS increased. T_g's of PVC and ABS determined from the loss modulus peaks were found to be 83°C and 106°C. The peaks of loss modulus of the PVC/ABS(SP200) blends were observed at 87°C from the blend containing 10 wt% of ABS(SP200) and this value increased to 93°C in the blend having 50 wt% of ABS(SP200). Moreover, a small shoulder of loss modulus peak was observed between 110°C -115°C which was more clearly seen with increasing the ABS. This peak was assigned to the T_g of the ABS-rich phase in the blends.

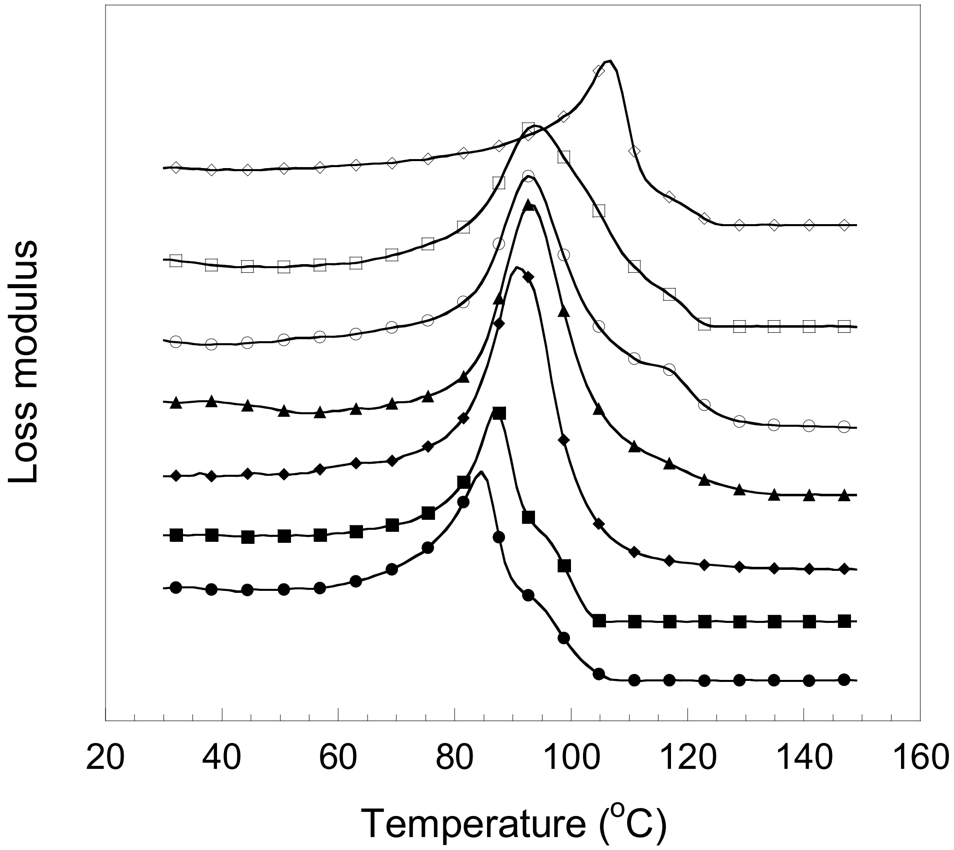


Figure 6.12: Loss moduli of PVC/ABS(SP200) blends at various mass ratios:

(●) PVC (■) PVC/SP200 90/10 (◆) PVC/SP200 80/20 (▲) PVC/SP200 70/30 (○) PVC/SP200 60/40 (□) PVC/SP200 50/50 (◇) SP200 (ABS).

Loss tangents of the PVC/ABS blends shown in Figure 6.13 exhibited two peaks of T_g more clearly than the the loss modulus curves. The value of T_g determined from a peak of loss tangent was observed to be higher than the T_g from a loss modulus peak. For example, T_g of PVC and ABS were located at 94°C and 120°C, respectively whereas the PVC/ABS(SP200) blend at 50 wt% content of ABS exhibited two peaks at 96°C and 116°C. The observed shift of the T_g's of the PVC/ABS blends towards each other was an important characteristic of the partially miscible nature of these blend systems. The second peak at higher temperature was also more pronounced with increasing the ABS content of the blends and was assigned to the T_g of the ABS-rich phase as described in the previous section.

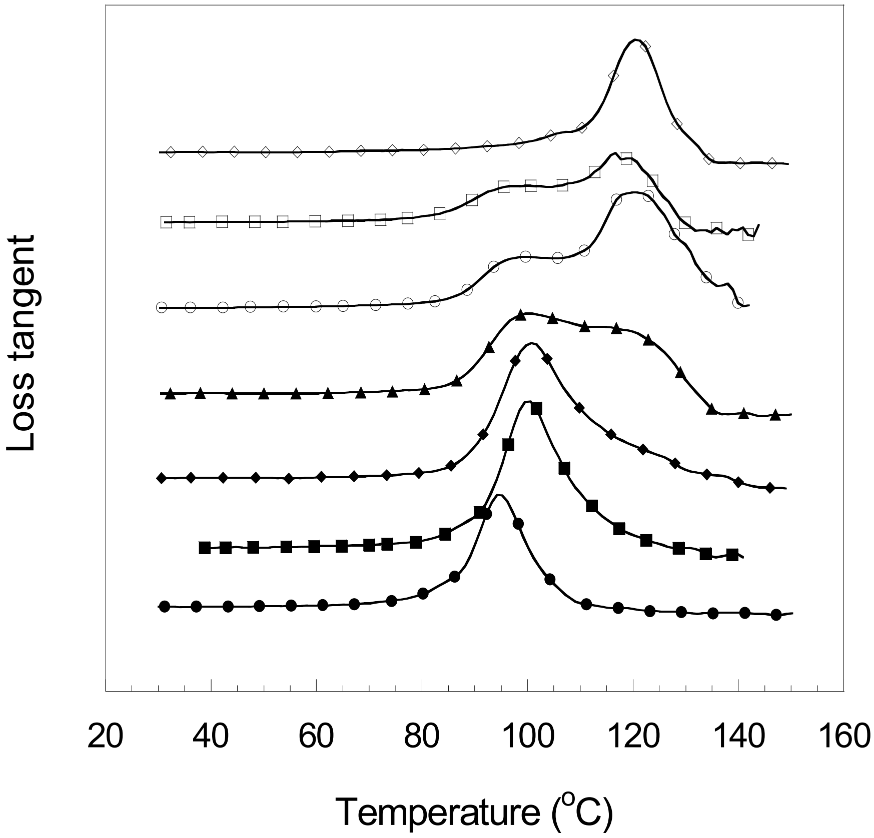


Figure 6.13: Loss tangents of PVC/ABS(SP200) blends at various mass ratios:

(●) PVC (■) PVC/SP200 90/10 (◆) PVC/SP200 80/20 (▲) PVC/SP200 70/30
(○) PVC/SP200 60/40 (□) PVC/SP200 50/50 (◇) SP200.

Figure 6.14 showed temperature dependence of storage modulus from dynamic mechanical analysis of the blends. At glassy state of all samples (40°C), storage moduli of the neat PVC, and ABS(SP200) were determined to be 3.08 and 2.23 GPa. PVC/ABS blend at 10 wt% of ABS provided the storage modulus of 2.94 GPa and the values systematically decreased to 2.46 GPa at 50 wt% of ABS(SP200) as shown in Figure 6.15. The trend was also consistent with the tensile and flexural modulus values discussed in the previous section.

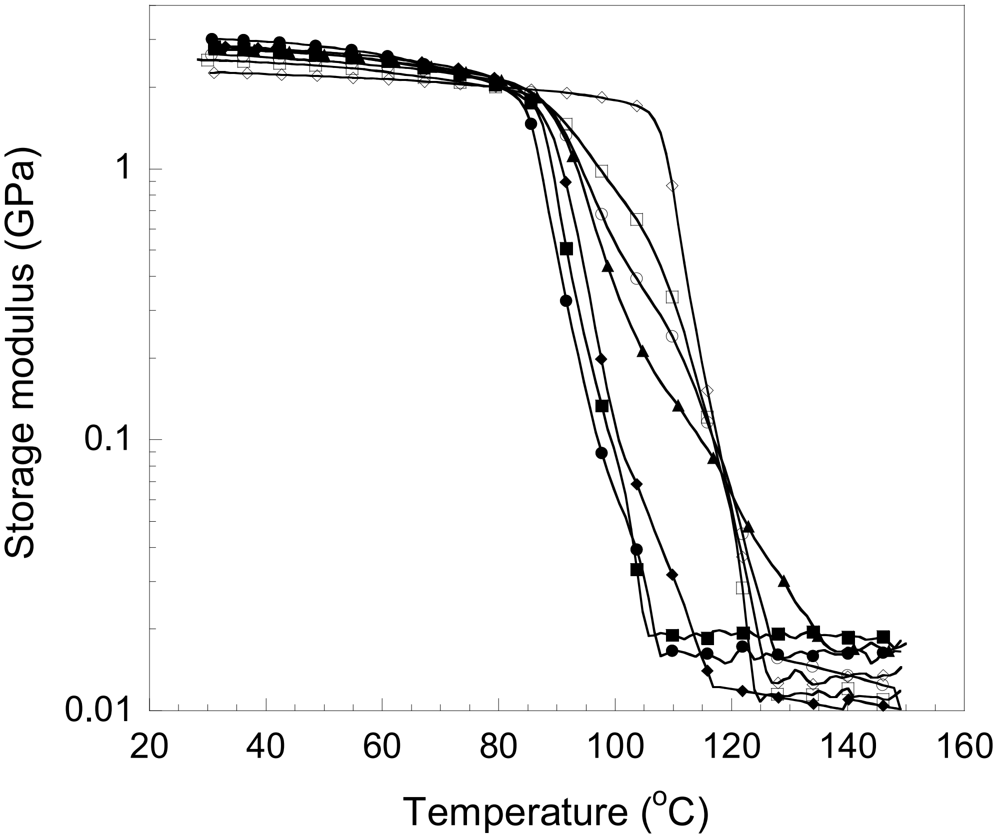


Figure 6.14: Storage moduli of PVC/ABS(SP200) blends at various mass ratios:

(●) PVC (■) PVC/SP200 90/10 (◆) PVC/SP200 80/20 (▲) PVC/SP200 70/30 (○) PVC/SP200 60/40 (□) PVC/SP200 50/50 (◇) SP200.

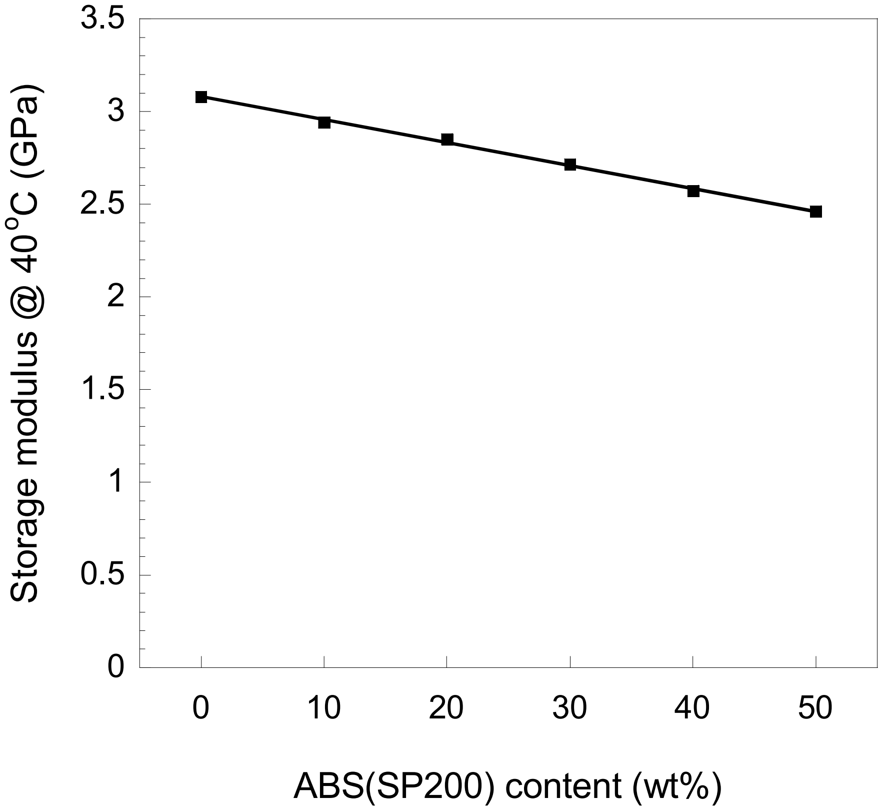


Figure 6.15: Storage moduli at 40°C of PVC/ABS(SP200) blends at various mass ratios.

6.2.2.3 Effects of ABS Content on Heat Distortion Temperature and Vicat Softening Temperature of PVC/ABS Blends

The effects of ABS(SP200) contents ranging from 0% to 50 wt% on the HDT and the vicat softening temperature of PVC/ABS(SP200) blends are shown in Figure 6.16. From this figure, the HDT and the vicat softening temperatures of the PVC/ABS(SP200) blends were found to systematically increase with increasing of ABS content. It was observed that the heat distortion temperature (HDT) of the neat PVC and ABS(SP200) were 68°C and 79°C, respectively. For the blend systems, as expected, both temperatures of the PVC increased with the ABS(SP200) content from 69°C at 10 wt% of the ABS(SP200) to 73°C at 50 wt% of the ABS(SP200). In the case of vicat softening temperature, the obtained values were higher than those obtained from HDT experiment. The vicat softening temperature of the neat PVC and ABS(SP200) were found to be about 77^{o}C and 93°C, respectively. The vicat softening temperature of the blend at 10 wt% of ABS was determined to be 79°C and the value increased to 84°C at 50 wt% of ABS content. Therefore, the addition of ABS(SP200) in the

PVC/ABS(SP200) blends tended to enhance the HDT and the vicat softening temperatures of the blends, providing the wider service temperature to the PVC. In the other hand, ABS can substantially improve the thermal stability to PVC. This characteristic can be explained from the possible diffusion of the SAN fraction of ABS into the PVC and thus increased thermal properties such as HDT and vicat softening temperatures of the blends. The improvement comfirmed the observations on the glass transition temperatures either from DSC or DMA experiments of these polymer blends.

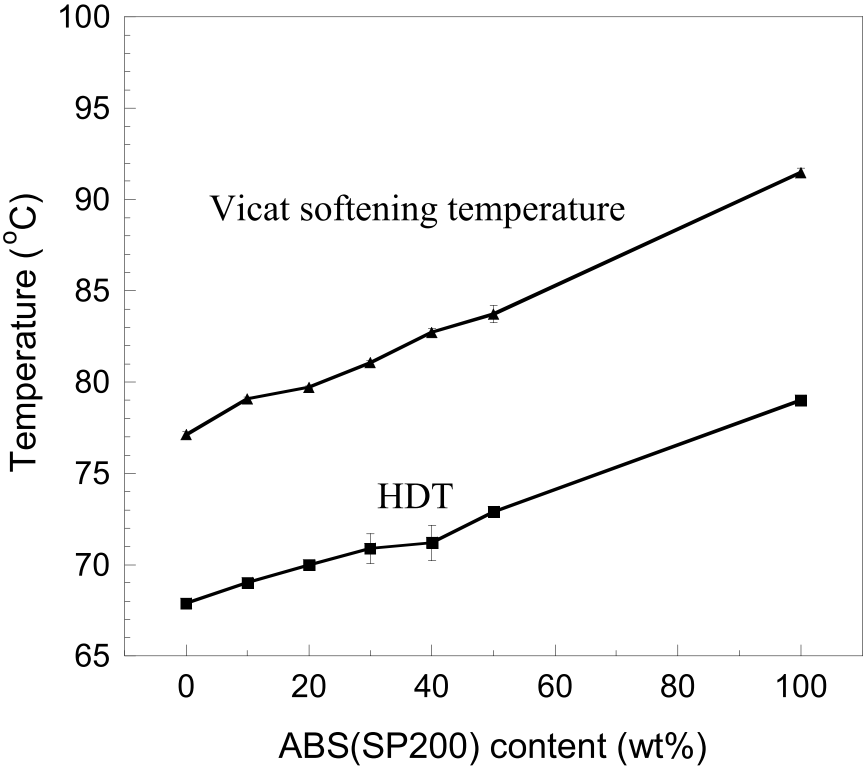


Figure 6.16: HDT and vicat softening temperatures of PVC/ABS(SP200) blends at various mass ratios: (▲) vicat softening temperature (■) HDT.

6.2.3 Effects of ABS Content on Physical Properties of PVC/ABS Blends

In Figure 6.17, density of the PVC/ABS(SP200) blends at various ABS contents at 10wt% were determined to be about 1.34 g/cm^3 and decreased with an increase of ABS(SP200) content to 1.18 g/cm^3 at 50wt% of the ABS. This result was relatively well predicted by the rule of mixture of the blends calculated based on the measured density of the PVC of 1.38 g/cm^3 and the density of the ABS(SP200) of 1.04 g/cm^3. The agreement between the theoretical and the experimental values suggested the negligible amount of void in the blend samples. Moreover, due to its low density, ABS provided lighter weight than PVC.

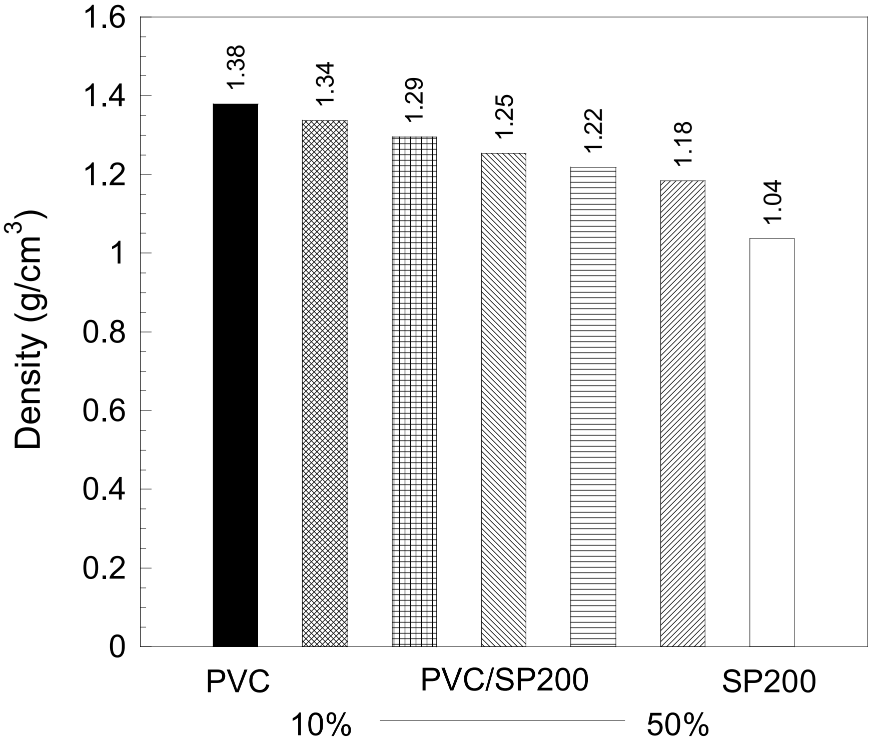


Figure 6.17: Densities of PVC/ABS(SP200) blends at various mass blending ratios:
(■) PVC (▩) PVC/SP200 90/10 (▦) PVC/SP200 80/20,
(▧) PVC/SP200 70/30 (▤) PVC/SP200 60/40 (▨) PVC/SP200 50/50
(□) SP200.

In general, all organic polymeric materials will absorb moisture to some extent resulting in swelling, dissolving, leaching, plasticizing and/or hydrolyzing events which can result in discoloration, embrittlement, loss of mechanical, or electrical properties etc. In this study, the water absorption properties of ABS(SP200) blended with PVC at various contents of 0 to 50 wt% of ABS were also examined. As seen in Figure 6.18, the water absorption experiment was also performed up to the saturation state. From Table 6.5, at twenty-four hour immersion, PVC and ABS(SP200) absorbed water only about 0.04 wt% and 0.2 wt%, respectively. For PVC/ABS(SP200) blends, their water absorption were found to increase with increasing ABS(SP200) content, likely due to the presence of a highly polar moiety of an acrylonitrile component in ABS. The long-term water immersion of all polymers was performed for more than 30 days, however, all specimens provided water absorption values of than 1 wt%.

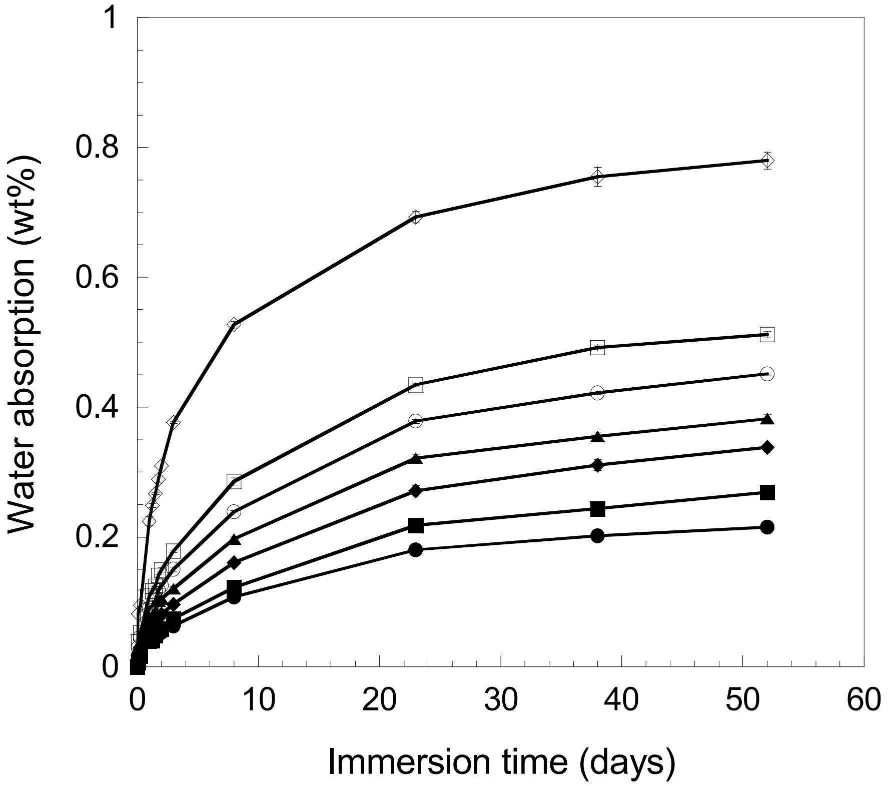


Figure 6.18: Water absorption of PVC/ABS(SP200) blends at various mass blending ratios: (●) PVC (■) PVC/SP200 90/10 (◆) PVC/SP200 80/20 (▲) PVC/SP200 70/30 (○) PVC/SP200 60/40 (□) PVC/SP200 50/50 (◇) SP200.

Table 6.5: Average water absorption of PVC, ABS(SP200) and PVC/ABS(SP200) blends at various mass ratios.

Samples	**Average water absorption***		
	at 2 hour immersion (wt%)	**at 24 hour immersion (wt%)**	**long-term (51 days) immersion (wt%)**
PVC	0.02	0.04	0.22
PVC/SP200 90/10	0.02	0.04	0.27
PVC/SP200 80/20	0.02	0.06	0.34
PVC/SP200 70/30	0.02	0.08	0.38
PVC/SP200 60/40	0.03	0.09	0.45
PVC/SP200 50/50	0.04	0.11	0.51
SP200	0.08	0.22	0.78

* The deviation of the average value is very small (less than 0.01 wt%).

In terms of processability, it is well known that ABS can significantly improve flow behaviors of some rather viscous polymers with poor processability like polycarbonate (PC). In the PVC/ABS blends, the processing temperature should not exceed 200°C because of the potential degradation of PVC. The effect of ABS on the flowability of PVC was also observed here. Figure 6.19 shows the required pressure or stress for extruding our PVC/ABS blends as a function of ABS contents at a constant extruding speed of 30 mm/min and extruding temperature of 190°C obtained by a plastometer. From the curve, the lower the required pressure, the lower the viscosity of the blends were. Therefore, with increasing the ABS contents in the blends, the viscosity tended to decrease systematically as seen in Figure 6.19.

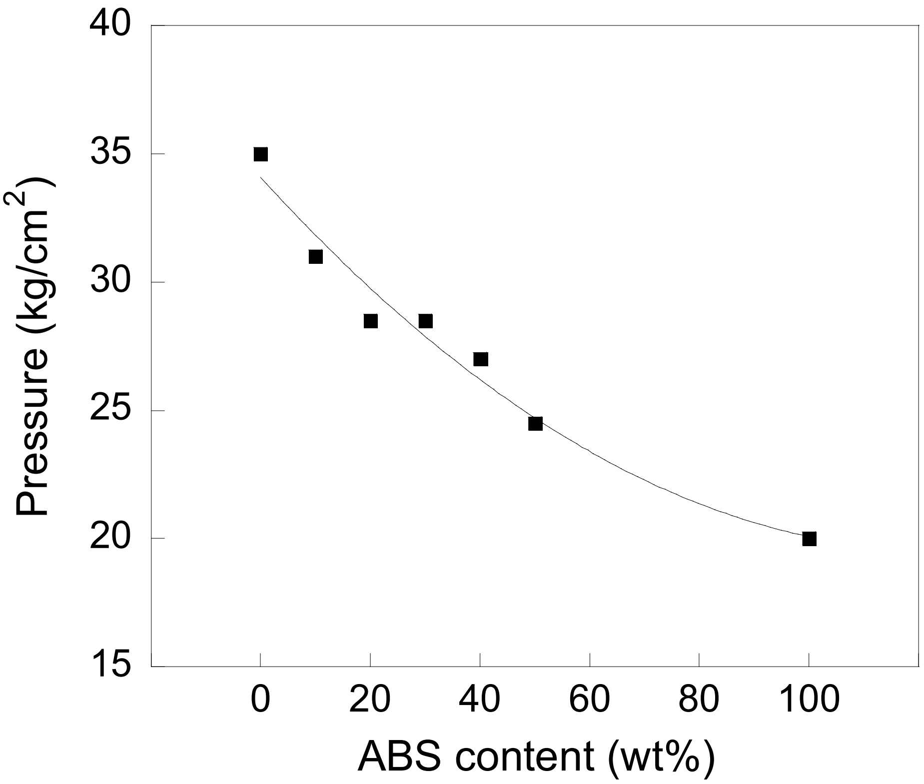


Figure 6.19: Melt rheology of PVC/ABS blends at temperature of 190°C.

In the next section, we selected PVC/ABS(SP200) at a mass ratio of 50/50 for further investigation as a matrix for wood composite preparation since it provided the highest impact strength with suitable thermal and mechanical characteristics for wood composites.

6.3 Effects of Woodflour Content on the Properties of PVC/ABS(SP200)/Wood Composites

6.3.1 Effects of Woodflour Content on Mechanical Properties of PVC/ABS(SP200)/Wood Composites

6.3.1.1 Tensile Properties

The tensile properties of PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents in a range of 0 wt% to 50 wt% were depicted in Figure 6.20. It can be observed that the tensile modulus of the PVC/ABS(SP200)/wood systematically increased with increasing woodflour content. In Table 6.6, the tensile modulus of unfilled PVC/ABS(SP200) was determined to be 2.36 GPa while the PVC/ABS(SP200)/wood composite showed the tensile modulus ranging from 2.99 GPa for 10 wt% of woodflour and increased to 5.58 GPa for 50wt% of woodflour. The enhancement of the tensile modulus of the wood polymer composites was due to the reinforcing effect which led to restriction of mobility of the polymer chains from an addition of a more rigid woodflour filler which having modulus in the range of 10-15 GPa [46].

In terms of tensile strength, PVC/ABS(SP200) matrix rendered tensile strength of 43 MPa. An addition of woodflour into the matrix resulted in the decrease in tensile strength to 35 MPa at 10 wt% of woodflour loading and to 30 MPa at 50 wt% of woodflour loading. The decrease in tensile strength values was possibly due to a formation of a weaker interfacial bonding and some microscopic defects between the woodflour and the PVC/ABS matrix [47].

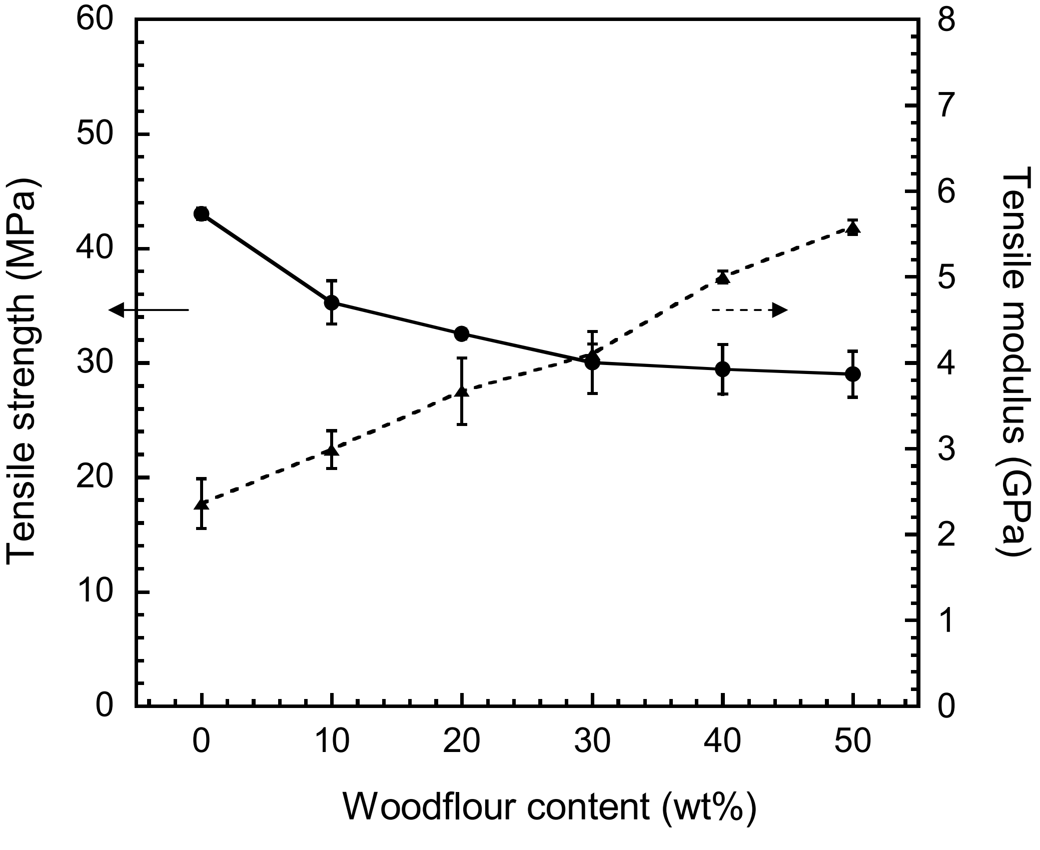


Figure 6.20: Tensile properties of PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents.

Table 6.6 Tensile properties of PVC/ABS(SP200)/wood composites blends at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents.

Samples	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PVC/SP200 wood 0%	2.36 ± 0.08	43.0 ± 0.6	18.9 ± 7.20
PVC/SP200 wood 10%	2.99 ± 0.07	35.3 ± 1.9	2.7 ± 0.24
PVC/SP200 wood 20%	3.67 ± 0.12	32.5 ± 0.4	1.9 ± 0.16
PVC/SP200 wood 30%	3.87 ± 0.39	29.0 ± 2.7	1.3 ± 0.19
PVC/SP200 wood 40%	5.00 ± 0.22	29.4 ± 2.2	1.0 ± 0.14
PVC/SP200 wood 50%	5.58 ± 0.29	30.3 ± 1.2	0.7 ± 0.02

According to the study of Sombatsompop and coworkers, PVC/wood composite containing woodflour at 41.2 wt% exhibited the tensile modulus which decreased from 0.7 GPa for the neat PVC to 0.3 GPa [39] and tensile strength of the PVC/wood composite decreased from 34 MPa of the PVC matrix to 7 MPa of the obtained wood composite. Our PVC/ABS/wood composite system, at a woodflour content of 40 wt% and without any surface treatment, showed a relatively high tensile strength value up to 30 MPa and a tensile modulus as high as 5 GPa [40]. Furthermore, as compared to the system of the polyolefin/wood composites, our PVC/ABS(SP200)/wood composite also provided substantially higher tensile properties. For example, Selke and Wichman [48] studied the mechanical properties of wood fiber polyolefin composite systems. They reported that the tensile strength of HDPE matrix was about 29 MPa while an addition of wood fiber decreased the tensile strength to 22 MPa at 40 wt% wood content or about 24% reduction from that of HDPE matrix [39, 48]. In addition, the strength of high density polyethylene wood composites and polypropylene wood composite at 50 wt% of wood filler were reported by Yuan *et al.* [49]. They found that the tensile strength of HDPE/wood composite also evidently decreased from 22.6 to 15.7 MPa or about 31% decrease whereas that of PP/wood composite decreased from 36.6 to 21.6 MPa which corresponded to 42% reduction in the strength [49].

The elongation at break of the PVC/ABS(SP200)/wood composites as a function of the woodflour content is shown in Table 6.6. The elongation at break of PVC/ABS(SP200)/wood composites was found to decrease considerably with the presence of woodflour. The elongation at break of the PVC/ABS(SP200) matrix used in this experiment was approximately 19% as reported in the previous section and the value was decreased to about 2.68% even at only 10 wt% of woodflour. Beyond 20 wt% woodflour, the elongation at break of the PVC/ABS(SP200) wood composites slightly decreased further to 0.74% at the maximum content of 50 wt% woodflour. The considerable decrease of the elongation at break of our PVC/ABS(SP200)/wood composites with the presence of woodflour and the slight decrease further with increasing the woodflour content was also observed by various researchers and was probably caused by the presence of the rather rigid woodflour filler in the PVC/ABS(SP200) matrix and the insufficient interfacial interaction between the PVC/ABS(SP200) matrix and woodflour as discussed in the case of tensile strength of the composites. This relatively low interfacial adhesion in the composite led to the easy debonding and the initiation of cracks at the composite interface thus the low elongation at break of the specimens.

6.3.1.2 Flexural Properties

The effects of the woodflour content on flexural properties of PVC/ABS(SP200)/wood composites are shown in Figure 6.21. The flexural modulus which can be determined from the initial slope of the stress-strain curve of the PVC/ABS(SP200)/wood composite was found to increase with increasing the woodflour content. In Table 6.7, the flexural modulus of the unfilled PVC/ABS(SP200) used in this experiment was approximately 2.71 GPa and about twofold increased to about 5.44 GPa at the maximum woodflour content of 50 wt%. As expected, an addition of the woodflour showed a similar effect on an enhancement of the flexural modulus as in the case of tensile modulus of PVC/ABS(SP200)/wood composites. The similar improvement was also reported in the systems of HDPE and PP/wood composites [48, 49]. Furthermore, the flexural strength of the PVC/ABS/wood composites was also found to decrease with increasing woodflour content. From the results, the flexural strength of the unfilled PVC/ABS(SP200) at 50/50 mass ratio was determined to be 75 MPa and tended to decrease with an addition of woodflour i.e. 55.6 MPa in the composite containing 50 wt% of woodflour. The effect of woodflour content on the flexural strength of the composites was similar to that of tensile strength as discussed earlier. On the other hand, PVC/wood composite showed the flexural strength of 37 MPa, therefore, PVC/ABS(SP200)/wood composites proved to provide the higher flexural strength even at a relatively high woodflour loading up to 50 wt%.

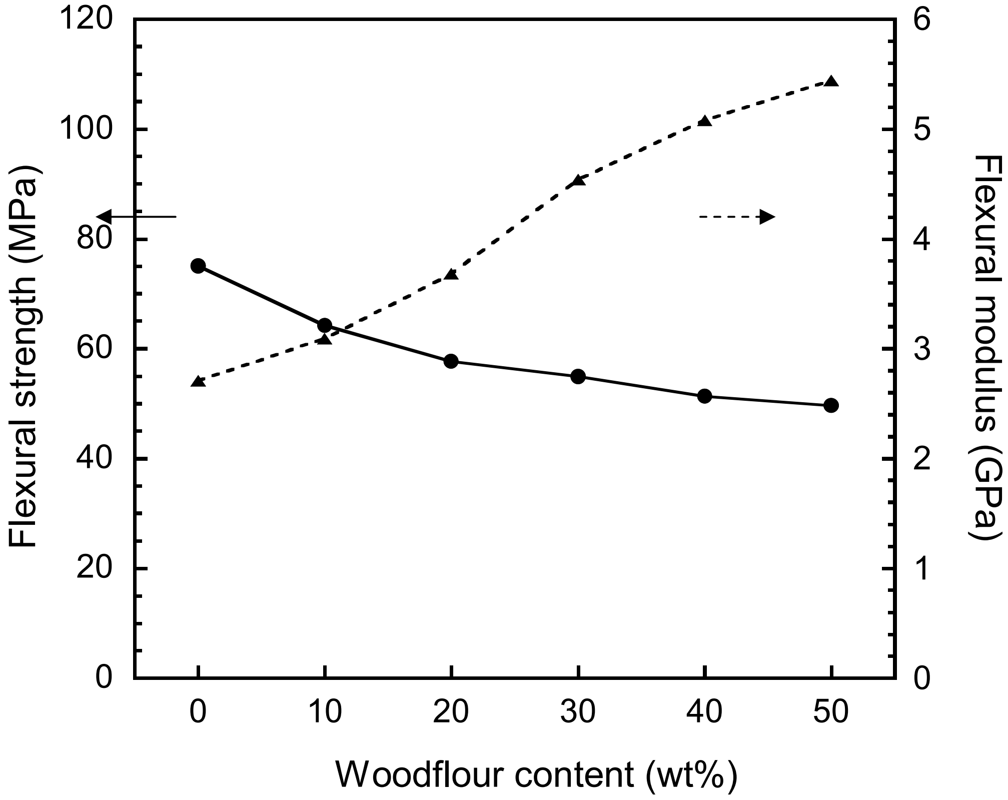


Figure 6.21: Flexural properties of PVC/ABS(SP200)wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents.

Table 6.7: Flexural properties of PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents.

Samples	Flexural modulus (GPa)	Flexural strength (MPa)
PVC/SP200 wood 0%	2.71 ± 0.03	75.0 ± 0.6
PVC/SP200 wood 10%	3.09 ± 0.24	64.2 ± 2.3
PVC/SP200 wood 20%	3.68 ± 0.13	57.7 ± 2.5
PVC/SP200 wood 30%	4.54 ± 0.07	56.9 ± 1.1
PVC/SP200 wood 40%	5.08 ± 0.63	51.3 ± 5.9
PVC/SP200 wood 50%	5.44 ± 0.44	49.6 ± 3.8

6.3.1.3 Impact Properties

Figure 6.22 showed the effect of woodflour content ranging from 0 wt% to 50 wt% on notched Izod impact strength of the PVC/ABS(SP200)/wood composites. It can be observed that the notched Izod impact strength of the PVC/ABS(SP200)/wood composites was found to decrease with increasing woodflour content. The PVC/ABS(SP200)/wood composite containing 10 wt% of woodflour showed the impact strength value as high as 9.98 kJ/m^2 and the impact strength decreased with an increase of woodflour content to about 5.40 kJ/m^2 at the 50 wt% of the woodflour. The similar behavior was also found in other wood composites system such as PE/wood and PP/wood composites [48,49]. In the case of PVC wood composite, the notched Izod impact strength of the PVC/wood composite at 50 wt% of woodflour was 4.53 kJ/m^2 which was slightly lower than that of the PVC/ABS/wood composite. As the woodflour content increased, the ductile portion (the polymer matrix) automatically reduced, thus decreasing the composites toughness [36]. The decrease of impact strength of natural fiber/polymer composites was usually derived from ineffective debonding and friction effects, especially for the composites without fiber surface treatments.

The impact strength of PVC/ABS/wood composites was found to provide substantially higher.value than those of typical polyolefin/wood composites. Selke and Wichman [48] studied wood polyolefin composites and found that the impact strength of PE/wood composite at 40 wt% of woodflour loading was about 4 kJ/m^2. In the case of PP/wood composites, Oskman and Clemons [50] studied the mechanical properties of PP woodflour composites. They reported that the composite at 40 wt% of woodflour loading showed the impact strength of only 2.6 kJ/m^2.

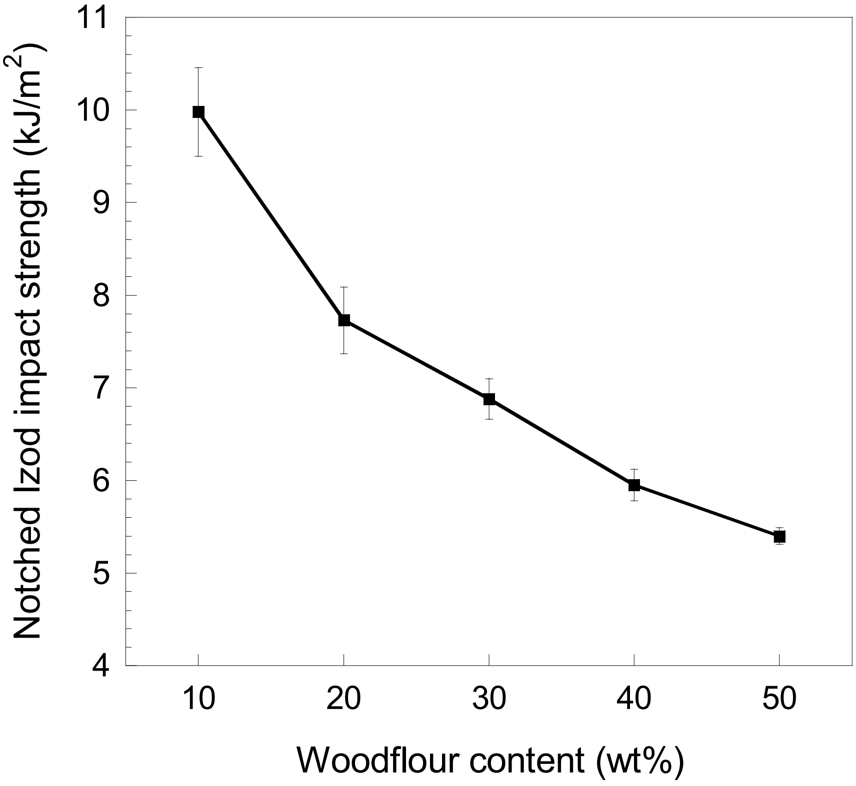


Figure 6.22: Impact properties of PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents.

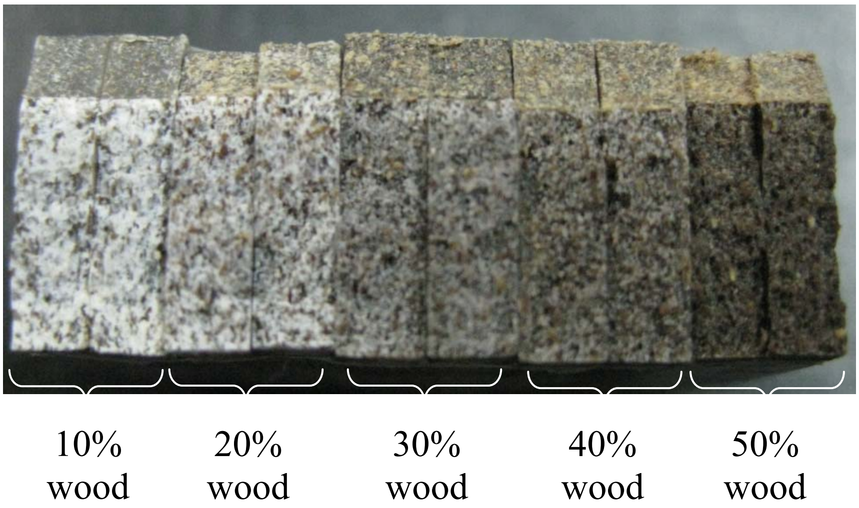


Figure 6.23: Fracture surface of PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents.

Moreover, the fracture surfaces of the composites were also examined and are illustrated in Figure 6.23. At higher woodflour content, it can be observed that the continuous area of polymer matrix was smaller with less plastic deformation area (whiten area), suggesting that the composites can absorb less impact energy thus the lowering of the impact properties.

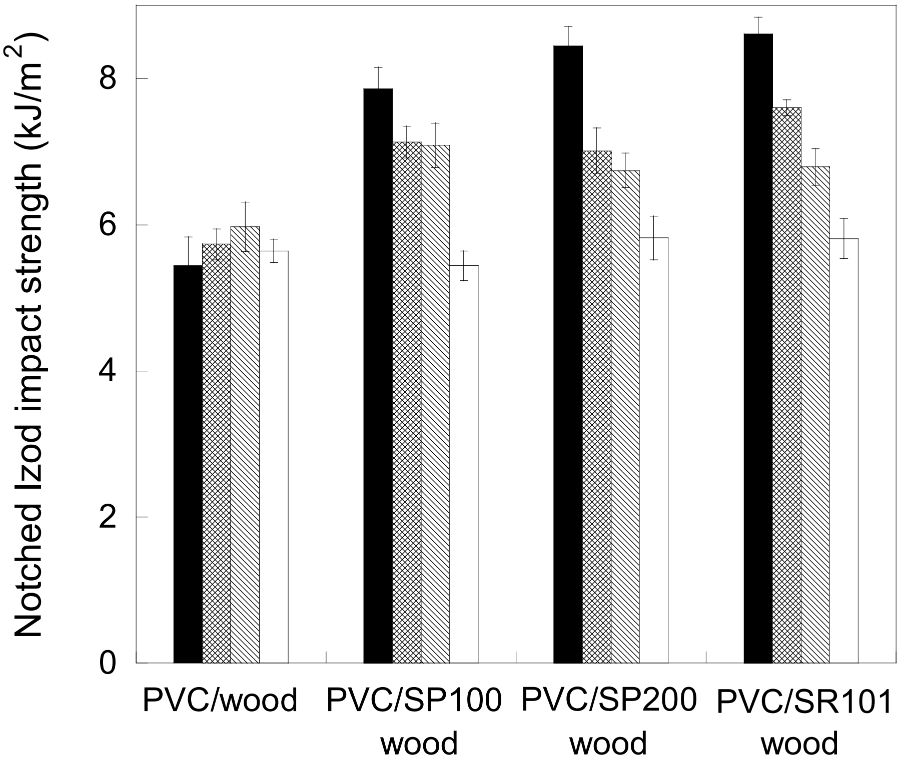


Figure 6.24: Impact property of PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents:
(■) woodflour 20 wt% (▩) woodflour 30 wt% (▧) woodflour 40 wt%
(□) woodflour 50 wt%.

In Figure 6.24, as compared to PVC/wood composites, PVC/ABS(SP200) wood composite at 20 wt% of woodflour provided the substantial enhancement on impact strength from the impact strength of PVC/wood composite having the value of 5.40 kJ/m^2 to the value of 8.5 kJ/m^2 of the PVC/ABS(SP200)/wood composite or about 57.4% increase. The enhancement on impact strength was, however, reduced to 22.8% (5.7 to 7.0 kJ/m^2) and 11.7% (6.0 to 6.7 kJ/m^2) at higher woodflour contents of 30, 40 wt%, respectively. When the woodflour content was 50 wt%, ABS was observed to show marginal enhancement on impact property of the obtained wood composites.

According to the study by Sombatsompop *et al.*, the silane treated fiber at a low woodflour content of 9.1% provided the improvement on impact strength in PVC/silane-treated woodflour composite i.e. from the value of 3.5 to 5.3 kJ/m^2 using the treated woodflour, whereas at higher woodflour content of 41.2%, the impact strength was improved to a much lesser extent from the value of 2.8 to that of 3.7 kJ/m^2 [40]. Zheng *et al.* [51] studied the interfacial treatment of natural fiber by benzoic acid and observed an improvement in Charpy unnotched impact strength of the PVC/wood composite. At 25% baggasse fiber content treated by 3% benzoic acid, the Charpy impact strength of PVC/benzoic acid-treated baggasse fiber composite was enhanced from 7.5 to 9.7 kJ/m^2. In addition, Sombatsompop *et al.* [52] studied the effect of glass fiber content on mechanical properties of PVC/wood composites. The 50 phr of 1% silane-treated woodflour in PVC/wood composite was reported to provide the notched Izod impact strength value at 2.8 kJ/m^2. Even when the composites were further reinforced by glass fiber at 10, 20, and 30 phr, the impact strength values were improved to be 3.7, 4.2, and 4.6 kJ/m^2, respectively. Finally, Mengeloglu *et al.* [9] studied the effects of impact modifiers on impact properties of PVC/wood composites. They found that methylmethacrylate-butadiene-styrene (MBS) and acrylic impact modifier (ACR) could enhance impact strength of PVC/wood composite from 2.0 kJ/m^2 to 7.0 kJ/m^2 at 33.3 wt% woodflour content. The impact strength of our PVC/ABS woodflour composite was thus observed to show relatively high value comparable to the PVC wood composite using surface treated natural fiber system.

As compared to other toughening techniques, an incorporation of ABS provided relatively substantial enhancement on impact properties of the composites, particularly at the loading below 50 wt%. It should be noted that, for a benefit of cost savings and minimal processing step, no chemical treatment was applied to the woodflour particles used in this work.

6.3.2 Effects of Woodflour Content on Thermal Properties of PVC/ABS(SP200)/Wood Composites

6.3.2.1 Effects of Woodflour Content on Thermoechanical Properties of PVC/ABS(SP200)/Wood Composites

Dynamic mechanical properties of the PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 were investigated at different woodflour contents (i.e. 0 wt%-50 wt%). The results are shown in Figure 6.25-5.27. The glass transition temperatures of PVC/ABS(SP200)/wood composites were determined from the peak of loss modulus as seen in Table 6.8. It can be observed that T_{g1} of PVC/ABS(SP200)/wood composites slightly increased from about 93°C of the unfilled PVC/ABS(SP200) to 94°C at 10 wt% of woodflour and systematically increased to 97°C at 50 wt% of woodflour whereas T_{g2} of the composites only slightly increased from 115°C to 117°C in the same woodflour loadings. The similar behavior was reported by Sombatsompop *et al*. [39].

The slight enhancement in T_g was possibly due to the presence of rigid woodflour in the polymer matrix and might imply that the addition of woodflour had a restriction effect on the motion of molecular chains of the polymer matrix due to impediment of a more rigid woodflour particle. Loss tangent peaks shown in Figure 6.26 confirmed the partially miscible characteristic of the blend matrix from the appearance of the two peaks of the PVC and ABS phases in every woodflour content.

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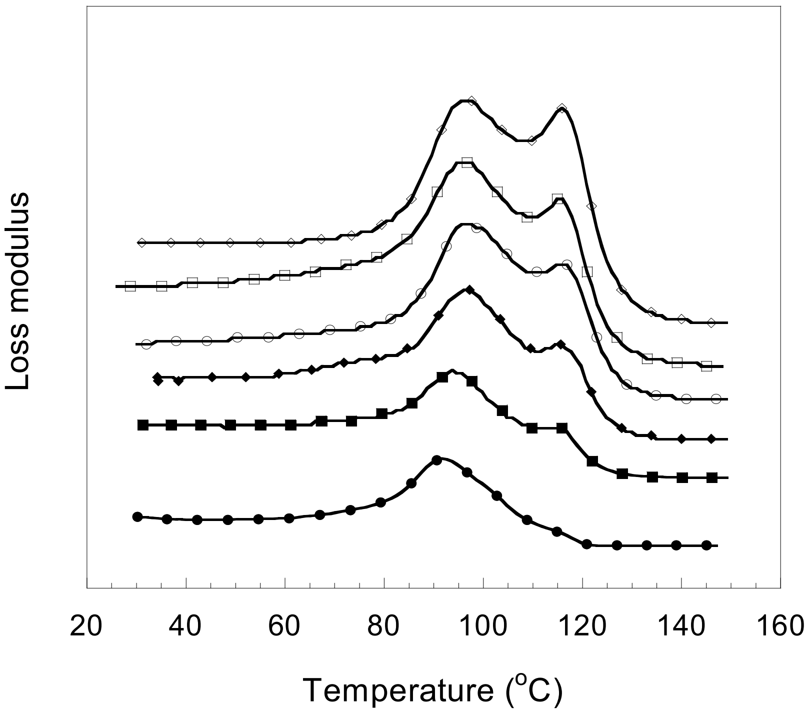


Figure 6.25: Loss moduli of PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents: (●) PVC/SP200 wood 0% (■) PVC/SP200 wood 10% (◆) PVC/SP200 wood 20% (○) PVC/SP200 wood 30% (□) PVC/SP200 wood 40% (◊) PVC/SP200 wood 50%.

Table 6.8: Glass transition temperatures of PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents from loss modulus.

Samples	**T_{g1} (°C)**	**T_{g2} (°C)**
PVC/SP200 wood 0%	93	115
PVC/SP200 wood 10%	94	115
PVC/SP200 wood 20%	95	115
PVC/SP200 wood 30%	97	117
PVC/SP200 wood 40%	97	117
PVC/SP200 wood 50%	97	117

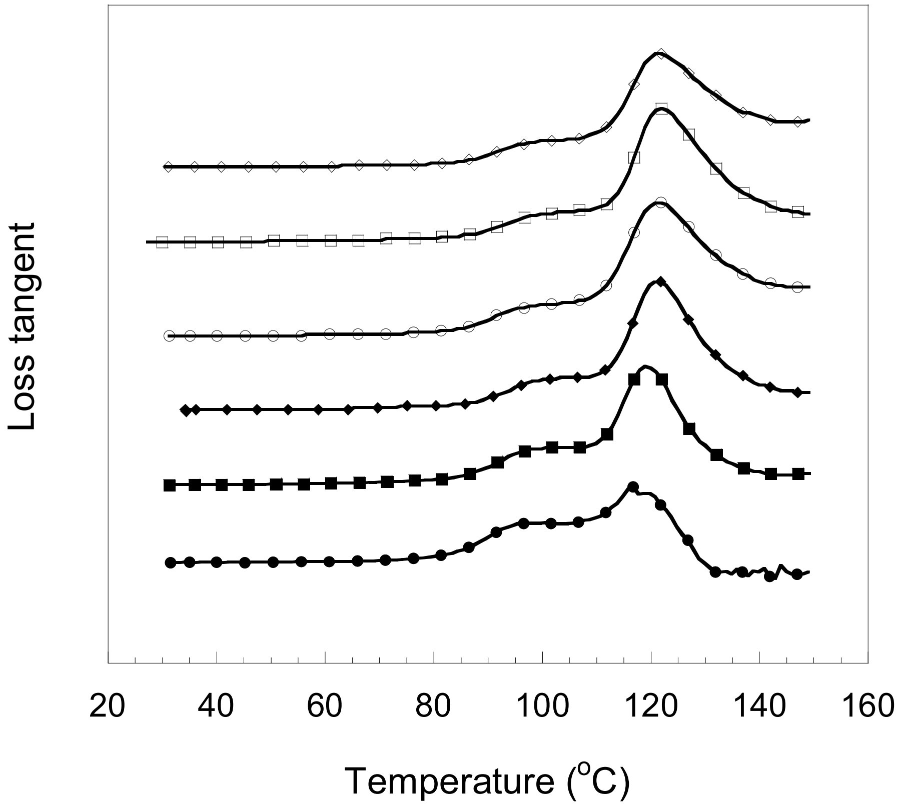


Figure 6.26: Loss tangents of PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents:
(●) PVC/SP200 wood 0% (■) PVC/SP200 wood 10%
(◆) PVC/SP200 wood 20% (○) PVC/SP200 wood 30%
(□) PVC/SP200 wood 40% (◇) PVC/SP200 wood 50%.

Furthermore, the temperature dependence of storage modulus of wood composite is illustrated in Figure 6.27. At glassy state of the composites (i.e. at 40°C) in Figure 6.28, the storage modulus of the PVC/ABS(SP200)/wood composites increased with increasing woodflour contents. This characteristic can be explained by a reinforcing effect due to the higher modulus value of the natural filler compared to that of the polymer matrix.

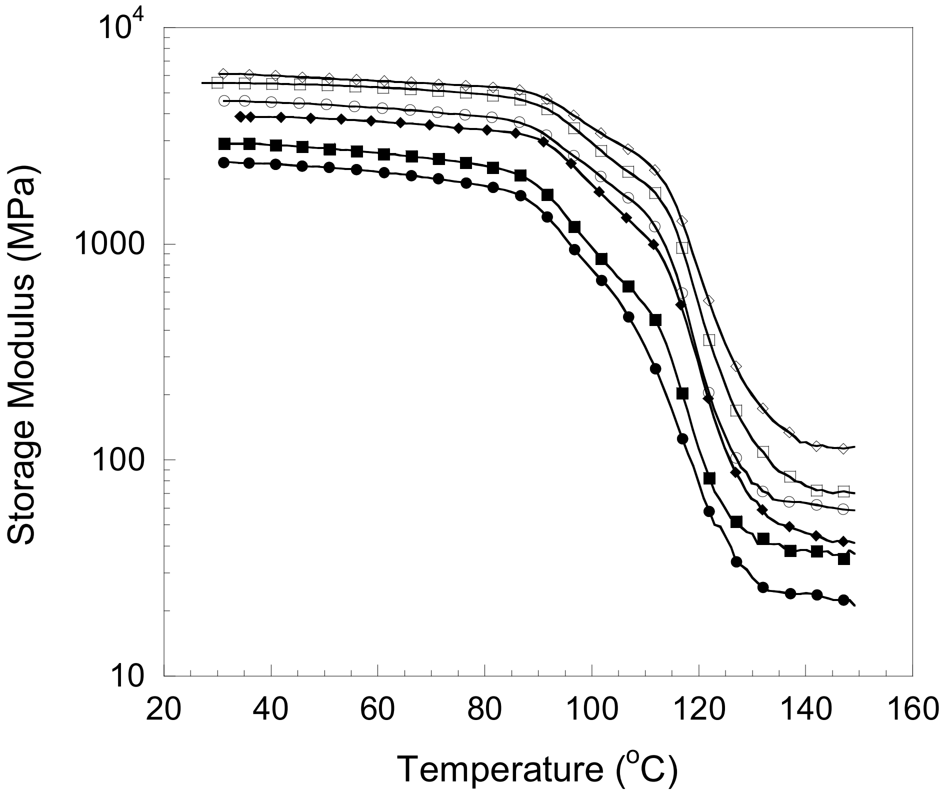


Figure 6.27: Storage moduli PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents: (●) PVC/SP200 wood 0% (■) PVC/SP200 wood 10% (◆) PVC/SP200 wood 20% (○) PVC/SP200 wood 30% (□) PVC/SP200 wood 40% (◇) PVC/SP200 wood 50%.

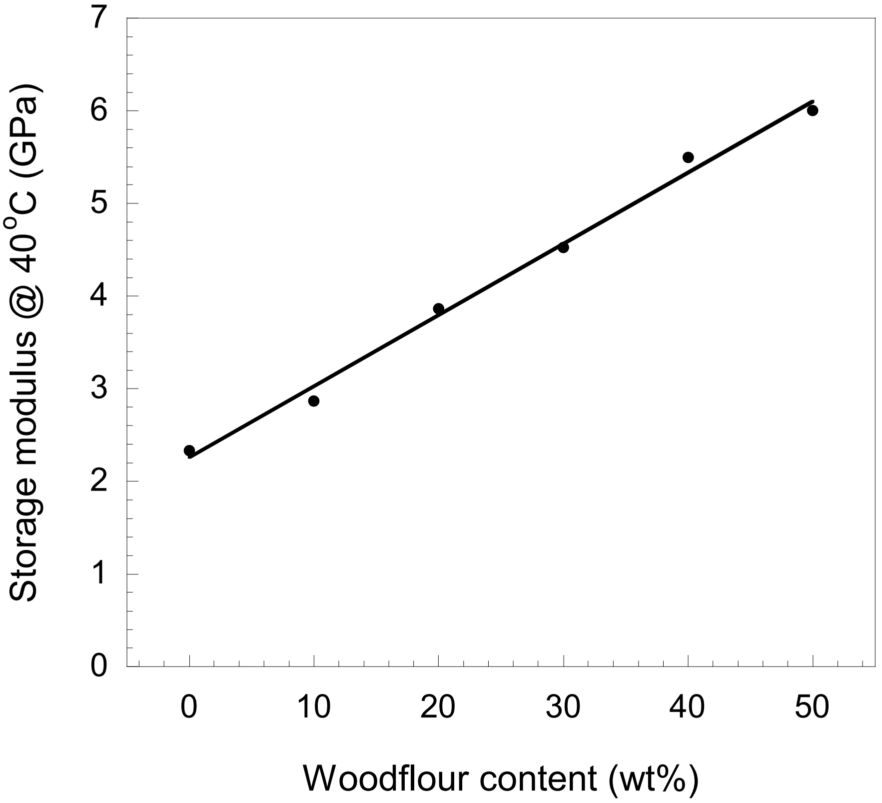


Figure 6.28: Storage moduli at 40°C of PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents.

6.3.2.2 Effects of Woodflour Content on Heat Distortion Temperature and Vicat Softening Temperature of PVC/ABS/Wood Composites

The effects of woodflour contents on vicat softening temperature and heat distortion temperature (HDT) of PVC/ABS(SP200)/wood composites are shown in Figure 6.29. It can be observed that the vicat softening temperature and HDT of PVC/ABS(SP200)/wood composites were found to increase with increasing woodflour contents. As shown in this figure, the vicat softening temperature of the unfilled PVC/ABS was determined to be about 84°C and the value was increased to about 98°C at the woodflour content of 50 wt%. The heat distortion temperature of the unfilled PVC/ABS(SP200) was determined to be 73°C and also substantially increased with the woodflour content to approximately 87°C at 50 wt% of woodflour. This trend had also been observed in other wood composite systems such as that reported by Kuan *et al.* [53]. As mentioned before, the rigid woodflour tended to restrict the chain mobility of PVC/ABS(SP200) matrix and thus increased the vicat softening temperature and HDT of the composites. The similar improvement was also noticed in the glass transition temperature of the composites with the same explanation.

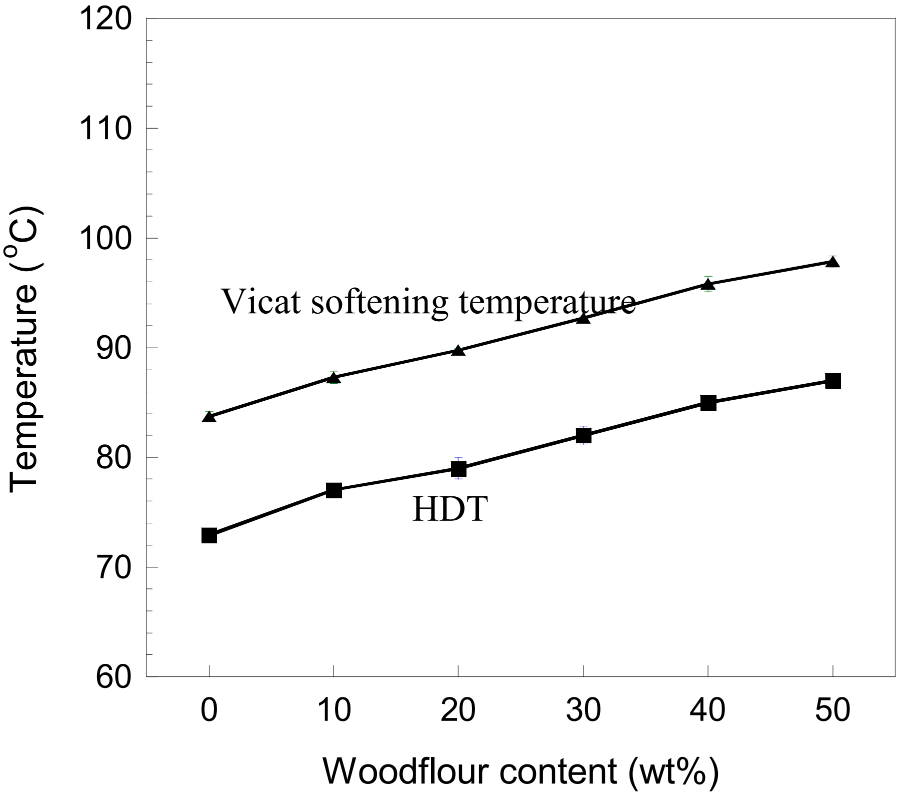


Figure 6.29: HDT and vicat softening temperatures of PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents: (▲) vicat softening temperature (■) HDT.

6.3.3 Effects of Woodflour Content on Physical Properties of PVC/ABS(SP200)/Wood Composites

In Figure 6.30, densities of the PVC/ABS(SP200)/wood composites at various woodflour contents at 10-50 wt% were investigated. The density of the unfilled-PVC/ABS(SP200) was determined to be 1.18 g/cm^3 and found to systematically increase with the increase of woodflour content to 1.24 g/cm^3.

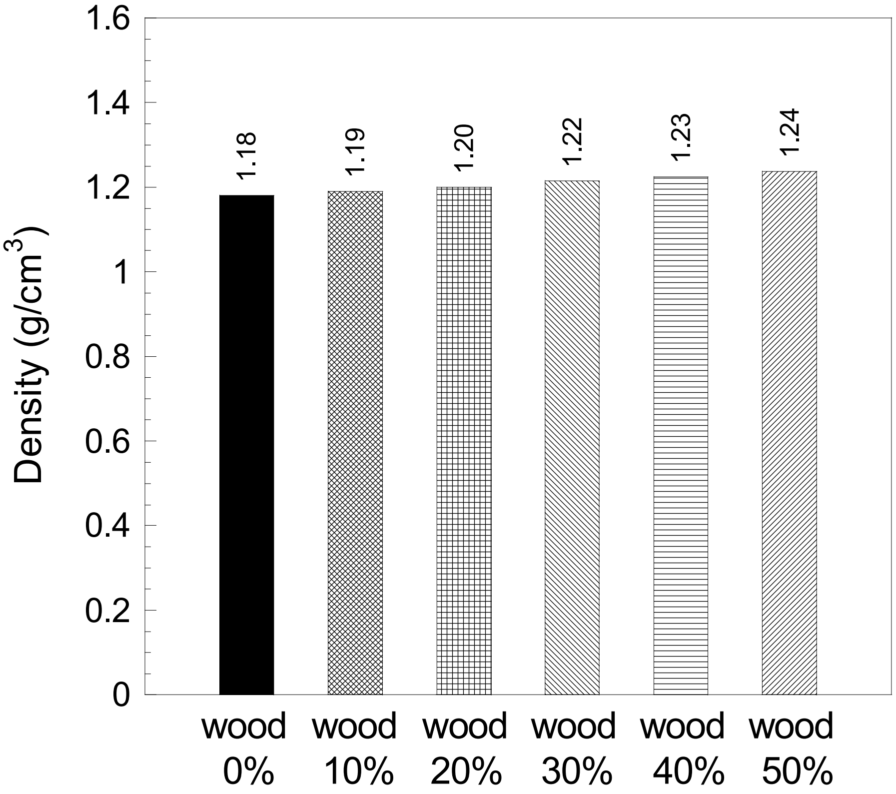


Figure 6.30: Densities of PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents: (■) PVC/SP200 wood 0% (▩) PVC/SP200 wood 10% (▦) PVC/SP200 wood 20% (▧) PVC/SP200 wood 30% (▤) PVC/SP200 wood 40% (▨) PVC/SP200 wood 50%.

The effect of woodflour contents ranging from 0 to 50 wt% on water absorption of PVC wood composites are shown in Figure 6.31 and Table 6.9. At 24 hour immersion, with, unfilled PVC/ABS(SP200) matrix absorbed water only about 0.1 wt%. The moisture absorption of PVC/ABS(SP200)/wood composites was found to increase with increasing woodflour content. For example, at 50 wt% woodflour loading, the water absorption was about 1.8 wt%. This relatively low water uptake in polymer wood composite was attributed to the ability of the polymer matrix to wet or cover most of woodflour surface so water cannot interact directly with the more hydrophilic woodflour filler. For the long-term immersion, the maximum water absorption belonged to PVC/ABS(SP200)/wood 50 wt% of woodflour with the absorption amount of 7.34 wt%. However, this value was still quite low as compared to the amount of water absorption in real wood which can be as high as 24-100% [1]. This was likely due to the hydroxyl group in the structure of cellulose and hemicellulose in woodflour which is highly hydrophilic by nature compared to the polymer matrix [47].With an increase of woodflour content, the gaps between the two phases would also increase as a result of the weaker interfacial bonding between the woodflour and the polymer matrix. Consequently, the degree of water absorption of the composite significantly increased with the woodflour loading. There are three main regions where the absorbed water in the composites can reside: the lumen, the cell wall and the gaps between woodflour and PVC/ABS matrix. To develop composites with better mechanical properties and to decrease their moisture uptake, it is necessary to make the woodflour more hydrophobic possibly by suitable treatment to strengthen interfacial interaction with the polymer matrix used.

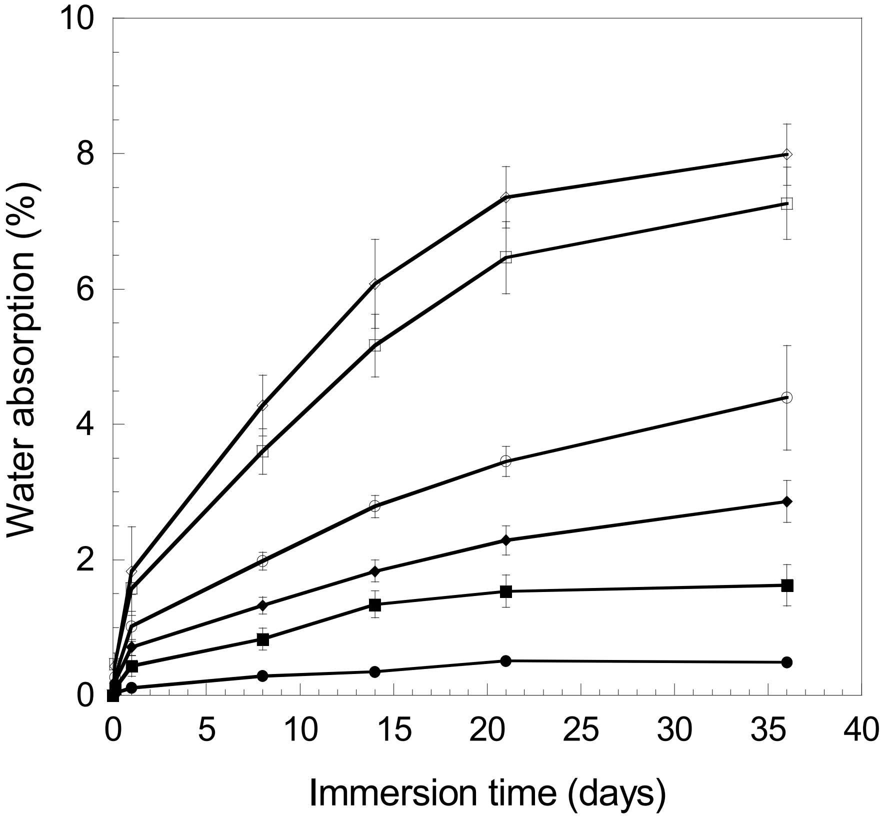


Figure 6.31: Water absorption properties of PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents:
(●) PVC/SP200 wood 0% (■) PVC/SP200 wood 10%
(◆) PVC/SP200 wood 20% (○) PVC/SP200 wood 30%
(□) PVC/SP200 wood 40% (◇)PVC/SP200 wood 50%.

Table 6.9: Average water absorption of PVC/ABS(SP200)/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents.

Samples	**Average water absorption**		
	at 2 hour immersion (wt%)	**at 24 hour immersion (wt%)**	**long-term (36 days) immersion (wt%)**
PVC/SP200 wood 0%	0.04 ± 0.01	0.11 ± 0.01	0.49 ± 0.01
PVC/SP200 wood 10%	0.10 ± 0.07	0.44 ± 0.12	1.63 ± 0.31
PVC/SP200 wood 20%	0.20 ± 0.08	0.71 ± 0.15	2.86 ± 0.31
PVC/SP200 wood 30%	0.27 ± 0.10	1.02 ± 0.09	4.40 ± 0.45
PVC/SP200 wood 40%	0.46 ± 0.07	1.58 ± 0.22	7.27 ± 0.53
PVC/SP200 wood 50%	0.44 ± 0.19	1.83 ± 0.66	7.99 ± 0.77

6.3.4 Effects of Woodflour Content on Weatherability of PVC/ABS(SP200)/Wood Composites

In Figure 6.32, after 20 days natural weathering test in Rayong Province, Thailand during April 22nd to May 12th 2010, PVC specimen became darker as compared to the controlled PVC whereas PVC/ABS blends showed less color change. For the wood composites, the color of wood composite significantly changed even only 20 days outdoor exposure and the change became more severe when the woodflour content increased. In Figure 6.33, after 50 days weathering, PVC specimen remained darker as compared to the controlled PVC whereas PVC/ABS blends exhibited no significant change in color. The result from the color measuring device (Ultrascan Pro) confirmed the general visual observation. In Figure 6.34, the color of unmodified-PVC was also significantly darker as compared to the PVC/ABS blends at 30 or 50 wt% where a change in lightness of the PVC/ABS/wood composite was also less than that of the unmodified PVC/wood composite. These evidences indicated that ABS could help improve weatherability of PVC/wood composites.

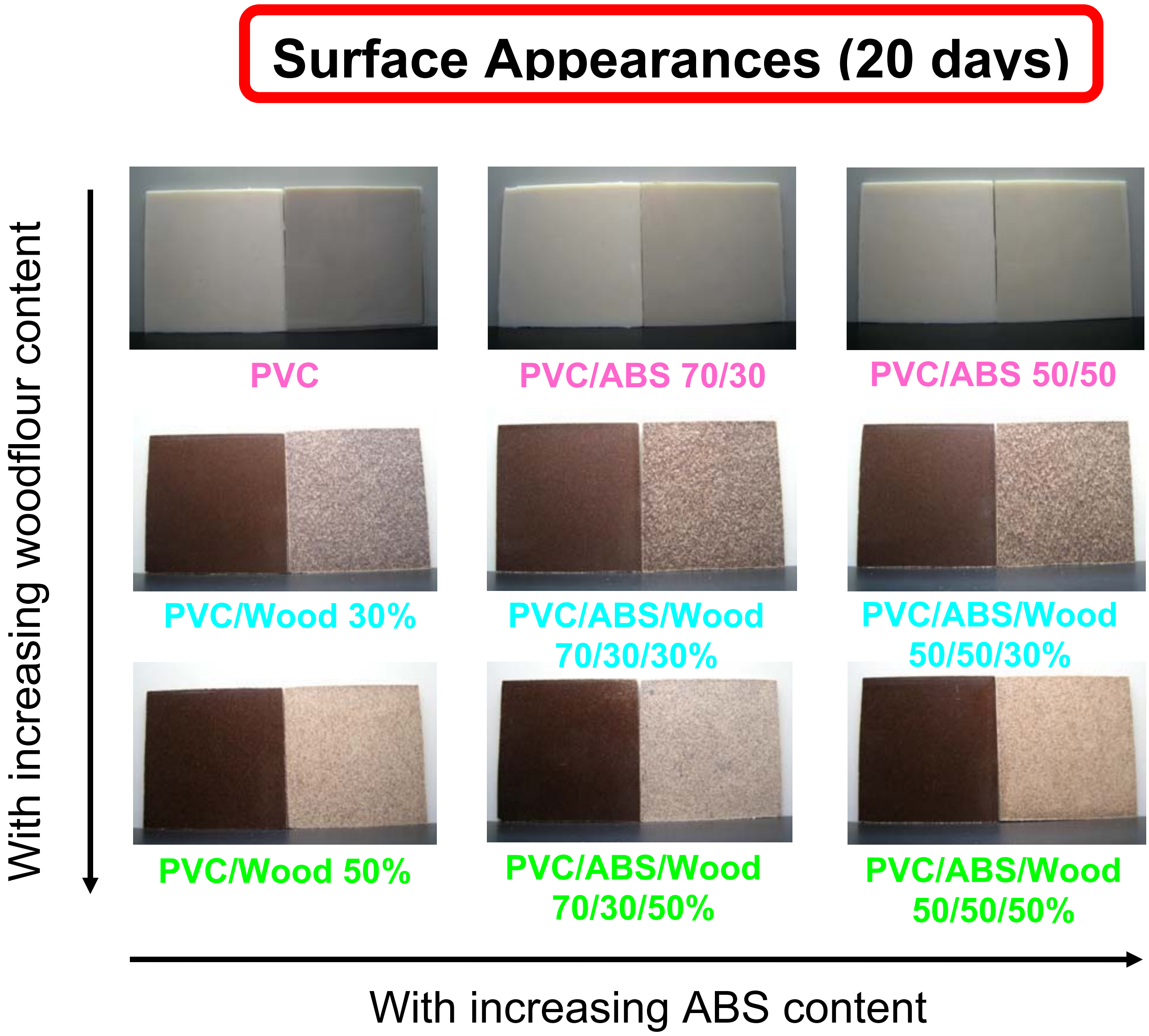


Figure 6.32: Color change of the PVC/ABS blends and their composites at 30% and 50% woodflour loading after 20 days exposure.

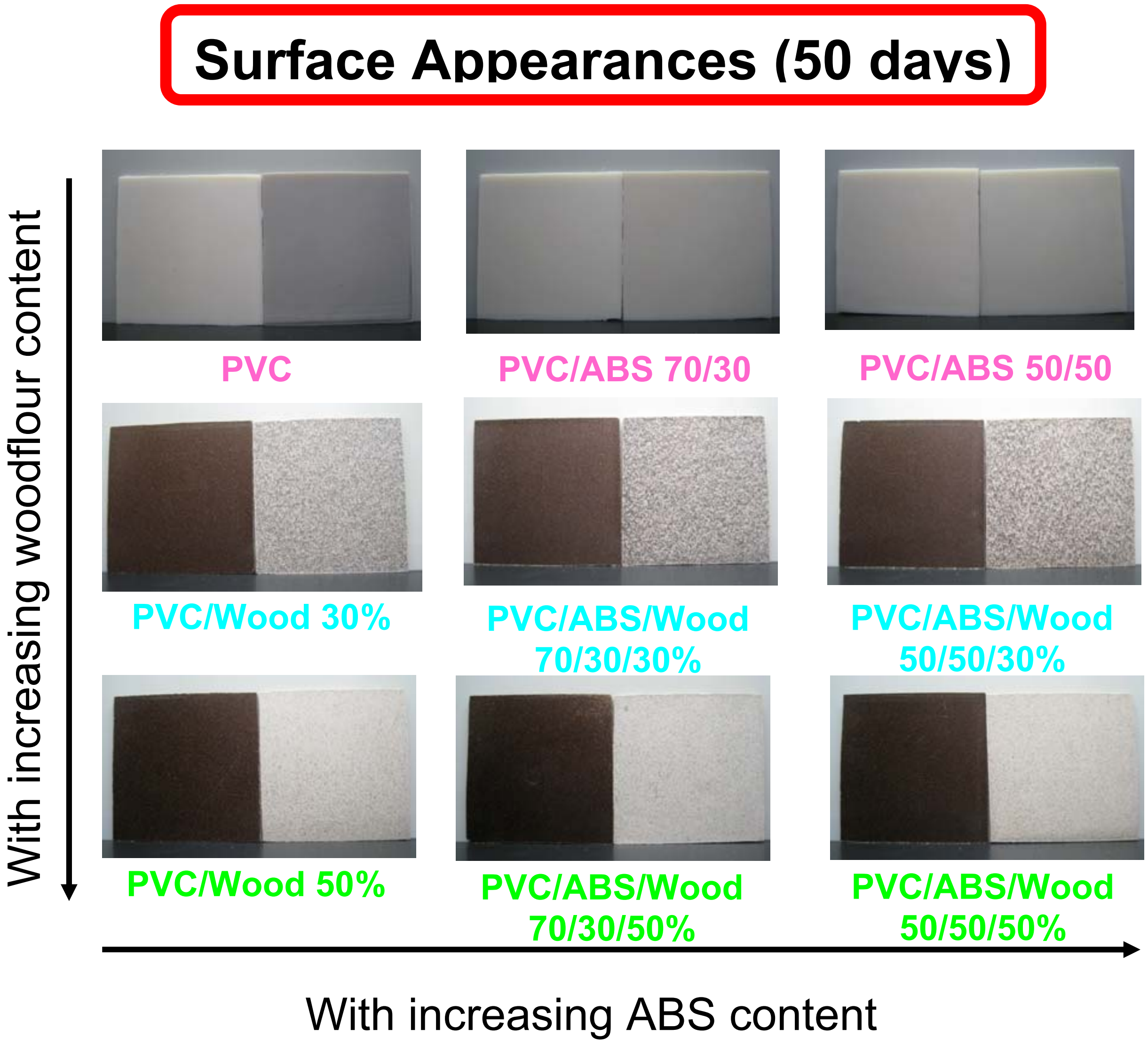


Figure 6.33: Color change of the PVC/ABS blends and their composites at 30% and 50% woodflour loading after 50 days exposure.

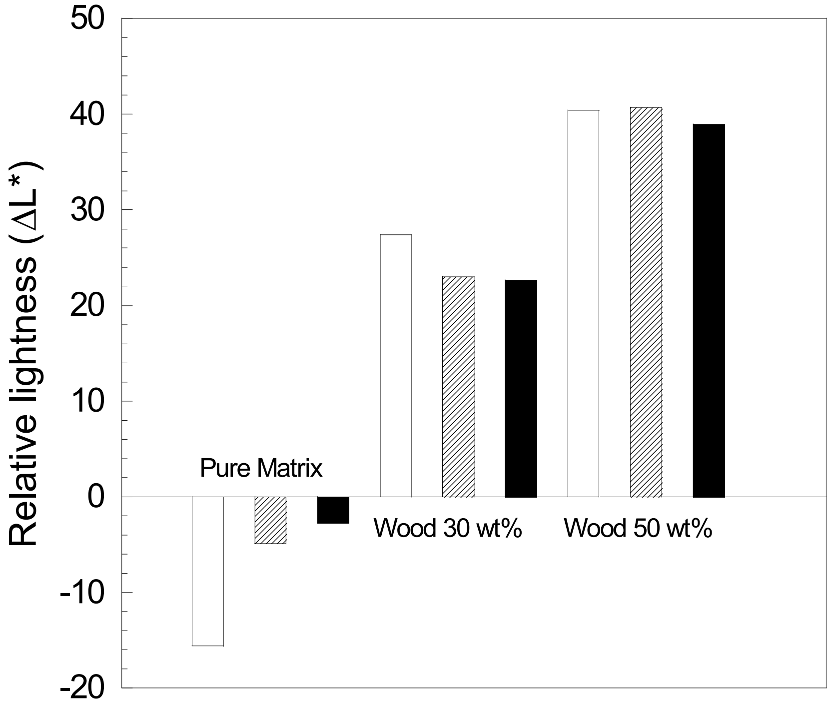


Figure 6.34: A change in relative lightness of the PVC/ABS blends and their composites at 30% and 50% woodflour loading after 50 days outdoor exposure.

The surface textures of 50 days weathering specimens were also characterized by optical microscope and SEM. The micrographs in Figure 6.35 revealed surface cracking of the matrix, possibly due to the photo-degradation of the polymer matrix itself and the mismatch of volumetric expansion of the woodflour and the polymer matrices. In Figure 6.36, the optical micrograph of PVC/wood composites at various content of ABS in the matrix at a fixed woodflour content of 30 wt% after 50 days weathering were illustrated. The results showed that unmodified-PVC/wood composites had more fading surface color than the PVC/ABS/wood composites at 70/30 or 50/50 compositions. This might be attributed to the more severe level of surface destruction occurred on the unmodified-PVC/wood composite specimen. Additionally, the impact fracture specimens were also characterized and the pictures were shown in Figure 6.37. The SEM micrographs showed the gap at the interfaces between the woodflour filler and the polymer matrix. It indicated that the gap between PVC/ABS blends and woodflour was wider than PVC/wood composite. In addition, the gap tended to be larger with increasing the ABS content in the blends. This was possibly due to the coefficient of thermal expansion of ABS was higher than that of the PVC used [54]. In summary, when focusing on the fading area, the pictures from optical microscope and SEM indicated that the fading of wood composite specimen occurred both from the photo-degradation and the expansion of woodflour leading to the matrix surface cracking.

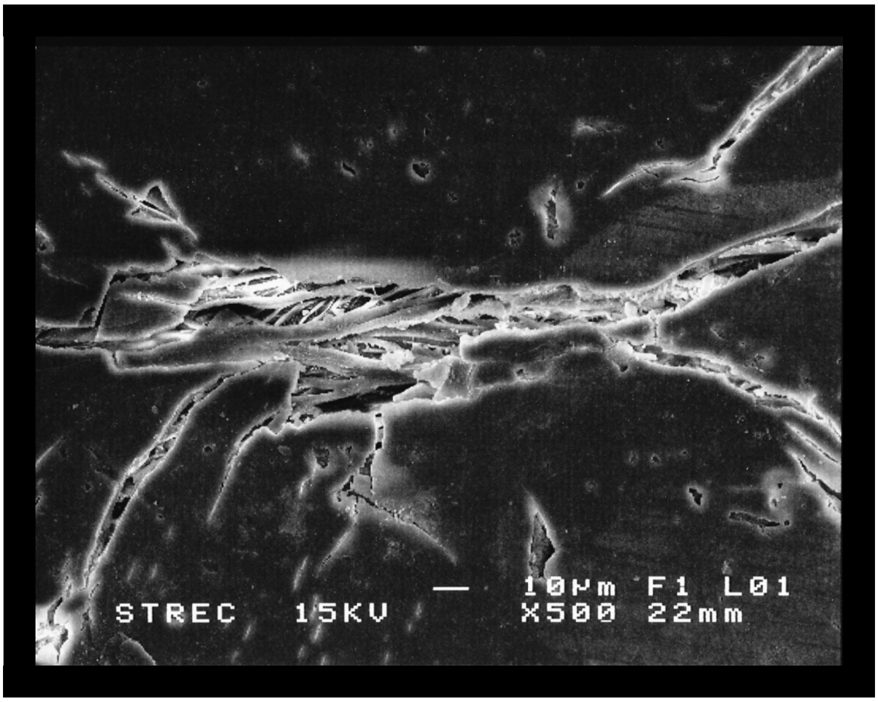
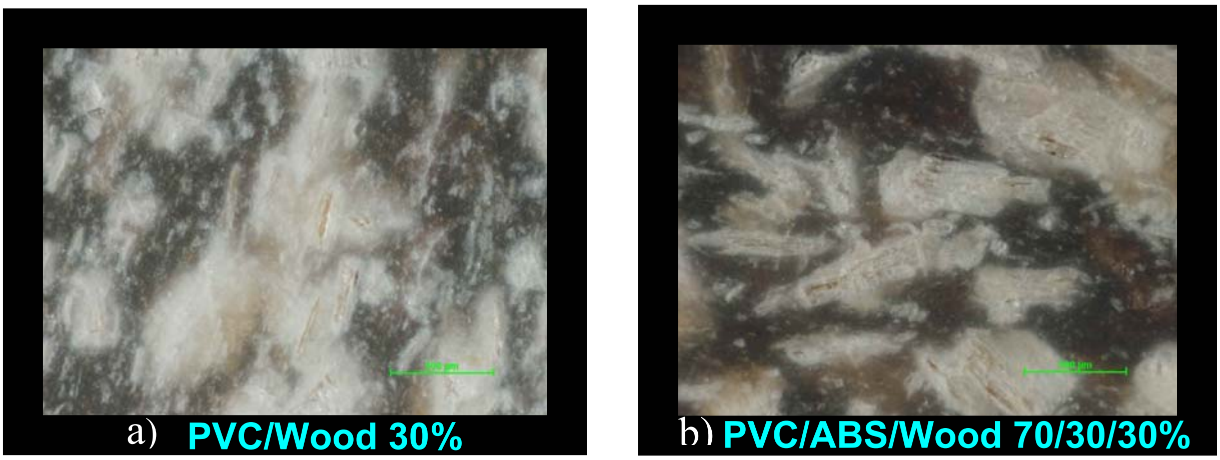


Figure 6.35: Scanning electron micrographs of the surface of the PVC/wood composite at 30 wt% woodflour content after 50 days exposure

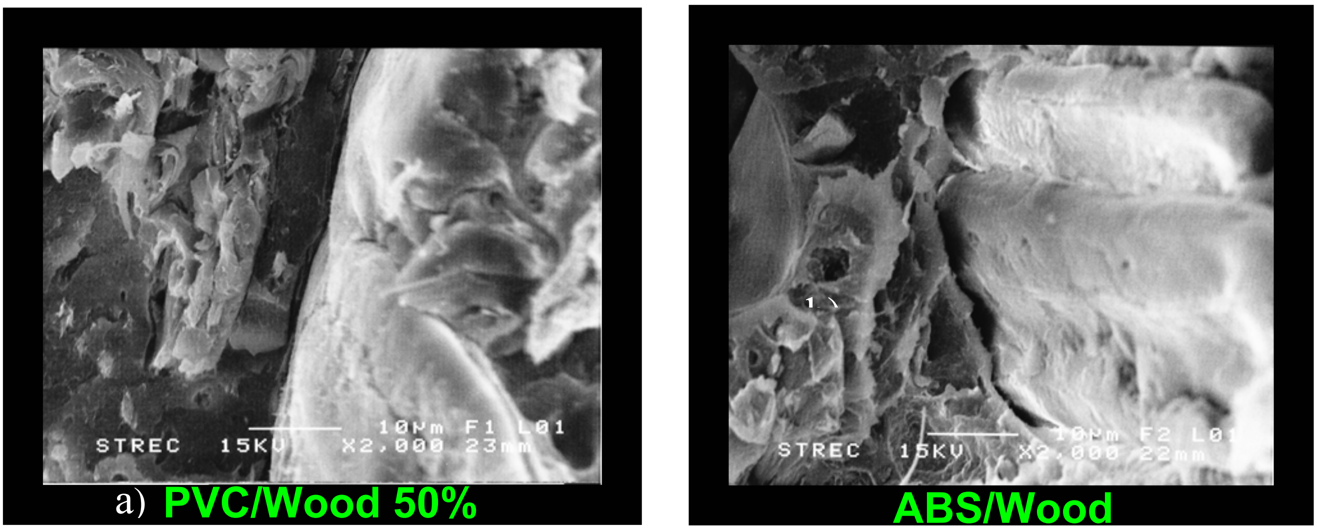


a) PVC/Wood 30%

b) PVC/ABS/Wood 70/30/30%

c) PVC/ABS/Wood 50/50/30%

Figure 6.36: Optical micrographs showed the surface of the specimens after 50 days exposure at a fixed 30 wt% woodflour loading with various matrix: a) PVC/wood composite b) PVC/ABS wood composite at 70/30 mass ratio c) PVC/ABS wood composite at 50/50 mass ratio



c)

Figure 6.37: SEM micrographs showed the interfacial adhesion between matrix and woodflour at 50 wt% woodflour loading with various matrix: a) PVC/wood composite b) ABS/wood composite c) PVC/ABS wood composite at 50/50 mass ratio.

PART TWO

Impact Property Enhancement of PVC-Wood Composites Using Acrylonitrile Styrene Acrylate

(31st August 2010 – 30th August 2011)

7. Introduction

7.1 General Introduction

Throughout history, wood has remained an important material because of its unique characteristics and useful properties. Virgin wood products are important materials used for the construction work. The ideal advantages of wood in building construction are low density, remarkable durability, dimensional stability, and hardness. The grain patterns and colors make it an esthetically satisfying material. In addition, wood has ability to resist oxidation, acid, saltwater, and other corrosive agents [55]. Despite the suitable properties for structural applications, their high water adsorption, thickness swell, and bio-deterioration have limited weathering use. To solve these problems, addition of thermoplastics to wood composites has an influence on ultimate properties of wood plastic composites (WPCs) [56].

WPCs are made by compounding cellulose fiber and plastic resin with other additives (lubricants, coupling agents, pigments, antioxidants, UV stabilizers, antimicrobial agent, etc.) and manufacturing in a process such as extrusion or compression or injection molding. WPCs possess the desirable properties of both wood and plastic. Generally, addition of wood to a thermoplastic matrix results in an increase in mechanical properties and thermal stability of composites, whereas the thermoplastic component contributes moisture barriers to the wood components, decreasing water adsorption and swelling characteristic [56]. Due to its competitive price, the absence of knots and splinters, acceptable mechanical properties, good durability, low maintenance, resistance to termites, and better fire resistance over traditional materials, wood plastic composites have become a large market volume of building products and one of the most rapidly expansion segments of the building products industry, especially for decking, railing, and related outdoor structures [1]. The WPC decking products have presented an annual growth sale at a blasting rate of over 30% per year over the last 10 years [57]. In 2006, WPCs were projected to grow at a rate of 23% in term of volume, approximately $1.2 billion in market [58]. By 2011, the market for wood composite decking is expected to exceed $2 billion, or a third of the overall decking market [59]. The two major factors of the existence of WPC materials are: (a) to make the composite material less expensive and (b) to obtain material with overall better properties compared to both neat plastic and wood [5]. Furthermore, the addition of wood fiber makes WPC having functions and appearance resemble to wood [8]. Nowadays, WPCs are widely used in decoration, building and construction such as decking, railings, fencing, landscaping timbers, cladding and siding, park benches, molding and trim, window and door frames, and indoor and outdoor furniture. Wood filled in WPCs can be particulate or fibrous shape. Particulates can be used to increase mechanical properties and reduce polymer material used. Fibers are used to increase stiffness and strength of the composite. Thermoplastics used in WPCs can be both amorphous and semi-crystalline structures which have melting or softening temperature less than the degradation temperature of wood (210°C) and at the same time having properties necessary for the WPC materials to pass the building standard [5]. This thermal criterion limits to polyolephins family such as polystyrene (PS), low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), and polyvinyl chloride (PVC) [56].

Polyvinyl chloride (PVC) is an important component of products which meet the demand of human needs. Because of its versatility, low cost, energy efficiency, and long life cycle, Polyvinyl chloride becomes appropriate products in so many applications especially in building and construction market [60]. PVC-based WPC is stronger and stiffer than polyethylene- and polypropylene-based WPC. Addition PVC is inherently flame resistant, PVC-based WPC also has ability in flame retardant. Key application of PVC-based WPC includes siding, window profile, deck, fence materials and floor coverings. Compared to other-based WPC, PVC has some inherent disadvantages. It has the high glass transition temperature which causes PVC brittle at ambient temperature [1]. To gain more flexibility and impact strength of Polyvinyl chloride, impact modifiers are used as additives for many applications.

Impact modifiers are rubbery in nature. They have a lower modulus than the host polymer. Adding impact modifiers as dispersed rubbery phase makes the polymer can absorb more impact energy. The dispersed rubber phase dissipates the impact energy in order to stop crack propagation. In order to reach the high impact performance, the rubber phase must be well dispersed and the impact modifier must be compatible with the host polymer. A variety of impact modifiers are available depending on the host polymer and the required properties. When choosing impact modifier, the balance of impact property, flow, stiffness, weatherability, toughness, thermal stability and cost, must be considered. Impact modifier market had globally volume about 540 million kg includes styrenic copolymer such as acrylonitrile butadiene styrene (ABS), acrylonitrile styrene acrylate (ASA), and methyl methacrylate-butadiene-styrene (MBS) as the largest volume about 45% of the market. Acrylics have about 30% of the market. Elastomers and thermoplastic elastomers make up about 10% of the market, and other types have the remainder. In the event of PVC-based WPC which always be used as construction materials, mechanical properties and weathering are guardedly considered [61]. Weathering is the tendency of materials to maintain impact and color when exposed to ultraviolet light. When the PVC-based WPC is used for long period in outdoor applications or under fluorescent light, photoyellowing or degradation of properties will occur. Discovering weatherable impact modifiers for PVC becomes more significant study. In comparison of the important impact modifiers for PVC, EPDM and acrylic modifiers are weatherable, while MBS and ABS are not. Although Acrylic modifiers are weatherable, they have poor low temperature impact resistance. Therefore, the preferable material for outdoor applications is ASA, which has higher weathering resistance than ABS.

Acrylonitrile styrene acrylate (ASA) is a styrene acrylonitrile copolymer modified with an acrylate rubber. It has mechanical properties similar to those of ABS in aspects of excellent resistance to ultraviolet light. ASA resins are widely used in industrial applications, for example, coating, adhesives, and paints. Furthermore, ASA can be blended with many polymers (such as PVC in this study) to make alloys and compounds obtain the benefit from ASA's weather and impact resistance [62]. Due to special acrylic ester rubber in the matrix, ASA resin provides resistance to UV radiation and atmospheric oxygen. Furthermore, under long period of exposure to UV, moisture, heat and impact, ASA shows very low level of yellowing and slightly decreases in toughness [63]. In recently, ABS copolymers are used as effective impact modifiers for PVC in many researches due to high thermal stability and superior impact resistance of the obtained blend. However, for outdoor applications, stabilized ABS still shows the decrease in impact strength after long period of exposure due to the presence of unsaturated structure, this problem can solve by using ASA copolymer that absences unsaturated structure in polymer chains.

In this research, the synthesis of PVC/ASA blends and their composites filled with woodfiber were carried out. The physical, mechanical, and thermal properties of the blends and composites were determined.

7.2 Composite Materials

Composites are considered to be the combination of materials which the components retain their characteristics in the composite on a macro scale. Each component must not dissolve or merge into each other completely, but they are addicted together by interaction force. The constituents of a composite may be found in various forms. In many of them, discrete units are embedded in and bonded together by a continuous matrix. In others the matrix may be discontinuous, as in the bonding layers of laminate. The composite may contain one or more types of discrete units, and they may be arranged in a regular repetitive pattern or their distribution may be random.

The major classes of composites can be classified as polymer matrix composites (PMCs), metal matrix composites (MMCs), ceramic matrix composites (CMCs), carbon-carbon composites (CCCs), intermetallic composites (IMPs). Wood plastic composite is one of the broad fields of polymer matrix composites [64].

7.3 Wood Plastic Composites

Figure 7.1: Wood plastic composites raw materials [65].

Wood plastic composites are the composites that contain wood (of any form) and either thermoset or thermoplastic polymer. Traditional wood products have a sensitivity to water adsorption (24-100 wt%) [1], thickness swell, high flammability (Limiting Oxygen Index: LOI=20-22) [2], and biodeterioration. To overcome the extreme moisture absorption in nature of wood, hydrogen-bonding sites must be limited. Adding thermoplastic to wood composites significantly affects on moisture behavior of the materials and results in extremely moisture resistance whereas, wood fillers improve strength and stiffness to wood composites.

WPCs are true composite materials and exhibit both properties of wood and plastic. The tensile strength of WPCs gradually decreased with the addition of wood fibers. In contrast, the tensile modulus increased with fiber addition [56]. The high moisture resistance of WPCs is a result of the composites structure. In WPCs, wood particles are completely coated by plastic as a thin layer. Moisture can only be absorbed into exposed part of wood and is not transmitted across the plastic layer. This result is that WPCs are extremely moisture resistance, have little thickness swell in water and do not suffer from fungal or insect attack. Wood content and particle size also influence on mechanical properties. Comparing fibers, particles, and flour, the strength reduction appears as the filler increase. Both strength and stiffness increase with increasing fiber length if adhesion between the wood and matrix is good. However effective dispersion is necessary when using wood fibers. Both flexure and tensile modulus increase with increase fiber loading [56]. As mentioned above, the properties of WPCs can meet the product requirements by varying the type and the level of wood or the type of plastic. Some properties of WPCs compared with virgin wood and plastic are summarized in Table 2.1.

Table 7.1 Combination of WPCs properties from wood and plastics [12].

Property	Wood	WPCs	Plastics
Humidity resistance	--	+	++
Maintenance free	--	++	++
Elaborate design	--	++	++
Rigidity	++	++	-
Impact resistance	++	--	+
Aging	--	-	++
Fire properties	-	+	++ (PVC)
Cost	+	+	-

* (++) excellent, (+) good, (-) poor, (--) bad

Since the invention of polymers, wood fiber has been compounded with polymers to improve performance. Beginning in the early 1900s, the first commercial composite marketed under the trade name Bakelite was composed of phenol-formaldehyde and wood flour [66]. Interestingly, in this composite in the United States during the mid-1980s was desired to develop materials from renewable sources due to a strong environmental concern. First, wood plastic composites were a combination of recycled wood flour or chips and binders then the new generation has rapidly developed to obtain good mechanical properties, high dimensional stability, and can be produced more complex shapes. Resins used in manufacturing these composites include polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyvinyledene fluoride (PVdF), polyphenylene oxide (PPO), polybutylene terephthalate (PBT), acrylonitrile-styrene-acrylate (ASA), acrylonitrile-butadiene-styrene (ABS), polycarbonate (PC), and others [67].

The applications of WPCs are largely in finished products such as door frames and components, window frame and components, exterior cladding, decking, docks and railing, skirting boards, stairs and hand rails, fencing and fence posts, garden furniture and architecture, and office furniture

7.4 Plant Fiber

Wood is a tree-dimensional biopolymer composite that is composed of cellulose, hemicelluloses, lignin, and minor amounts of extractives. In general, the coniferous species (softwoods) have a higher cellulose content (40–45%), higher lignin (26–34%), and lower hemicellulose (7–14%) content as compared to deciduous species (hardwoods) (cellulose 38–49%, lignin 23–30%, and hemicellulose 19–26%) [68]. Table 2.2 lists the composition and major functions of these constituents. The mechanical properties of plant fibers are lower when compared to other inorganic fibers. However, because of their low density, the specific properties such as strength and stiffness of plant fibers are comparable to those of inorganic fibers. Moreover, plant fibers are nonabrasive to mixing equipment, less concern to health and safety during handing than other fibrous materials. Additionally, the biodegradability and the price of plant fibers are very attractive in large volume engineering markets such as the automotive and construction industry.

Table 7.2 Composition of wood [67].

Component	Composition (wt%)	Polymeric Nature	Water Affinity	Role
Cellulose	44%-50%	Linear, crystalline	Hydrophilic	Strength
Hemicellulose	20%-25%	Branched, amorphous	Hydrophilic	Bind microfibrils, structural reinforcement
Lignin	20%-30%	Amorphous	Hydrophobic	Stiffness
Extractives	0%-10%	Polymeric	Hydrophobic	Encrusting

7.4.1 Plant Fiber Composition and Structure

Cellulose

Cellulose is the primary component of the cell wall. Structure of cellulose is a linear chain of 1,4-β anhydroglucose units, which contain alcoholic hydroxyl group (Figure 7.2). Cellulose molecules are completely linear and can form intermolecular and intramolecular hydrogen bonds with macromolecule itself and also other cellulose or polar molecules. This bonding results tightly packed crystalline structure of celluloses called microfibrils. Most of the noncrystalline cellulose and the surface of crystalline cellulose are accessible to water, while the rest of the crystalline is nonaccessible. Although the chemical structure of cellulose from different natural fibers is the same, the degree of polymerization (DP) varies. The mechanical properties of a fiber are significantly dependent on the DP. Native cellulose is resistant to strong alkali but is easily hydrolyzed by acids to water-soluble sugars. Cellulose is relatively resistant to oxidizing agents. It can retain its properties to 190ºC and loses about 10% of its strength when exposed for 10 min at 200ºC.

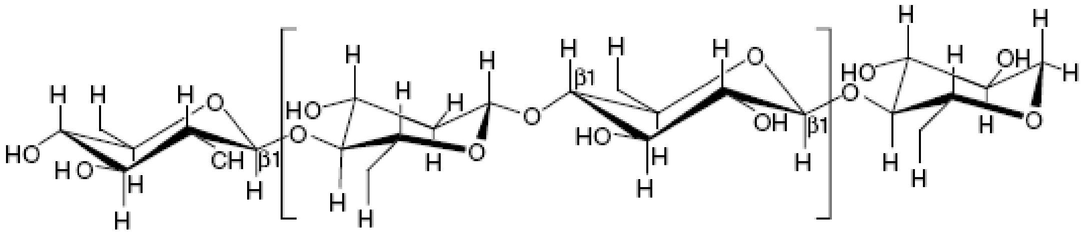


Figure 7.2: Structure of cellulose [69].

Hemicellulose

The content of hemicelluloses in wood is approximately 30% of the total mass of cell wall. Hemicellulose is a short chain with a degree of polymerization in the low hundreds and so is a low-molecular-weight (LMW) polymer. It primarily serves as connecting agent that links or bonds the microfibrils providing additional structural reinforcement to the wood fiber cell wall. It varies from relatively unbranched, alkali-resistant species to relatively nonlinear, soluble type. The nature and proportions of hemicellulose found in different wood varies but tends to follow broad consistent patterns.

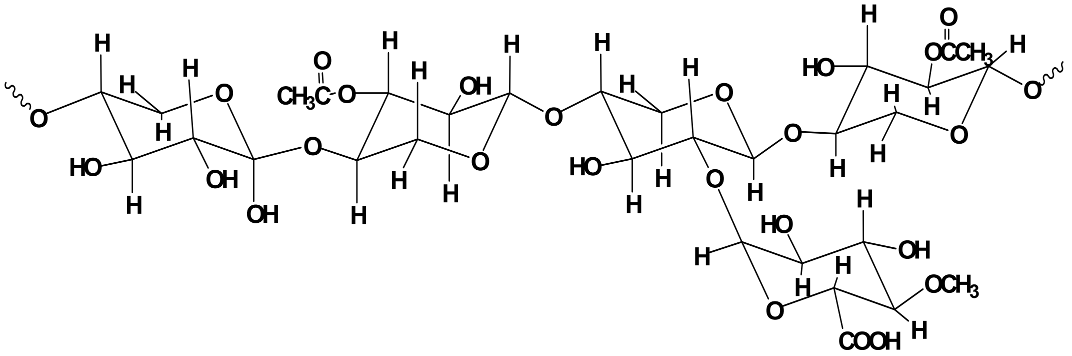


Figure 7.3: Structure of hemicellulose [69].

Lignin

The lignin content of hardwoods is usually in the range of 18–25%, whereas the lignin content of softwoods varies between 25 and 35%. Lignin is the compound that gives rigidity to the plants. Lignin structure is a three-dimensional copolymer of aliphatic and aromatic constituents with apparently no ordered arrangement. It is characterized by high carbon but low hydrogen content. Hydroxyl, methoxyl, and carbonyl groups have been identified. Lignin has been found to contain five hydroxyl and five methoxyl groups per building unit. It is believed that the structural units of a lignin molecule are derivatives of 4-hydroxy-3-methoxy phenylpropane. Lignin is amorphous and hydrophobic in nature. It is a thermoplastic polymer, exhibiting a glass transition temperature of around 90°C and beginning to soften at temperature 165-175°C. It is not hydrolyzed by acids, but soluble in hot alkali, readily oxidized, and easily condensable with phenol.

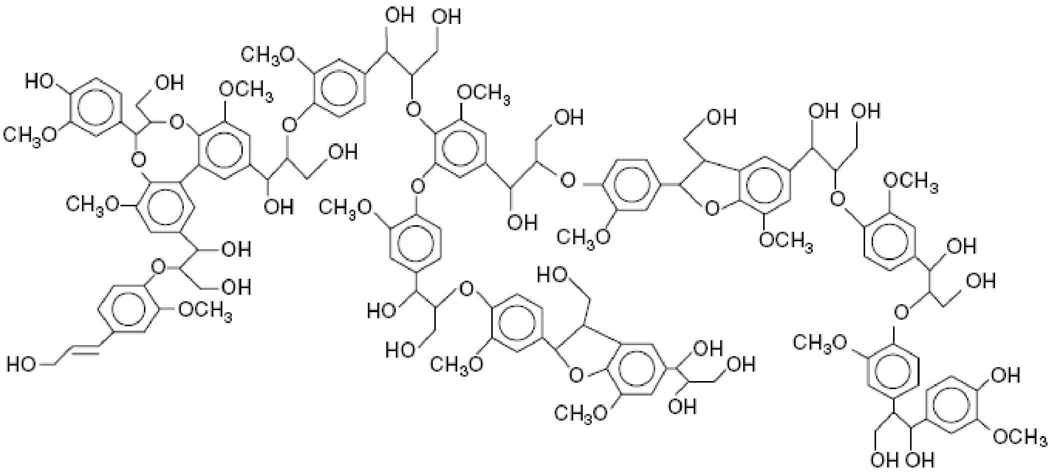


Figure 7.4: Structure of lignin [69].

7.4.2 Coconut (*Cocos nucifera*) Fibers

Coconut or coir fibers are fruit fibers obtained from the fibrous husk covering coconut fruits. The term *coir* is derived from kayar, a rope or cord. Production areas of coconut fruits are mostly found along the coastal regions in the wet tropical areas of Asia such as in the Philippines, Indonesia, India, Sri Lanka, Malaysia, and Thailand. On average, 7.5-8.2 kg of coir fiber can be obtained from 100 coconuts. The color of coconut fibers ranges from reddish-brown for fibers obtained from ripe nuts to golden yellow from not completely ripened nuts, which permit better grade coconut fibers. Typical properties of coconut fibers are listed in Table 7.3.

Table 7.3 Typical properties of coconut fiber [69].

Property	Coconut Fiber
Density (g cm 3)	1.15-1.46
Diameter (μm)	100-460
Tensile Strength (MPa)	131-220
Young’s Modulus (GPa)	4-6
Elongation at Break (%)	15-40

Figure 7.5: Coconut tree in Thailand.

Due to high content (40-50%) of lignin (but low in cellulose (32-43%)), coconut fibers are flexible, strong, and highly durable. Coir is one of the toughest plant fibers available. It is highly abrasion and fungal and bacterial resistant. Furthermore, coconut fiber is naturally insulating, sound absorbing, and difficult to ignite [69].

7.5 Polyvinyl chloride (PVC)

7.5.1 What is PVC?

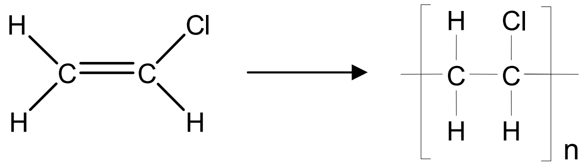


Figure 7.6: Polymerization of vinyl chloride monomer [70].

Poly(vinyl chloride) (PVC) is a polymer prepared from vinyl chloride monomer (VCM). It practically comes in two main sizes depending on production process. Worldwide, PVC manufactured by the suspension method is about 70%, 20% of it is produced by emulsion method, and others are produced by bulk and solution polymerization. Suspension polymerizations give 100-180 μm of particle size, whereas the emulsion polymerization gives latex of particle size 0.1-3.0 μm [70].

(a) (b)

(a)

Figure 7.7: a) PVC resin and b) PVC compound [71,72].

PVC is one of the most widely used thermoplastics. It contains chlorine atom which imparts a strongly polar to the PVC polymer chain, and the essentially syndiotactic conformation of the repeating unit in the chain leads to a limited level of crystallinity. With the reasons above, PVC has good mechanical properties. It is very durable, abrasion and moisture resistant, withstands corrosion, and has excellent fire resistance properties. Moreover, it is cheap, and lightweight. PVC resin can be also combined with many additives and modifiers.

These make PVC able to be used either in rigid compounds or plasticized PVC. Rigid PVC is mostly used in building and construction applications such as pipe siding, window profiles. For flexible PVC, the range of physical properties varies widely, depending on the plasticizer content. A PVC compound may contain, besides the polymer, the following ingredients: stabilizers, plasticizers, lubricants, fillers, and processing aids.

Figure 7.8: PVC products [73,74].

The main disadvantage of PVC is its low heat resistance. Additive-free PVC can degrade easily when exposed to heat or ultraviolet light. Degradation of PVC occurs by elimination of hydrogen chloride accompanied by the generation of conjugated double bonds, called polyenes. This degradation process mainly causes discoloration, deterioration of mechanical properties, and lowering of the chemical resistance. Degraded PVC is a brittle red-brown material unsuitable for any further use. The dark color caused by the relatively high visible light absorption coefficients of the polyenes. In order to use in practical applications, stabilizers are applied to provide the necessary protection against heat, light and weathering [75].

7.5.2 Polyvinyl chloride as Wood Composite Matrix

PVC is one of the most widely used plastic in many applications including pipes, electric wires, window profiles, and siding. Recently, PVC based WPC becomes more attractive because of it acceptable mechanical properties, moisture and fungus resistance, durability, wood-like appearance, and recyclability [76].

One of beneficial properties of PVC is that it is inherently flame resistant. Flame spread index for a PVC-based WPC is obviously low when compared to HDPE- based WPC. Rigid PVC is stronger and stiffer than polyethylene and polypropylene. Flexural modulus and compressive strength of PVC is also higher compared to polypropylene and HDPE. Moreover, PVC is cost effective than the others [1]. Some weakness of this material includes low impact strength and thermal stability, and narrow processing temperature. PVC-based WPC make 4% of decking and 22% of railing products [1].

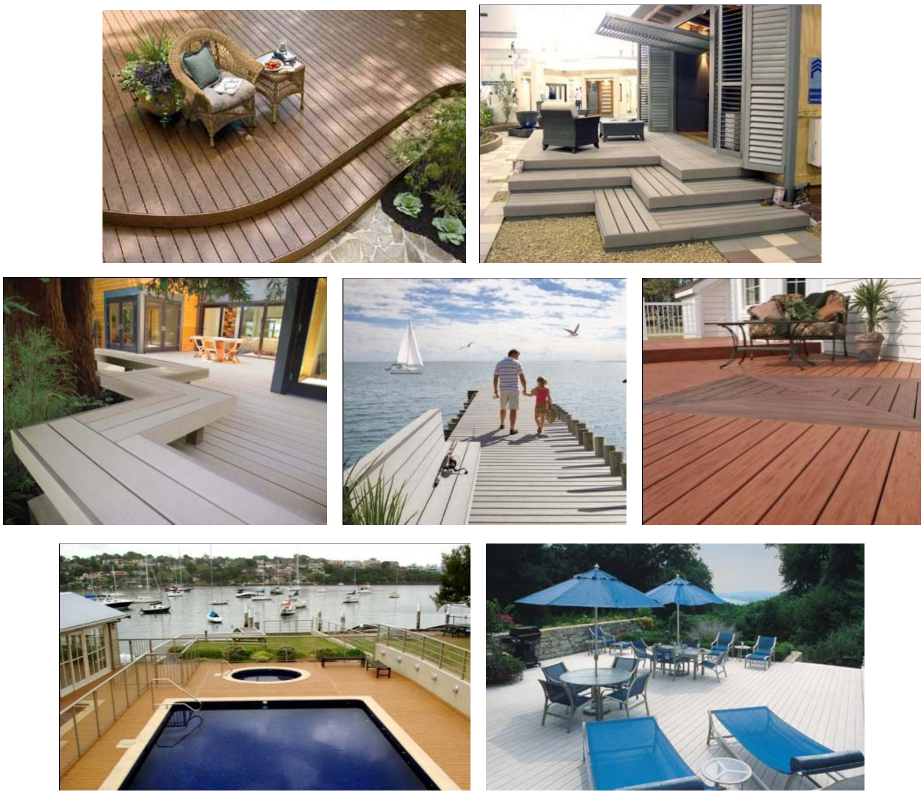


Figure 7.9: Wood plastic composite products [77].

7.5.3 Suspension PVC Resins

Suspension PVC particles are complex and irregularly shaped with the length of diameter about 100-150 microns. The substructure of the suspension PVC grain presented in Figure 2.10 consists of agglomerates, domains and microdomains. This combined structure results in porosity that allows low-melting additives to penetrate into the grain in a compounding process. Typical applications include injection molding, extrusion, extrusion blow molding, and calendaring.

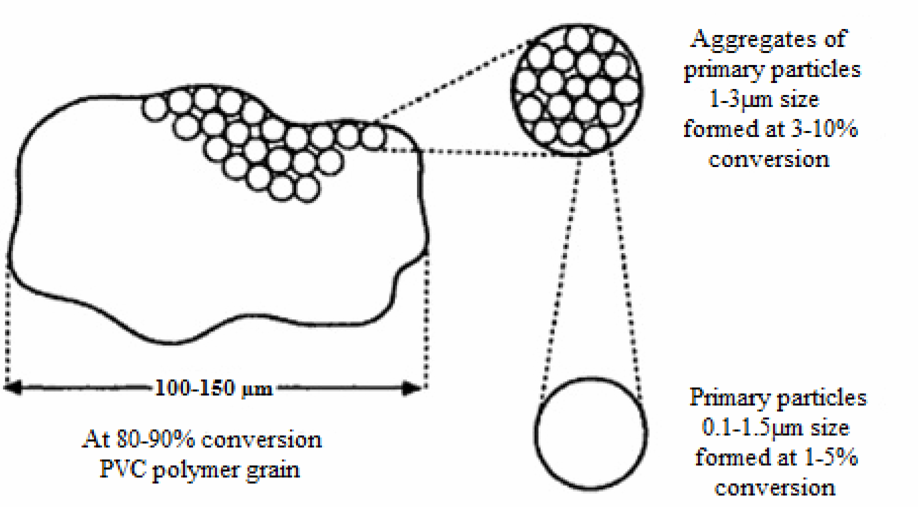


Figure 7.10: Structure of a suspension PVC particle [75].

Siamvic 258 RB, a suspension PVC type produced by Public Company Limited, is used as PVC resin in this study. Siamvic 258 RB is a low K value resin suitable for rigid PVC processing such as good thermal stability, good initial color, no tendency to stick on hot metal surface, and very low level of fish-eyes. Moreover, it generates very low dust during transportation and pneumatic filling of silos, suitable for dry blend preparation providing a regular feed to processing engines, and it is easy to process even at low temperature [22]. Some properties of the Siamvic 258 are listed in Table 7.4.

Table 7.4 Characteristics of suspension PVC resin (Siamvic 258 RB) [22].

Characteristic	Unit	Value (*)	Standard
Viscosity index	ml/g	82	ISO 1628-2
K-value (cyclohexanone)	-	58	DIN 53726
Polymerization degree	-	680	JIS K6721
Bulk density-compaction	kg/l	0.56	ISO 1068
Volatile matter	%	≤ 0.3	ISO 1269
Particle size (sieve analysis)	micron	120-150	ISO 1624

(*) In the case of certain characteristics the values given in this table are means based on a large number of individual measurements distributed around the means in a range corresponding to the normal manufacture and measurement tolerances. These values should not be considered as specifications.

7.5.4 PVC Additives

Due to its versatility, PVC has been successful as a commodity thermoplastic, whether for use as flexible PVC, or in a rigid moulding application. Many different types of additives are incorporated in to PVC compound to improve physical, mechanical, and chemical properties for particular application such as highly wood plastic composite.

Heat stabilizers

Due to the low thermal stability of PVC, heat stabilizer is the most essential additive in PVC compounds. Heat stabilizers are used to prevent oxidation of PVC by heat during processing and also in application. This results in improving its resistance to discoloration during processing, and helps maintain physical properties of the end product. Decomposition of PVC occurring either in the presence or absence of the stabilizer is initiated by heat, light, and mechanical stress to form alkyl radicals. The free radicals can react to cause the polymer to degrade, causing embrittlement, melt flow instability, loss of tensile properties, and discoloration. Once the degradation called the dehydrochlorination mechanism is initiated, the progressive unzipping of neighboring chlorine and hydrogen atoms can occur along the polymer chain. The consequence is the formation of allyl chloride structure which in turn is catalyzed by release of HCl. The change of PVC color is caused by the formation of conjugated double bond during this process [75]. There are a number of different types of heat stabilizer systems for PVC, depending on the type and products of oxidation. Metallic salts were originally used to stabilize PVC, the most common being based on barium, cadmium, lead, or zinc, often mixed together to obtain a synergistic effect. Organometallic compounds are also used, mainly based on tin. A third group is non-metallic organic stabilizers, in which phosphites play an important role, improving transparency, initial color, and light fastness [78].

Lubricants

Rigid PVC are highly viscous in the melt phase, and has a tendency to stick to the hot metal surfaces of processing equipment which can cause heat buildup, high torque on the screws, and high energy consumption. To overcome these problems, lubricants are incorporated into PVC. Lubricants are usually classified as external or internal. External lubricants are largely insoluble in PVC. They work externally by migrating to the surface of the polymer melt during processing and lubricating the melt from the metal of the processing equipment. Internal lubricants are mostly soluble in PVC. They work internally by lubricating the movement of PVC molecular chains past one another during processing.

However, most lubricants have some combination of both external and internal characteristics. An incorporation lubricant into PVC results in reduced shear, reduced equipment wear, increased production rates, and reduced energy consumption [79].

Processing aids

Processing aids are used as additives to facilitate the melt processing of PVC. During processing, the processing aids adhere to the PVC grains increasing the efficiently of forces transmitted to the grains. This results in less breakdown of the grains into primary particle units and a more homogeneous melt. In general, processing aids are compatible and easily entangle with PVC. Due to their long chains, processing aids can interact with PVC to produce a stiffer and more elastic melts. Increased rupture stress and extensibility are provided by the addition of processing aids, which makes PVC melts more resistance to rupture, prevents the surface of PVC melt from tearing as it exits the die [19].

7.6 Acrylonitrile Styrene Acrylate (ASA)

Acrylonitrile styrene acrylate (ASA) resin is one of the styrenic copolymers used for housings, covers and other applications which require excellent surface feature and outstanding weatherability combined with high impact resistance and stiffness. ASA is composed of a poly(styrene acrylonitrile) matrix modified with small rubber particles. Its structure is typically core-shell structure modifier with a cross-linking polyacylate (usually poly(butyl acrylate)) core and a grafted styrene-acrylonitrile shell acting as compatilizers between the rubber particles and the PSAN matrix in the ASA resin. Architecture and morphology of acrylonitrile styrene acrylate are exhibited in Figure 7.11 and Figure 7.12 respectively.

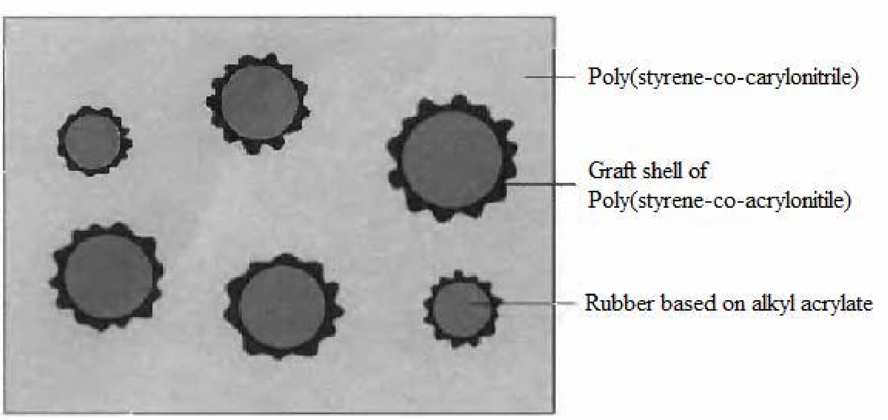


Figure 7.11: Architecture of acrylonitrile styrene acrylate [80].

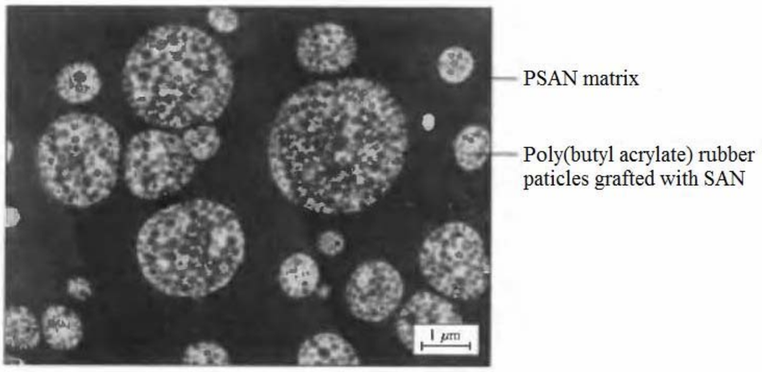
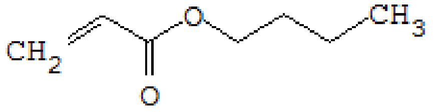
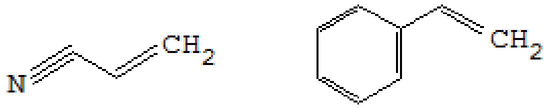


Figure 7.12: Transmission electron micrograph of ASA [80].

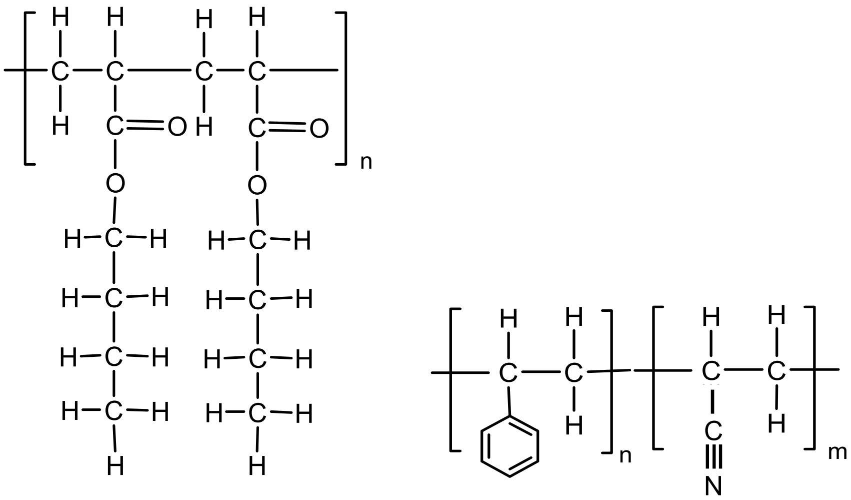
Polybutylacylate is transparent, chemical, and weather resistant materials. Polyacrylate or acrylic elastomer characterizes in heat resistance and oil resistance. It can retain its properties at a temperature of 170-180°C under dry air or in oil. Due to its saturated chain, acrylic rubber also has excellent weatherability and ozone resistance [81]. Styrene acrylonitrile copolymer is inherently transparent polymer, with high heat resistance and excellent gloss and chemical resistance. Moreover, it has a good hardness, rigidity, dimensional stability, and relatively high tensile and flexural strengths. When SAN is grafted on the poly(butyl acrylate) backbone, ASA has the useful SAN properties o and solvents, while the elastomeric component contrib y of withstanding the environmental conditions [70].



Butyl Acrylate



(a) Acrylonitrile Styrene



(b) Poly(butyl acrylate) Polystyreneacrylonitrile

Figure 7.13: (a) Monomer of ASA, (b) Poly(butyl acrylate) and Polystyreneacrylonitrile.

In comparison with ABS, the double of polybutadiene incline to oxidation and crosslinking due to oxygen, UV radiation or heat. This results in deterioration of the rubber, leading to loss of impact strength and discoloration. In contrast, the butyl acrylate rubber of ASA is free of double bond which gives ASA clear advantages in terms of weatherability and resistance against heat aging (Figure 7.14). Further advantages of ASA over ABS are its better chemical resistance and higher resistance against environmental stress cracking, especially against alcohols and many cleaning agents

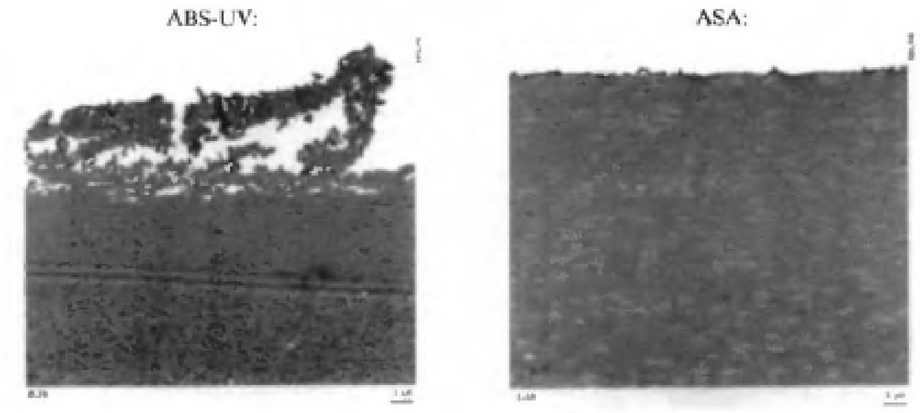


Figure 7.14: Electomicrographs of a cross-section perpendicular to the exposed side of ABS and ASA after 500 hrs of UV exposure (Xenotest, ISO 4892-2A) [80].

ASA also exhibits advantages over other thermoplastic housing materials such as polycarbonate, PBT and polypropylene. The low moulding shrinkage of ASA and of PC is advantageous for housings and covers, because warpage problems are almost nonexistent with these products. However, PC has only a limited resistance against environmental stress cracking, for example by alcohols and cleaning agents, and it yellows much more than ASA during outdoor exposure. Compared with polypropylene, a material widely used because of its low price, ASA has advantages in terms of stiffness, impact strength, heat distortion temperature, and weatherability. Further, owing to its high moulding shrinkage, polypropylene has a high tendency to warp during or after processing, and it is much more sensitive to scratches than ASA. Thus, because of its superior physical properties, and because it can be easily processed by injection moulding or extrusion, ASA has widespread use and can be found in a large variety of applications [80].

Owning to its favorable combination of properties, ASA has become an important plastic material. Now it is being used for many interior and exterior applications. The largest area of application for ASA is the automotive sector. Almost all automotive manufacturers use ASA for unpainted exterior parts such as mirror housings, radiator grills, cowl vent grills and pillar covers. A further important field of application for ASA is the household sector. Typical applications include housings and covers for sewing machines and kitchen appliances, garden equipment such as lawnmower housings, and parts for lawn and garden. In the building sector, ASA has found various applications such as window frames and sanitary equipment [80].

Figure 7.15: ASA applications.

In this work KIBILAC PW-997S, ASA extrusion grade, was being used. PW-997S is suitable for extrusion applications, which is used in constructions and automobiles. The properties of PW-997S are listed in Table 7.5.

Table 7.5 Typical properties of PW-997S [82].

Properties	**ASTM Test Method**	**Unit**	**PW-997S**
Tensile Strength at 1/8”,6 mm/min	D638	kg/cm^2 (lb/in^2)	450 (6380)
Flexural Strength at 1/4”,2.8 mm/min	D790	kg/cm^2 (lb/in^2)	660 (9330)
Izod Impact Strength at 1/8”,23ºC	D256 (Notched)	kg-cm/cm (ft-lb/in)	40 (7.4)
Melt Flow Index at 220ºC,10Kg	ISO1133	g/10min	4
Gloss	D525	%	93
Specific Gravity at 23ºC	D792	-	1.07
Vicat Softening Temp at 1/8”,50ºC/hr	D1525	ºC(ºF)	105(221)
H.D.T at 1/4”,120ºC/hr	D648	ºC(ºF)	85(185)

The data are intended as a general guide only and do not necessarily represent results that may be obtained elsewhere.

7.7 PVC/ASA Blends

Most of ASA produced is used for blending with a lower cost PVC resin. The blend is used in profile extrusions and coextrusions. Application of ASA/PVC blend is siding, mobile home skirts, window profiles, vending, automotive exterior trim, etc. This blend results significantly better impact strength, better heat distortion temperature and better color retention than PVC. In addition, the blend has cost advantages over the neat ASA. Typical properties of ASA/PVC blends are shown in Table 7.6.

Table 7.6 Properties of PVC/ASA blends [83].

Properties	**ASTM Test Method**	**Unit**	**GELOY 1220 GEC**	**SUPREL 9301 Vista**
Density	D792	kg/m^3	1200	1200
Water Absorption, 24 hrs	D570	%	0.1	
Flexural Modulus	D790	MPa	2140	2760
Flexural Strength	D790	MPa	60	
Tensile Strength at Yield	D638	MPa	46	43
Elongation at Break	D638	%	25	
Rockwell Hardness	D785		R96	R106
Notched Izod Impact, at 23°C	D256	J/m	1080	425
Heat Deflection Temperature, at 1.82 MPa	D648	°C	76	76

7.8 Principles of Toughening

7.8.1 Toughening Mechanisms

In a polymer science context, toughness is defined as the ability to resist fracture by absorbing energy. It is usually expressed in terms of the work done in a unit area of fracture surface. Several thermoplastics, both of the commodities kind [polystyrene (PS), polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), polypropylene (PP), polyvinylchloride (PVC) etc.] and engineering polymers [polyamides (PA), polyesters (PE), polycarbonates (PC), polyimides (PI), and etc.] exhibit glass transition temperatures (T_g) higher than or close to room temperature. As a result, at room temperature, they exhibit the shortcoming of brittle impact behavior, which limits their commercial end-uses. To overcome this problem, suitable rubber modifiers are added into the homopolymer matrices. These will induce locally diffused microscopic mechanisms of deformation, and make the matrix capable of dissipating large impact energies without catastrophic failure. In general impact modifiers have some required characteristics such as a sufficiently low Tg, of elastomeric behavior at room temperature, optimum particle size with a suitable particle size distribution, a homogeneous dispersion and a good adhesion to the thermoplastic matrix. Well dispersed rubber particles are able to induce in the thermoplastic matrix different mechanisms of toughening include crazing, shear yielding, and combination of crazing and shearing yielding.

Crazing

Rubber particles, with an optimum size, homogeneously dispersed in a very rigid matrix (brittle amorphous polymers, such as PS and SAN) can enhance capable of dissipating impact energies to the matrix, this results in a multicraze initiation and termination mechanism. Within the matrix, crazes initiate occurs at the rubber particle equators where a very high stress concentration is built up. Through the application with an external load, they undergo propagation and the termination occurs when they impinge upon neighboring rubber particles. The microcrazes, diffused throughout the deformation zones of the body, are perpendicular to the direction of the applied stress and are accompanied by a marked stress whitening effect. A craze is similar to a microcrack but differs in being bridged across by several microfibrils, made by oriented polymer chains, which can maintain a certain load. The molecular weight of the matrix is an important parameter for crazing. Below a critical molecular weight, no chain entanglements, no stable crazes can be formed. The fracture under a sufficiently high load is determined by the rupture of the craze fibrils, once a crack of critical size has been developed [84].

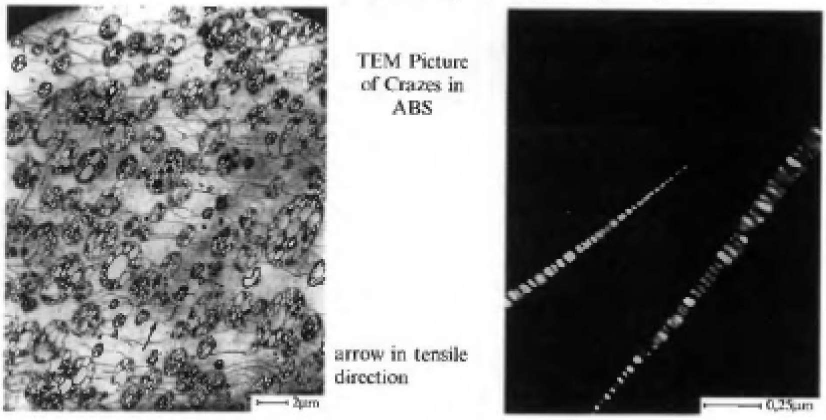


Figure 7.16: Transmission electron micrographs picture of crazes in ABS [80].

Shear yielding

In homogeneous polymers shear deformation consists of a distortion of the body shape without significant volume change. In semi-crystalline materials shear yielding is localized and occurs by slip on particular planes of maximum shear stress. In non-crystalline materials the shear yielding is much more scatter than in the previous case, requiring large co-operative chain movements. In toughened materials a diffused shear yielding is the main energy dissipation phenomenon, preceded or followed by rubber particle cavitation (the particle must be very small, of sub-micron sizes). Particle cavitation induces a stress whitening effect, visible along the largest deformation patterns of the body. Semi-ductile polymer matrices, such as PVC, ABS, ASA, PC, and PA undergo diffuse shear yielding [84].

Crazing and shear yielding

Crazing and shear yielding occur in most cases simultaneously and the differences in behavior. In HIPS, crazing predominates over shear yielding, whereas in ABS or PVC both phenomena coexist. Moreover their relative significance depends on variables such as: temperature, strain rate, matrix nature and composition and others. An effective interaction exists between the two mechanisms: the molecular orientation within a shear band, roughly parallel to the applied stress, is perpendicular to the plane of the crazes. This induces a synergistic effect by which shear bands can stop the craze propagation, increasing the material toughness [84].

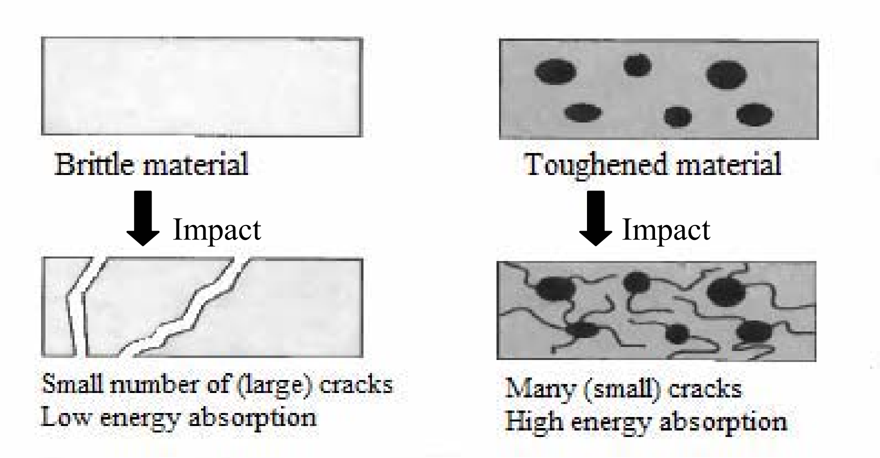


Figure 7.17: Formation of crazes after impact [80].

7.8.2 Core-Shell Impact Modifiers

Core-shell impact modifiers have commercially been used as PVC impact modifiers since 1958. A major distinction of core-shell impact modifiers from other types of impact modifiers is that their size is set during the production process and exists the same size after they are dispersed in a host matrix.

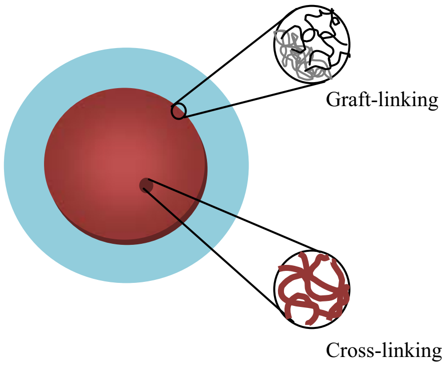


Figure 7.18: Diagram of typical core-shell modifier particle [85].

The architecture of core-shell polymers is described schematically in Figure 7.16. The core of these polymers made up of rubbery polymer whereas surrounding shell is rigid polymer that is grafted to the core. The materials commercially used as the rubbery core are poly(butyl acrylate) (PBA) or poly(butadiene). This center of the particles provides the soft second phase that induces toughening. The shell of the particles consists a glassy polymer which has a much higher glass transition temperature (T_g) than that of the core. The primary benefits of shell polymer are hard coating that keeps the rubbery core from adhering together and acting as an intermediate that merges the rubber core to the matrix. A key factor in the performance of core-shell impact modifiers is their adhesion to the matrices in which they are dispersed. A low value of the interaction parameter, indicative of miscibility, and also translates into effective toughening.

Major factors in core-shell toughening

Particle size: As a general rule, brittle glassy matrices that tend to craze benefit more from large rubber particle size. On the other hand, matrices that can absorb fracture energy via shear yielding are effectively toughened with relatively small-particle-size modifiers. Emulsion polymerization lends itself to the preparation of small particles, and therefore, core-shell polymers are more often used in shear yielding matrices, such as PVC and engineering thermoplastics.

Glass transition temperature: Maintaining a consistent T_g in the polymer core as well as in the shell is one of the key factors that determine the quality of an impact modifier. As a general rule for core-shell particles, rubber cores with lower glass transition temperatures induce better toughening at lower temperatures. A hard shell is grafted onto the latex particles to help isolation and provide compatibility with the host matrix.

Adhesion: The lack of miscibility of the most widely available PMMA or styrenic shells with engineering resins has prompted the need to use alternative strategies to enhance the dispersion and adhesion of core-shell particles in these types of polymers. The most well-known method is to take advantage of the end groups present in engineering polymers. Another option for enhancing the adhesion between the matrix and the shell is to add a compatibilizing agent, which is well-documented method [85].

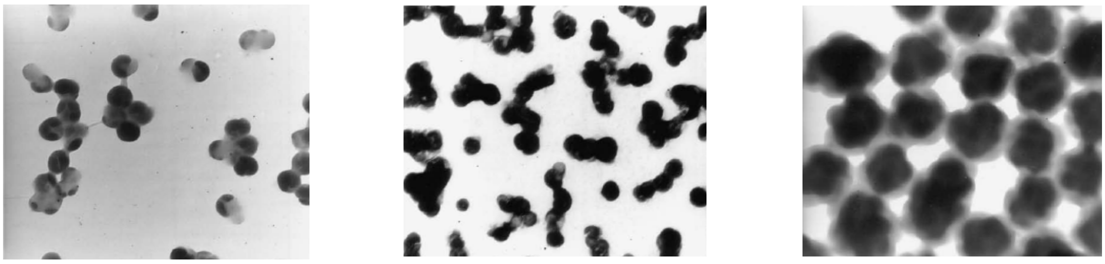


Figure 7.19: TEM micrographs of ASA latex particles prepared using different surfactants [62].

In rubber toughened plastics, the rubber particles constitute the dispersed phase in the polymer matrix. Their essential role is to act as a stress concentrator. When the toughened material is subjected to stress, the localized stress experienced by the matrix in the immediate vicinity of a rubber particle is magnified by the local stress concentration effect. The matrix will yield locally in response to this localized stress field, thus avoiding a global brittle catastrophic failure of the material. The concentration of stress that initiates the local yielding in the matrix is just the first step in a complex process; if the overall applied stress is increased further the matrix then continues to deform by shear yielding or crazing. Shear yielding involves the creation of bands of highly oriented, stretched material at 45 ° to the direction of the applied stress. Crazes are cracks, spanned by elongated fibrils of the material which can carry load and thus maintain the structural integrity of the material [86].

8. Literature Reviews

Megeloglu F., Matuana L. M., and King J. A. [9] analyzed the effects of types and levels of impact modifiers on the mechanical properties of rigid PVC/wood-fibers composites. The composites with impact modifier varied from 5 to 20 phr were used to investigate. Figure 8.1 indicates the effects of types and impact modifier contents on Izod impact strength of PVC/50 phr wood fiber composites.

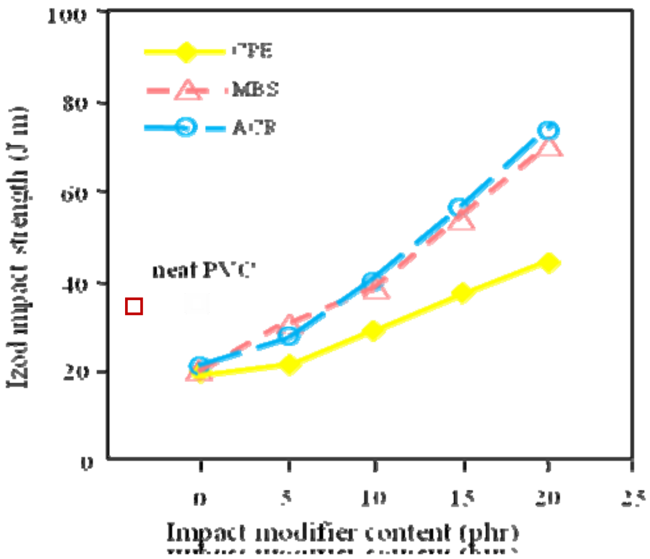


Figure 8.1: Effects of impact modifier types and contents on the impact properties of rigid PVC/wood-fiber composites [9].

First, without impact modification, it is found that introducing wood fiber to PVC matrix results in a lower performance of absorbing impact energy. As a consequence, each fiber in composite acts as a discontinuity capable of initiating cracks in PVC/wood composite. When introducing the impact modifiers to the matrix, the Izod impact strength of composites increases with the modifier content. Impact modifiers in rigid plastic act as an adhesive between PVC particles; this inhibits the matrix from brittle crack propagation. Moreover, in consideration of the effects of impact modifier types, cross-linked modifiers (MBS and all-acrylic) were able to improve more Izod impact strength in the composites than uncrosslinked modifier (CPE). That is attributed to the fact that CPE is sensitive to high temperature or prolonged processing time. The disadvantage of CPE modifier in generating impact performance may be attributed to its sensitivity to processing conditions.

According to this research, the impact modifier type and content played a major rule in impact properties of rigid PVC/wood composites. The impact values increased significantly with the modifier content for both crosslinked (MBS and all-acrylic) and uncrosslinked (CPE) modifiers. Currently, there are several types of impact modifiers which are used as impact enhancer in PVC matrix. The impact modifier used for PVC-based WPC has to be suitable for WPC applications.

Hassan A. and Haworth B. [87] studied the impact strength of unmodified PVC and acrylate modified PVC at various temperatures. The different particle sizes of acrylate/PMMA core-shell impact modifier were used in this study (A= 0.3 µm , B= 0.4 µm , and C= 0.2 µm).

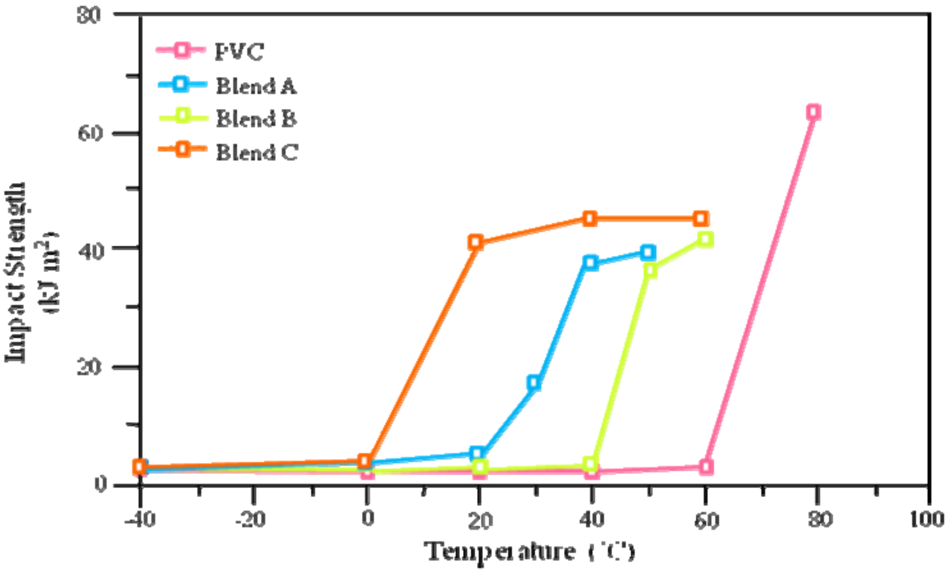


Figure 8.2: Effect of temperature on impact strength at testing speed 3 m/s [87].

Figure 8.2 illustrates the impact strength of samples at various temperatures. At low temperature range, the impact strength of all samples decreases slightly as the temperature decreases. When the ductile-brittle transition was reached, the impact value drops sharply. Unmodified PVC reaches firstly the transition in the range between 60 and 80 ºC. The result clearly shows the succed in shifting the ductile-brittle transition point to lower temperature in cooperated with acrylate rubber. Moreover, it is interesting to notice that each impact modifier size differs in shifting the range of ductile-brittle transition. In addition, the impact modifier C which has the smallest rubber particles size is demonstrated to be the most effective impact modifier for PVC in shifting the ductile-brittle conditions to a lower temperature. In summary, it is recognized that rubber particle size is an important factor in toughening of rubber-modified polymers.

Guo T. Y. et al [88] investigated the effects of core-shell structure particles of acrylate core-shell copolymer on the impact properties of poly(vinyl chloride). The core-shell impact modifier consisted of poly(n-butyl acrylate/methyl methacrylate) core and poly(methyl methacrylate/n-butyl acrylate) shell. Different acrylate core-shell structured particles were used as the PVC impact modifier for further evaluation of the toughening efficiency. Table 8.1 shows the core-shell structured particle contents.

Table 8.1 Recipes for the preparation of the core-shell structured particles [88].

Experiment No.	**Core**			**Shell**	
	MMA	BA	TAIC	MMA	BA
1	7	63	0.2	25	5
2	6	54	0.2	34	6

As shown in Figure 8.3, the impact strength significantly increases with the increase of additional contents of the impact modifiers. For the modifier from experiment no.1, the impact strength reaches the highest value (at 6-times of neat PVC), while impact modifiers from experiment no.2 reaches the highest impact strength (at 4-times of unmodified PVC) at 20 phr content. As the further addition, the impact strength then decreases. The sole difference between both impact modifiers is the component of the rubbery phase. Therefore, the ratio of rubbery phase to plastic phase has a major effect on the modified materials. In other words, the rubbery phase influences the toughening mechanism and is able to effectively improve the impact strength, only when the content reaches a certain amount. At the largest impact strength, it is noticed that even though the rubbery content is almost equivalent amounts, toughening efficiency is not similar. It could be concluded that the composition and structure of the modifier have a great effect on the toughening development.

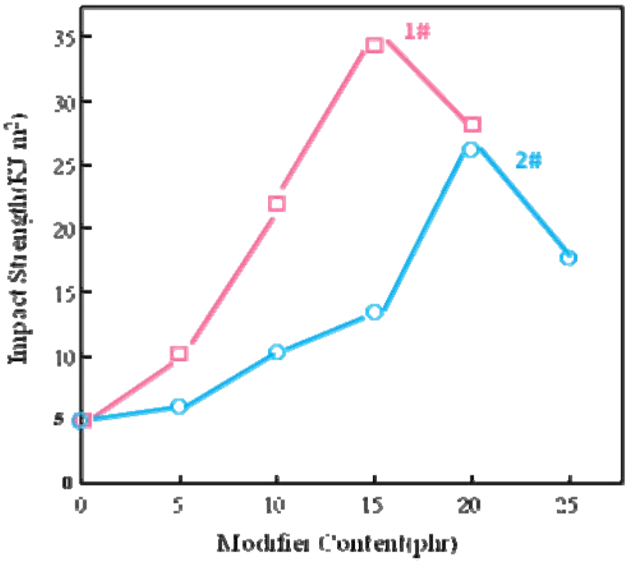


Figure 8.3: Effect of modifier content on the impact strength of the modified PVC [88].

The impact modifier used to contribute toughness to PVC matrix has been used in a wide range. ASA is one of the recently developed choices for outdoor applications. ASA is a core-shell polymer, consisting of acrylate rubber and poly(styrene acrylonitrile). Although the previous documents have been published the successful of acrylate rubber modified PVC. Compatibility between shell copolymer SAN and PVC matrix is necessary to be considered.

Lizymol P. P., Thomas S., and Jayabalan M [89] investigated the solution rheology of PVC/EVA, PVC/SAN, EVA/SAN, and PVC/EVA/SAN to study the compatibility. From the recent research, Singh and co-worker have concentrated on the compatibility of the polymer blends. They found that the plots between viscosity and shear rate deviate from linearity according to the degree of compatibility. Figure 8.4 is shown the variation of viscosity with composition of the blend. For compatible blends, viscosity of the blend will be equal to the value in the presence of shear. For the incompatible blend, the viscosity of the blend is lower than additive value in the presence of shear.

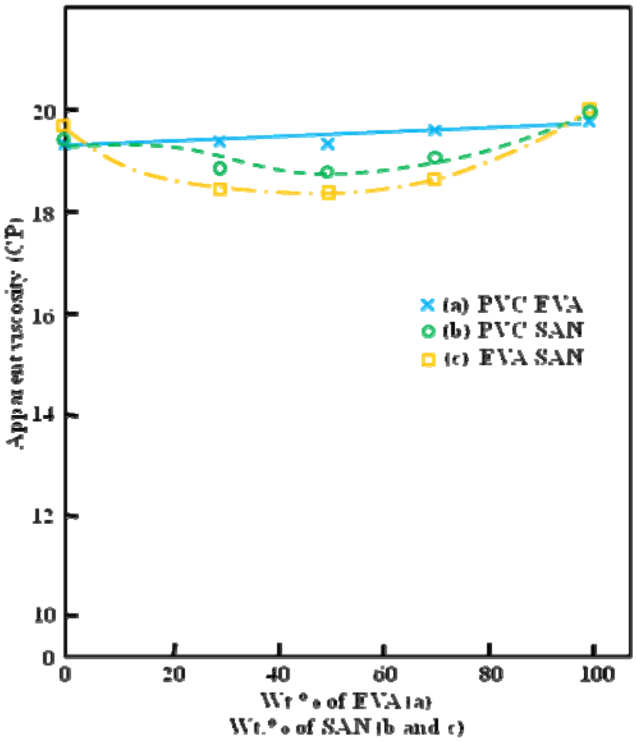


Figure 8.4: Variation of viscosity with composition of binary blends at a shear rate of 20 sec^{-1} : (a) PVC/EVA, (b) PVC/SAN, an (c) EVA/SAN [89].

It was found that, PVC/EVA blends have dilatancy behavior. The variation of viscosity with composition of the blend is plotted in Figure 8.4. The linear behavior of PVC/EVA blends indicates the compatibility of PVC/EVA blends, whereas PVC/SAN blends also exhibit dilatancy. The plot in Figure 8.4 indicates negative deviation from the linearity of PVC/SAN at high levels of the SAN, this characteristic exhibits the partial compatibility of PVC/SAN under shear. For the EVA/SAN blends the variation of viscosity with shear rate is not linear. This is attributed to the complete immiscible nature of EVA and SAN under shear.

PVC has been used in a wide range of applications. It is an important material applied in the building and construction industry, but the softening point of PVC is too low to allow its use. Additionally, PVC can discolor after prolonged periods outdoor applications. Many researchers have lately concentrated on ASA as core-shell impact modifier with the added advantage of enhanced weatherability. There are recent works which involve the addition a second phase ASA to the matrixes in order to improve the mechanical properties of the blends.

DeArmitt C. [90] has studied the development of Vicat/HDT of PVC. It was reported that ASA consists of SAN copolymer and acrylate rubber. SAN has a T_g higher than PVC and is compatible with PVC while acrylate rubber acts as dispersed rubbery phase which can absorb the impact energy exerting on the matrix. Figure 8.4 shows the softening point of PVC/ASA blends. PVC/ASA blends have intermediate HDT values and the relationship is linear to the levels of ASA loading. Therefore, it has been concluded that ASA can also be blended with PVC resulting in an increase in HDT.

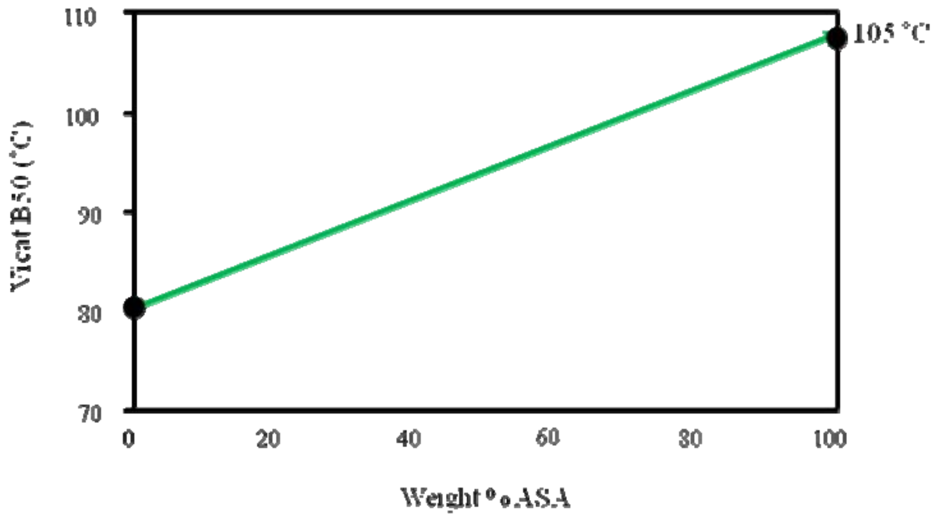


Figure 8.5: The relationship between wt% of ASA and softening point of PVC [90].

Benson C. M. and Burfoford R.P. [91] examined the morphology of ASA/PBT blends. This research focused on ASA/PBT system at ratios of 40/60, 50/50, and 60/40. ASA used in this study contained 42wt% rubber. It is found that processing temperature and composition of the blends are major factors that significantly effect on mechanical properties of the blends. When increasing the content of ASA in ASA/PBT blend, impact strength of blends exhibits more impact energy resistance. The two ASA-rich blends have better impact strength than PBT-rich blend. At the high processing temperature, the PBT matrix degrades rapidly at the temperature above 270ºC. A slight increase in tensile strength occurs as the temperature is increased. For the optimum properties between tensile strength and impact resistance, the 50:50 blends at lower temperature is best. Figure 8.6 and 8.7 show the tensile strength and impact resistance of ASA and PBT blends at different processing temperatures.

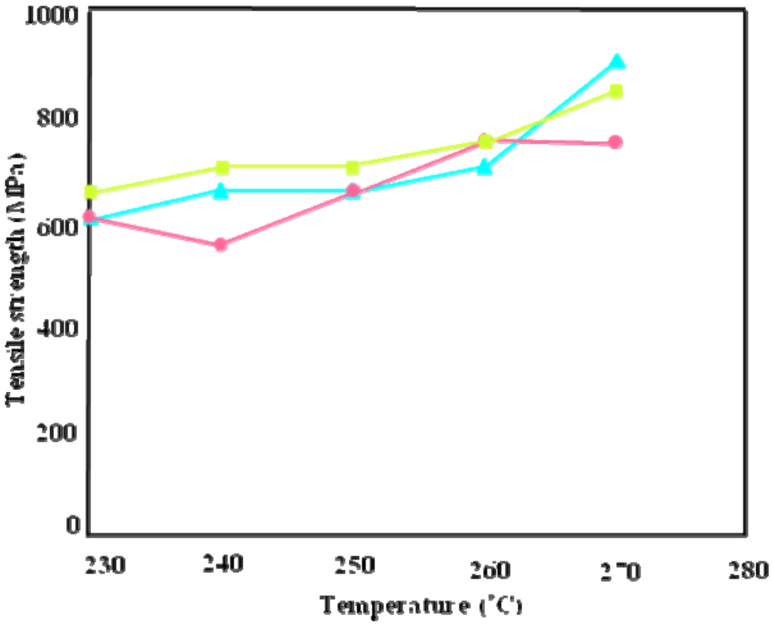


Figure 8.6: Tensile strength at break against processing temperature of the ASA/PBT blends: (■) 40:60, (●) 50:50, (▲) 60:40 [91].

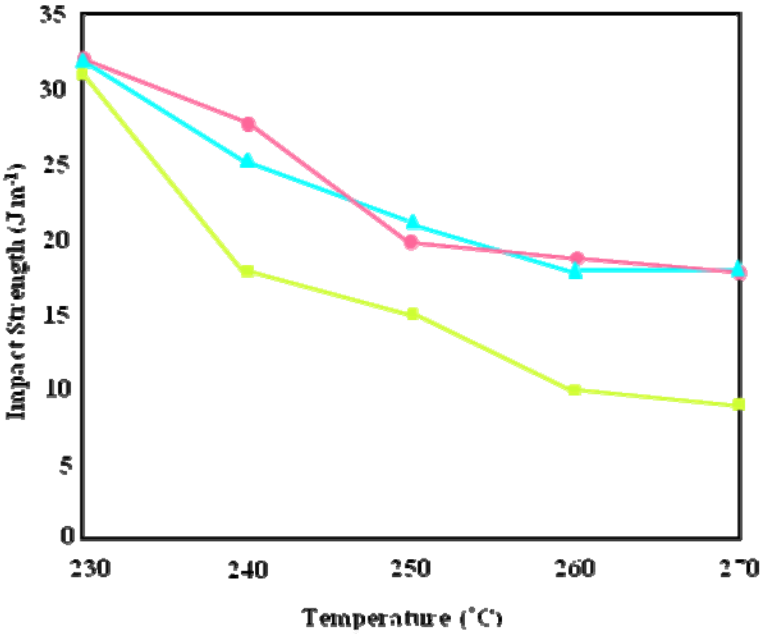
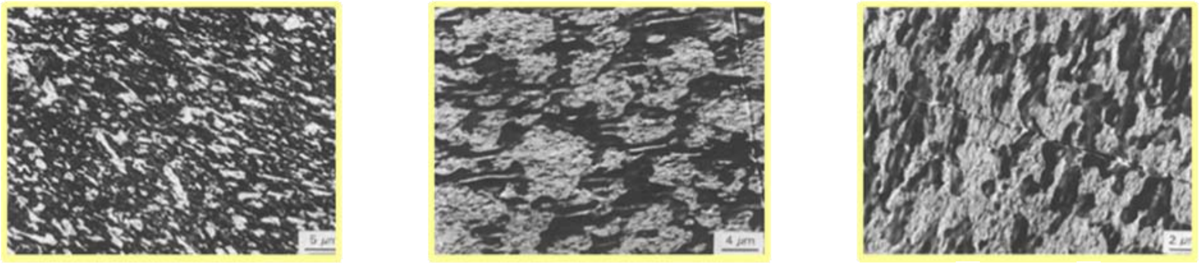


Figure 8.7: Impact resistance versus processing temperature of the ASA/PBT blends: (■) 40:60, (●) 50:50, (▲) 60:40 [91].



(a) (b) (c)

Figure 8.8: Transmission electron micrograph of ASA/PBT blends (a) 40:60, (b) 50:50, (c) 60:40 [91]

Figure 8.8 shows the morphology of ASA/PBT blends depicted by transmission electron microscope. In the 40:60 ASA:PBT blend, PBT is continuous in dark whereas ASA is formed as pockets within the continuous phase of PBT matrix. In addition, it is found that the rubber particles do not migrate into the PBT phase, but rather stay in SAN matrix. Similarly, in the 60:40 blends, ASA is continuous matrix containing dispersed PBT phase. For the 50:50 blends, the morphology of ASA/PBT blend indicates a co-continuous matrix. This blend refers maximum compatibility between ASA and PBT resulting in the best combination of tensile strength and impact resistance.

Besides, there are many studies in weather modified PVC by coextruding PVC with ASA. The sheet member has a top layer made of ASA and a bottom layer made of PVC.

U.S. Pat. No. 6,536,177 [92] claims a roofing panel comprising a top layer made of ASA materials (15 mm. thickness) and a bottom layer made of PVC (75 mm. thickness). Both layers are coextruded or bonded together. This roofing panel can meet roofing material performance such as good impact strength, good insulation, and highly weathering resistance.

Szamborski G. [93] studied on the weatherability and impact performance of acrylic-capped PVC siding. Weatherable polymers (acrylic containing) used for capping on PVC substrate in order to enchance weatherability of PVC silding were investigated. The samples 3 mm thickness with tolerances at ± 0.5 mm were studied on weatherability and impact retention in Florida and Arizona.

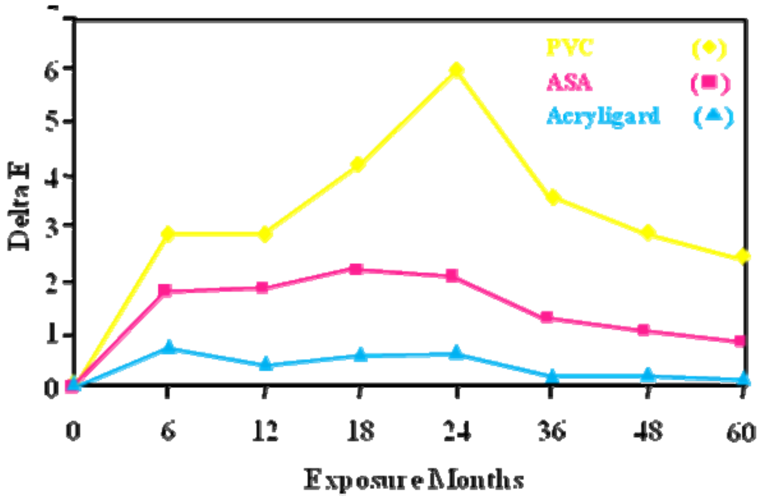


Figure 8.9: Outdoor weathering performance in dark beige L=58 color in Florida [93].

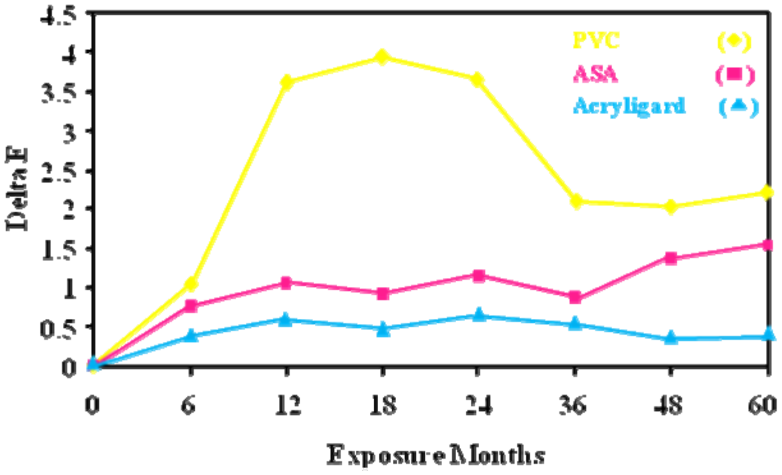


Figure 8.10: Outdoor weathering performance in dark beige L=58 color in Arizona [93].

As a result, neat PVC tends to yellowing with long period of outdoor exposure whereas ASA and Acrylic show excellent color hold ability, particularly in medium to dark color.

Figure 8.11 shows impact loss on weathering of PVC and Acrylic capped PVC. In case of nonvinyl capstrocks, impact loss is less drastic but still does occur.

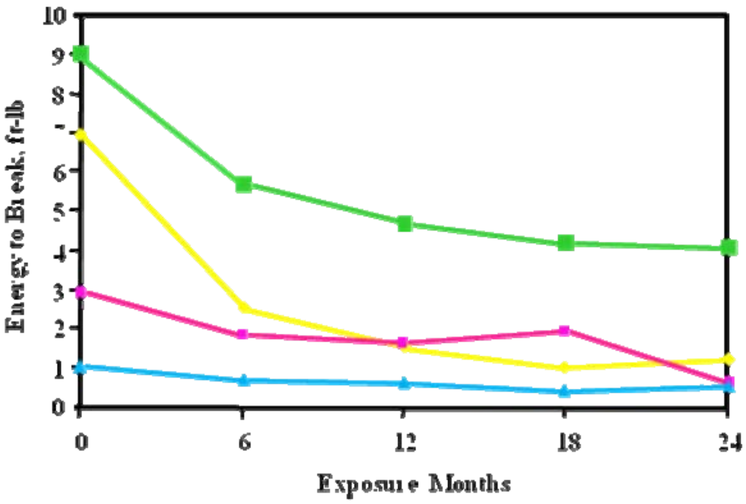


Figure 8.11: Impact strength retention of dark beige capstocks exposed in Arizona [93].

U.S. Pat. No. 09/488,172 [94] claims compositions which possesses substantial weatherability and impact resistance. A very useful ASA terpolymer material includes about 58.4% by weight of styrenic units, about 23.3% by weight acrylonitrile units, and about 18.3% by weight acrylate units. In composites, the matrixes may include ASA copolymer material from about 30% to about 90% and PVC material from 10% to about 50%. Wood compositions in the weatherable composites is in a range of about 1% to about 40% by weight, based on the total weight of the composition. More preferably, such particles have a size in the range of about 50 to about 150 U.S. mesh.

9. Objectives of this research

1. To develop high impact PVC-based wood substituted composites by using styrenic copolymers as impact modifiers.

2. To examine the effects of type and content of ASA on the other essential properties of both PVC/ASA blends as wood composite matrices.

3. To explore the effects of coconut fiber content on the mechanical, thermal and physical properties of the resulting PVC/ASA/coconut fiber composites.

10. Scope of the 2nd year research

1. Preparing PVC dryblend.
2. Preparing woodfiber. (*Cocos Nucifera*), i.e. drying, grinding, sieving, etc.
3. Preparing PVC/ASA at mass ratios of 100/0, 90/10, 80/20, 70/30, 60/40, and 50/50 by two roll mill at the temperature of 170°C.
4. Evaluating the optimum ASA content which results in the highest impact performance of PVC/ASA blends.
5. Preparing PVC/ASA at mass ratio which results in the highest impact performance of PVC/ASA blends at the processing temperature of 160, 170, and 180°C and evaluating the optimum processing condition which results in the highest impact performance of PVC/ASA blends and using this blends as the matrix for wood plastic composites
6. Investigating physical, mechanical and thermal properties of PVC/ASA blends on following properties: mechanical properties (tensile, flexural and impact strengths), thermal properties (glass transition temperature (T_g), heat distortion temperature (HDT), and Vicat softening temperature), and physical properties (density and water absorption).
7. Preparing PVC/ASA woodfiber composites at contents of woodfiber (0, 10, 20, 30, 40 and 50 wt%) by two-roll mills.
8. Investigating weatherability, physical, mechanical and thermal properties of PVC/ASA-wood composites.
9. Evaluating the optimal content of ASA as impact modifier in PVC/ASA blends.
10. Evaluating the maximum loading of woodfiber in the natural fiber-reinforced PVC/ASA composites.

11. Experimental

11.1 Materials

Polymers used in this study are polyvinyl chloride (PVC) and acrylonitrile styrene acrylate (ASA). Suspension grade PVC, Siamvic 258RB, with *K*-value 58 and degree of polymerization about 680 which obtained from Vinythai Public Company Limited., Thailand was used as polymer matrix for wood plastic composites. The additives used in PVC compound were Kane Ace 20 as processing aid, SAK-WP08-NP as heat stabilizer, Loxiol P1141 as internal lubricants, and calcium stearate as external lubricant. The additives, Kane Ace PA 20 (Processing aids), SAK-WP-08-NP (Heat stabilizers), and Calcium stearate (External lubricants) were provided by Vinythai Public Company Limited., Thailand and Loxiol P1141 (Internal lubricants) was supported by the Siam Chemical Solutions Co., Ltd. Thailand. Extrusion grade ASA resin, KIBILAC PW-997S, used as impact modifier in PVC wood composites system was purchased from Global Connections Co., Ltd., Thailand. KIBILAC PW-997S was produced and mainly supplied by Chi Mei Corporation. It was suitable for extrusion application with high impact performance such as in construction and automobiles

11.2 Methodology

11.2.1 Matrix Preparation

11.2.1.1 PVC Dryblend Preparation

In order to allow ease of PVC handing and further processing, powdered PVC resin was compounded with other additives including Kane Ace 20, SAK-WP08-NP, Loxiol P1141, and calcium stearate in high speed mixer. Kane Ace PA 20 (processing aids) was used to achieve better homogeneous melt of PVC and it can interact with PVC to produce a stiffer and more elastic melts which made PVC melts more resistance to rupture, prevented the surface of PVC melt from tearing. SAK-WP-08-NP (heat stabilizers) was used to prevent oxidation of PVC by heat during processing, in order to improve its resistance to discoloration during processing, and help to maintain physical properties of the end products. Moreover, to improve melt behavior, Loxiol P1141 (internal lubricants) and Calcium stearate (external lubricants) were also incorporated in to

PVC dry blend. During processing Loxiol P1141 can lubricate the movement between PVC molecular chains, while Calcium stearate was used lubricated the melt from the metal of the processing equipment. All additives were blended follow PVC formulation as shown in Table 11.1.

Table 11.1 PVC dryblend formulation.

Ingredient	Composition (phr*)	Composition (wt%)
PVC (Siamvic 258 RB)	100.0	88.9
Stabilizer (SAK-WP-08-NP)	4.0	3.6
Processing aid (Kane Ace PA 20)	6.0	5.3
Internal lubricant (Loxiol P1141)	2.0	1.8
External lubricant (Calcium stearate)	0.5	0.4
Total	112.5	100.0

PVC resin and four additives, which the amount of all ingredients should not exceed 35 kg., was blended in high speed mixer model Plasmec Turbomixer 100L at Vinythai Public Company Limited (Rayong) in Figure 11.1. The mixing process consists of two mixing tanks, operating with 2 steps of hot and cold mixers as following details:

Hot Mixing Step

- Added PVC resin and solid additives into the mixer.
- Stirred at low speed (400 rpm), the temperature of the mixture rose up due to frictional heat generation from between PVC particles.
- Stirred at high speed (1200 rpm) until the temperature was 70°C.
- Added liquid additive - Loxiol P1141, stirred until the temperature was 120°C.
- Discharging to a cold mixer.

Cold Mixing Step

- The hot dryblend was cooled by cooling water at temperature of 15-20°C
- Stirred until the temperature of dryblend was decreased to 35°C.
- Discharging to a container.

Figure 11.1: High Speed Mixer: Plasmec Turbomixer 100L with cooler (made in Italy).

Figure 11.2: Two-roll mills from Labtech Instruments Inc. [95].

11.2.1.2 PVC/ASA Blends Preparation

PVC dry blend was blended with ASA pellet by two-roll mills with 0.125 mm gap at at various temperatures of 160, 170, and 180ºC for 6 minutes to yield a homogeneous blends. The two-roll mills at Vinythai Public Company Limited (Rayong) were also shown in Figure 11.2. The total amount of material loading on two-roll mills should not exceed 300 g. Table 11.2

showed the amount of both PVC dryblend and ASA required at various compositions of PVC/ASA blend ranging from 10-50 wt% of ASA content. The obtained compound was preheated for 3 min and then pressed into sheet by compression molding at 170 ºC and pressure of 150 bar for 4 min. The compression-molded sheets were then cut into test pieces for further property evaluations.

Table 11.2 The amount of PVC and ASA required per 300 g loading on two-roll mills.

ASA content (wt%)	PVC dryblend (g)	ASA (g)
10	270	30
20	240	60
30	210	90
40	180	120
50	150	150

11.2.2 Composite Preparation

11.2.2.1 Preparation of Coconut Fiber

Natural fiber used in this research was obtained from the fruit of the coconut tree. Generally, coconut fiber is the seed-hair fiber obtained from the outer shell (endocarp), or husk, of the coconut *(Cocos nucifera)*. In this research, coconut fiber was cut by Fritsch pulverisette cutting mill 15 as shown in Figure 11.3 to reduce the fiber length to 3-8 mm. Then coconut fiber was dried in an oven for 24 hours at 105°C prior to composite preparation. Drying of fibers is a fundamental step since the presence of water reduces the adhesion between this filler and the matrix.

Figure 11.3: Fritsch pulverisette 15 cutting mill [43].

11.2.2.2 Preparation of PVC/ASA/Coconut Fiber Composites

In this research, the PVC/ASA at mass ratio of 50:50, which showed the greatest impact strength, was selected to use as wood composites matrix. The amount of PVC and ASA required for wood composites at various coconut fiber contents were shown in Table 11.3. The obtained mixtures were then mixed by two-roll mills with 0.25 mm gap at the same temperature that used to process the PVC/ASA matrix. The obtained compound was then preheated for 3 min and compression-molded at the temperature of 170°C and at the pressure of about 150 bar for 4 min. The compression molded sheets were then cut into test pieces for further property characterizations.

Table 11.3 The amount of PVC dryblend and ASA required at various fiber contents.

Fiber content (wt%)	PVC dryblend (g)	ASA (g)	Coconut fiber (g)
10	135	135	30
20	120	120	60
30	105	105	90
40	90	90	120
50	75	75	150

11.3 Characterizations of Polymer Blends and Wood Composites

11.3.1 Mechanical Characterization

11.3.1.1 Notched Izod Impact Property Measurement

Notched Izod Impact is a single point test that measures a materials resistance to impact from a swinging pendulum. Izod impact is defined as the kinetic energy needed to initiate fracture and continue the fracture until the specimen is broken. The specimen is clamped into the pendulum impact test fixture with the notched side facing the striking edge of the pendulum. The pendulum is released and allowed to strike through the specimen. Izod Impact strength of the specimens was obtained by Impact Tester (Yasuda) according to ASTM D256. The dimension of the test specimen was 12.7×60×3.2 mm^3, the specimen thickness was 3 mm, and the depth under the notch of the specimen was 10 mm.

11.3.1.2 Tensile Property Measurement

Tensile properties were obtained by a universal testing machine (Instron Instrument, model 5567) according to ASTM D638. The test specimens were a dumbbell shape with a uniform thickness. They were tested using a crosshead speed of 6 mm/min with the pre-load of 150 N giving a straight tensile force. The tensile modulus defined as the ratio of stress to strain which was determined from the initial slope of the stress-strain curve whereas the tensile strength is the ultimate stress. Five specimens from each blend and composite were tested and the average values were reported.

11.3.1.3 Flexural Property Measurement

Flexural modulus and flexural strength of the composites specimens were measured by a universal testing machine (Instron Instrument, model 5567) according to ASTM D790. Three-point bending test was carried out at room temperature at the crosshead speed of 1.2 mm/min with the support span of 48 mm. The dimension of the specimen was 3.2×12.7×64 mm^3. Five specimens from each blend and composites were examined and the average values were reported.

11.3.2 Thermal Characterization

11.3.2.1 Differential Scanning Calorimetry (DSC)

The DSC measurements were carried out with the TA instruments model DSC 2910. The sample weight was approximately 8-9 mg. The temperature was equilibrated at 30°C and the samples were heated from 30 to 150°C with the heating rate of 10°C/min. Nitrogen gas flow rate was maintained at 50 ml/min.

11.3.2.2 Dynamic Mechanical Analysis (DMA)

Thermal characteristic of polymer blends and its composites was examined by a dynamic mechanical analyzer (NETZSCH, DMA242). The dimension of the specimen was rectangular with 50 mm length, 10 mm width, and 2 mm thickness. The three point bending mode of deformation was used under a test temperature range from 30°C to 150°C with a heating rate of 2 K/min. The test amplitude and frequency were 30μm and 1Hz, respectively. The glass transition temperature was taken as the temperature of the maximum in the loss modulus and the loss tangent plots.

11.3.2.3 Heat Distortion Temperature (HDT)

Heat distortion temperature was defined as the temperature at which a standard test bar deflected a specified distance under the load applied at its center to give maximum stresses. It was used to determine short-term heat resistance. It distinguished between materials that were able to sustain light loads at high temperatures and those that lose their rigidity over a narrow temperature range. The specimen was placed under the deflection measuring device. The specimen was then immersed in a silicone oil with a means of raising the temperature at 120°C/h or 2 ± 0.2°C/min until they deflected 0.25 mm following ASTM D648. This temperature was recorded as the deflection temperature under flexural load of the test specimen.

11.3.2.4 Vicat Softening Temperature

The vicat softening temperature was the temperature at which a flat-ended needle penetrates the specimen to the depth of 1 mm under a specific load. The temperature reflects the point of softening to be expected when a material is used in an elevated temperature application. A test specimen was placed in the testing apparatus so that the penetrating needle rested on its surface at least 1 mm from the edge. A load of 50N was applied to the specimen. The specimen was then lowered into a silicon oil bath at 30°C. The bath was heated at a rate of 50°C/h until the needle penetrated 1 mm following ASTM D1525. The temperature at which the needle has penetrated to a depth of 1 ± 0.01 mm was recorded as the vicat softening temperature.

11.3.3 Physical Properties

11.3.3.1 Density Measurement

The density of the coconut fiber polymer composites was measured by a water displacement method, ASTM D792. The dimension of the specimen was 20 x 20 x 3 mm^3. All specimens were weighed both in air and in water. Then, the density was calculated from the following equation:

$$\rho = \left(\frac{A}{A - B} \right) \times \rho_0$$

where ρ is the density of the specimen (g/cm^3), A and B are weight of the specimen in air and in the auxiliary liquid (g) (demineralized water was used in this study) ρ_0 is the density of the auxiliary liquid at the given temperature (g/cm^3).

11.3.3.2 Water Absorption and Thickness Swelling Measurement

Water absorption measurement was conducted following ASTM D570, using specimen in the form of a disk 50.8 (2 in.) in diameter and 3.2 mm (1/8 in.) in thickness. Three specimens were conditioned in an oven at 50°C for 24h, cooled in a desiccator, and then weighed. The specimens were then immediately immersed in distilled water and were weighed periodically. Based on the initial mass of each specimen, the amount of water absorbed was calculated form the following equation:

$$WA(\%) = \left(\frac{M_e - M_o}{M_o} \right) \times 100$$

where WA is water absorption at time t (%); M_e and M_o are the mass values of the specimen after and before immersion, respectively.

In the water immersion tests, thickness of each specimen was also measured for determination of the thickness swelling (TS) by using the following equation:

$$TS(\%) = \left(\frac{T_t - T_o}{T_o} \right) \times 100$$

where TS, is thickness swelling at time t (%), T_t and T_o are thicknesses at time t and dried condition mm, respectively.

11.3.4 Natural Weathering Test

11.3.4.1 Color Change Measurement

This test method originally resulted from the consolidation of separately published methods for instrumental evaluation of color differences. The total difference, ΔE_{ab}^*, between two colors each given in terms of lightness (L*) and chromaticity coordinate (a* and b*) is calculated following ASTM D 2244 by Ultrascan Pro (Hunter Lab, USA) which measures both reflected and transmitted color and meets CIE (International Commission on Illumination):

$$\Delta E_{ab}^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

The magnitude, ΔE_{ab}^*, gives no indication of the character of the difference since it does not indicate the relative quantity and direction of hue, saturation, and lightness differences. The direction of the color difference is described by the magnitude and algebraic signs of the component ΔL^*, Δa^* and Δb^*.

$$\Delta L^* = L_1^* - L_0^*, \Delta a^* = a_1^* - a_0^*, \Delta b^* = b_1^* - b_0^*$$

Where L_0^*, a_0^* and b_0^* refer to the initial values, and L_1^*, a_1^* and b_1^* refer to the final values of a specimen. The signs of the components ΔL^*, Δa^* and Δb^* have the following approximate meanings:

$+\Delta L^*$= lighter, $-\Delta L^*$ = darker
$+\Delta a^*$ = redder (less green), $-\Delta a^*$ = greener (less red)
$+\Delta b^*$ = yellow (less blue), $-\Delta b^*$ = bluer (less yellow)

11.3.4.2 Scanning Electron Microscope

Surface texture of the wood composites before and after weathering test was studied using a Scanning Electron Microscope (SEM: JSM-5800LV, JEOL) with an acceleration voltage of 15 kV. The weathering surface of each specimen was coated with thin gold film prior to testing.

12. Results and discussion

In order to investigate the enhancement in impact properties of PVC/wood composites, the effects of ASA content and processing temperature on mechanical properties, thermal properties, and physical properties of PVC/ASA blends were thoroughly examined. Then the effects of addition of coconut fiber on characteristics of PVC/wood composites using ASA as impact modifier were investigated.

12.1 Effects of ASA Content on the Properties of PVC/ASA Blends

12.1.1 Mechanical Properties

12.1.1.1 Impact Properties

The effects of ASA content ranging from 0 wt% to 50 wt% on notched Izod impact strength at room temperature of PVC/ASA blends are presented in Figure 12.1. From the figure, we can see that the neat PVC exhibited a notched Izod impact strength value of 6.8±0.5 kJm^{-2} whereas that of ASA was around 47.0±3.1 kJ m^{-2}. Interestingly in PVC/ASA blend systems, the impact strength of the blends with a maximum value as high as 77.6±4.0 kJ m^{-2} was obtained at ASA content of 50 wt%. The strength was observed to increase with an increase of ASA content up to 50 wt% and then decreased. The remarkable improvement of impact strength of the PVC/ASA blends was possibly due to an ability of ASA to form optimal energy dissipation phase morphology i.e. co-continuous phase, with the PVC in the polymer blend [10]. When the polymer blend was subjected to an external stress, the elastomeric phase in ASA might be able to effectively initiate and terminate crazes. With this crazing, energy was transformed into deformation of the rubber particles in the ASA followed by the formation of voids in the rubber phase itself. However, further deformation can effectively be stopped by other rubber particles [80]. As also seen in the figure, the impact strength increased slightly when ASA content was less than 30 wt% and the sharp increase in impact strength was observed with ASA content greater than 30 wt%. The point of drastic change in impact strength of the PVC/ASA blend systems is called a brittle-ductile transition.

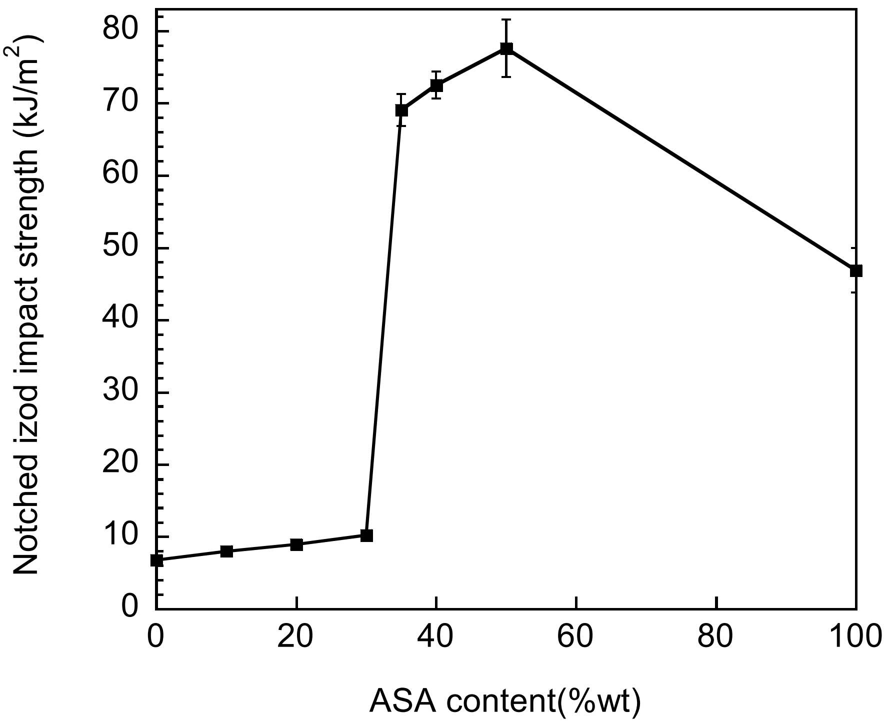


Figure 12.1: Impact strength of PVC/ASA blends at various mass blending ratios.

In this case, ASA content is a major factor that induces the brittle-ductile transition. At the ASA content of 0-30 wt%, the impact strength was low and brittle fracture was observed with little stress whitening zone as shown in Figure 12.2. Beyond 30 wt% of the ASA, ductile fracture with a pronounced stress whitening zone can be clearly seen. Stress whitening is the phenomenon possibly resulted from crazing in the matrix, internal cavitation of the rubber particles or debonding at the matrix-particle interface [96]. This transition behavior in impact strength of our PVC/ASA blend was also observed in other particle toughened polymers [96-97] Sharma and coworkers [42] reported that the maximum impact strength can be achieved in this kind of polymer blend at the critical volume fraction of the elastomer phase. However, when this critical elastomer content is exceeded, impact strength drops. At the peak value of impact strength, optimum balance between sufficient elastomer content and the preferred combination of toughening mechanisms such as multiple crazing with interacting shear deformation might be attained.

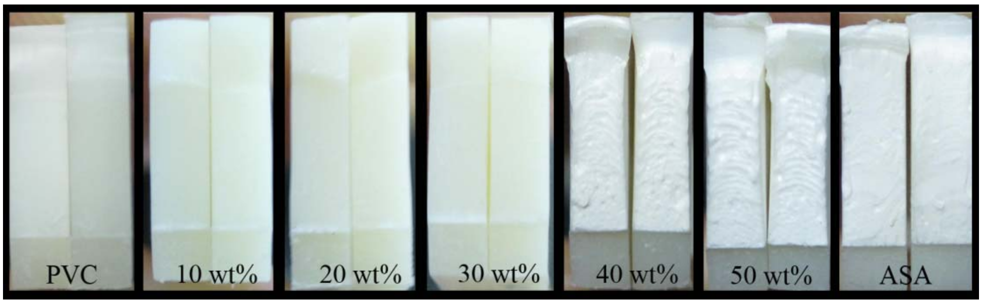


Figure 12.2: Fracture surface of PVC/ASA specimens after notched Izod impact tests at various mass blending ratios.

12.1.1.2 Tensile Properties

The tensile properties of PVC/ASA blends with various ASA contents are reported in Table 12.1. In the case of tensile properties, we can see that the tensile modulus of PVC was found to be 2.18 GPa whereas that of ASA was 1.57 GPa. As the PVC content increased, tensile modulus of PVC/ASA blends was found to systematically increase due to more rigidity of PVC than ASA following the rule of mixture. Similar observation was also reported in PC/ABS blend [10, 98] and PVC/ABS blend [99].

Our PVC exhibits tensile strength of 53.0±0.3 MPa which is substantially higher than that of ASA (38.0±0.9 MPa). Moreover, the tensile strength of the PVC/ASA blends rendered the values between that of neat PVC and neat ASA as being predicted by the rule of mixture, indicating substantial interfacial interaction between the two polymers. Similar behavior was also observed in the PVC/ABS blend, PC/ABS blend [10, 98], PC/ASA/SAN blends [97] and HDPE/UHMWPE blends [100]. However, negative deviation in tensile strength was observed in PET/ASA system which was reported to be rather incompatible (poor interfacial interaction) in nature [91]. Lastly, the tensile elongation of the ASA was found to be lower than that of PVC. With increasing the ASA fraction in the PVC/ASA blend, a decrease in the elongation at break was observed. This is due to the fact that the PVC possesses a greater elongation at break than the ASA used.

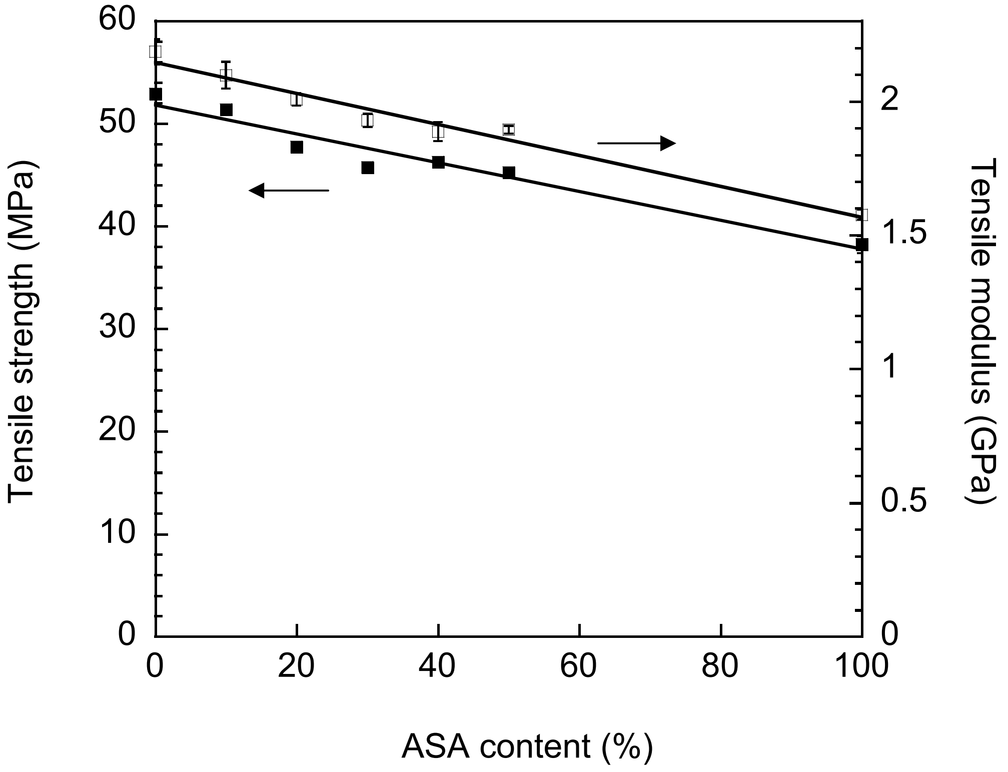


Figure 12.3: Tensile properties of PVC/ASA blends at various mass blending ratios: (■) tensile strength (□) tensile modulus.

Table 12.1 Tensile properties of PVC/ASA blends at various mass blending ratios.

Samples	**Tensile modulus (GPa)**	**Tensile strength (MPa)**	**Elongation at break (%)**	**Energy at break (J)**
PVC	2.18 ± 0.05	53 ± 0.3	112.6 ± 28.8	222 ± 59
PVC/ASA 90/10	2.10 ± 0.05	51 ± 0.4	83.9 ± 23.9	153 ± 44
PVC/ASA 80/20	2.01 ± 0.02	48 ± 0.5	62.3 ±31.0	119 ± 60
PVC/ASA 70/30	1.93 ± 0.02	46 ± 0.3	41.8 ± 24.2	73 ± 43
PVC/ASA 60/40	1.89 ± 0.03	46 ± 0.2	23.5 ± 7.1	40 ± 12
PVC/ASA 50/50	1.89 ± 0.01	45 ± 0.4	12.6 ± 3.6	21 ± 6
ASA	1.57 ± 0.02	38 ± 0.9	5.6 ± 0.9	8 ± 1

12.1.1.3 Flexural Properties

The flexural properties of the PVC/ASA blend systems at varied ASA content is also reported in Table 12.2. From the table, the modulus and strength of the blend samples under flexural load of the PVC/ASA blends showed a similar trend to that of tensile modulus and strength. The flexural modulus of the blend systems was found to increase from 2.73 GPa at 50 wt% PVC content to 3.00 GPa at 90 wt% PVC content due to the higher rigidity of the PVC while those of the neat PVC and the neat ASA were determined to be 3.20 GPa and 2.23 GPa, respectively. In case of flexural strength, the PVC/ASA blends at various blending ratios exhibited the flexural strength at 79 MPa for the blend containing 10 wt% ASA. With increasing ASA content, the flexural strength decreased to 69 MPa for the blend containing 50 wt% of the ASA while the flexural strength of the PVC and the ASA was determined to be 87 MPa and 63 MPa, respectively. This behavior is similar to that of ABS/SAN blends [101]. From the result, the effect of the ASA content on PVC/ASA blends tended to follow the additivity rule confirming good interfacial interaction between the two phases as described in the tensile test.

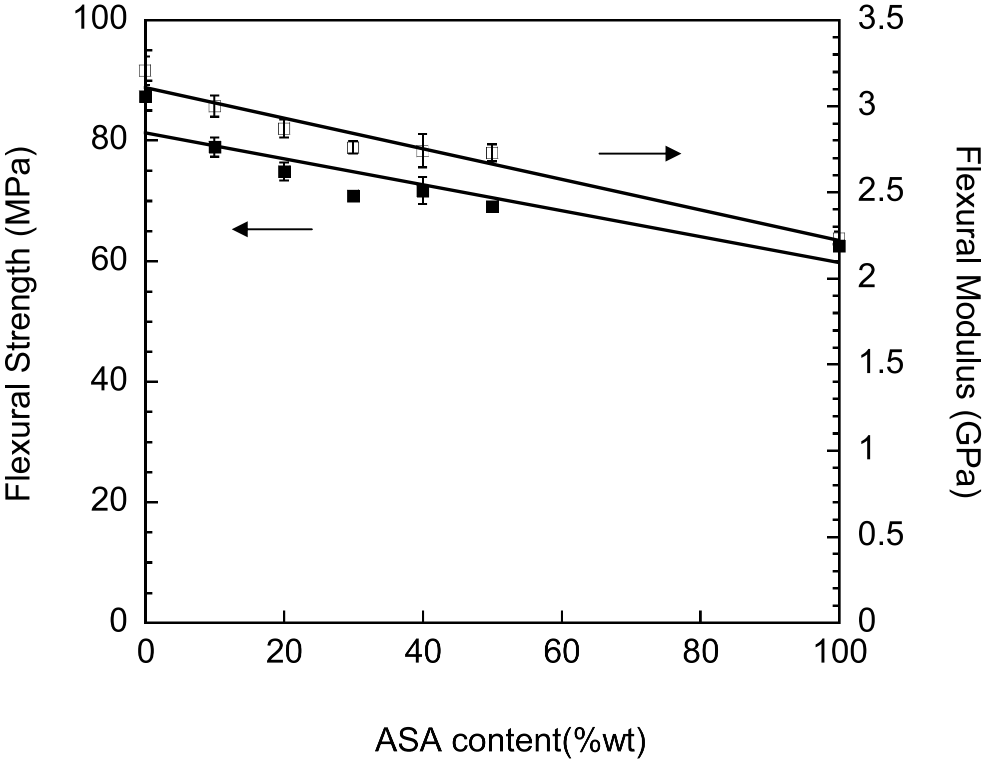


Figure 12.4: Flexural properties of PVC/ASA blends at various mass blending ratios: (■) flexural strength (□) flexural modulus.

Table 12.2 Flexural properties of PVC/ASA blends at various mass blending ratios.

Samples	Flexural modulus (GPa)	Flexural strength (MPa)
PVC	3.20 ± 0.08	87 ± 1.0
PVC/ASA 90/10	3.00 ± 0.06	79 ± 1.6
PVC/ASA 80/20	2.87 ± 0.05	75 ± 1.5
PVC/ASA 70/30	2.76 ± 0.04	71 ± 0.8
PVC/ASA 60/40	2.74 ± 0.10	72 ± 2.2
PVC/ASA 50/50	2.73 ± 0.05	69 ± 0.3
ASA	2.23 ± 0.04	63 ± 0.6

12.1.2 Thermal Properties

12.1.2.1 Differential Scanning Calorimetry

In order to study the thermal behavior which changed in the blends at different blending ratio of PVC to ASA, glass transition temperature (T_g) was investigated under differential scanning calorimetry (DSC) technic. From the DSC curve, glass transition temperature is represented graphically in the thermal curve as a shift in the baseline which is a change in the heat capacity of the polymer as the amorphous regions melt. The DSC thermograms of PVC, ASA and their blends with ASA contents in a range of 10-50 wt% are shown in Figure 12.5 and also summarized in Table 12.3. The thermographs of the neat PVC clearly showed a single T_g at 81°C whereas that of ASA showed a single T_g at 107°C that represents to T_g of SAN phase in ASA matrix. Moreover it has been reported that the Tg of the rubber phase polybutylacrylate is at about -40°C [102] that disappeared in this temperature range of analysis. The thermographs of PVC/ASA blends showed two distinct Tg in the whole composition range. As increasing ASA content, the T_g's of PVC phase clearly observed to shift to higher value from 81°C for the neat PVC to about 84°C at 50 wt% of the ASA content while the T_g's of ASA in the blends were more difficult to observe due to some exotherm peak of PVC that disappeared with increasing of ASA content near T_g of ASA in the blend. This exotherm peak was determined to be recrystallization behavior in Berens and Hodge study [103]. A similar behavior was also observed by Bensemra *et al.* [99]. The enhancement in T_g of PVC implied the ability to diffuse into PVC phase of SAN component in ASA matrix due to their similar polarity and partially miscible nature of these blend [88].

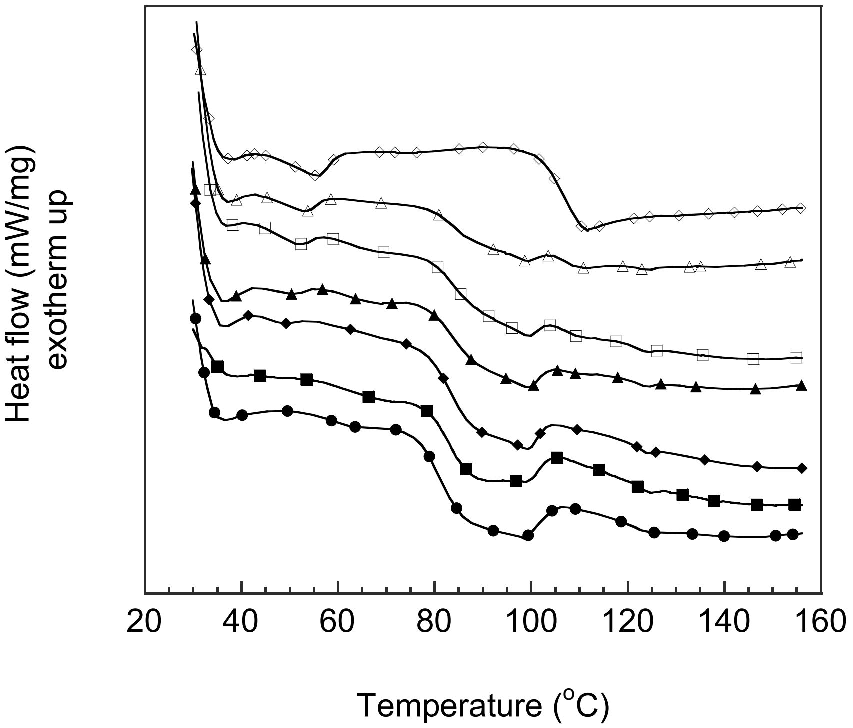


Figure 12.5: DSC thermograms of PVC/ASA blends at various mass blending ratios: (●) PVC (◇) ASA (■) PVC/ASA 90:10 (◆) PVC/ASA 80:20 (▲) PVC/ASA 70:30 (□) PVC/ASA 60:40 (△) PVC/ASA 50:50.

Table 12.3 Glass transition temperatures obtained from the midpoint of step change of PVC/ASA blends at various mass blending ratio from DSC curves.

Samples	**T_{g1} (°C)**	**T_{g2} (°C)**
PVC	80.7	-
PVC/ASA 90:10	82.8	106.9
PVC/ASA 80:20	82.9	107.7
PVC/ASA 70:30	83.0	107.0
PVC/ASA 60:40	83.7	107.1
PVC/ASA 50:50	84.0	107.1
ASA	-	107.0

5.1.2.2 Dynamic Mechanical Analysis

Figure 12.6 exhibits storage modulus (E′) as a function of temperature of the PVC/ASA blends. From this figure, storage modulus at room temperature of PVC was determined to be 2.9 GPa while that of ASA was about 2.0 GPa. The higher storage modulus at room temperature of the neat PVC compared to that of the ASA is consistent with those of tensile and flexural test discussed in the previous section. Furthermore increasing the amount of ASA in PVC from 0 wt% to 50 wt% led to a systematic decrease in storage modulus of the blends from 2.9 GPa to 2.3 GPa. However, as heating continued in the DMA test, PVC was observed to lose their rigidity at elevated temperature more readily than ASA and their blends. The greater change in slope of the modulus curve vs. temperature of PVC compared to ASA is one parameter indicating better thermal stability of the latter. The enhancement in thermal stability of the blends was thus obtained due to the superior thermal stability of ASA to PVC.

The temperature dependence of the tan δ peak of PVC/ASA blends at different ASA content is illustrated in Figure 12.7. Glass transition temperature (T_g), determined from the peak of the tan δ, of the neat PVC and the neat ASA were found to be 96°C and 121°C respectively. For the PVC/ASA blends, heavily overlapped with only one dominant peak was observed when ASA content in the blends is less than 30 wt%. However, when the ASA content was greater than 30 wt%, two clearly separated peaks of the PVC-rich phase (T_g1) and of the ASA-rich phase (T_g2) existed. Furthermore, the positions of both peaks tended to shift towards each other in the obtained polymer blends. For example, T_g1 of the PVC-rich phase was found to increase from 98°C to 102°C with the increase of ASA content while T_g2 of the ASA-rich phase was found to shift to lower temperature from 119°C to 117°C at the blend composition of 30 wt% of ASA. This behavior suggested the partially miscible nature of the ASA with PVC. Normally, the shifting of T_gs of two individual components towards each other means the improved compatibilization while the final single broad relaxation denotes the complete compatibilization [104]. In our work, the incorporation of ASA chains into PVC chains might provide an enhanced interfacial adhesion between the PVC and ASA domains from the partial miscibility of the blends observed. The similar shifting in T_g has also been reported in PVC/ABS and PC/ABS systems [10, 98].

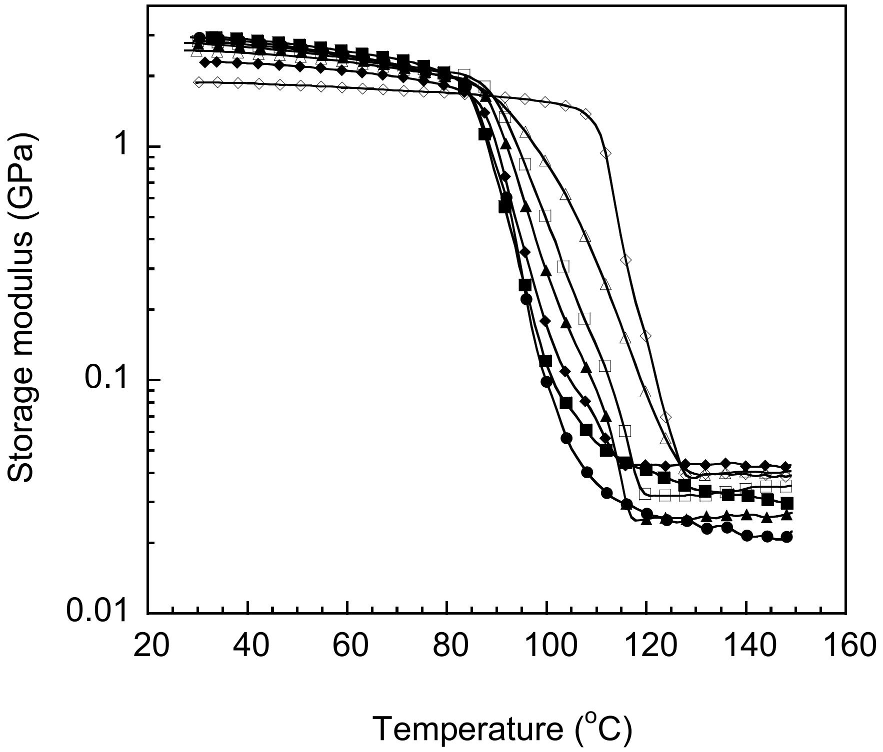


Figure 12.6: Storage modulus of PVC/ASA blends at various mass blending ratios: (●) PVC (◇) ASA (■) PVC/ASA 90:10 (◆) PVC/ASA 80:20 (▲) PVC/ASA 70:30 (□) PVC/ASA 60:40 (△) PVC/ASA 50:50.

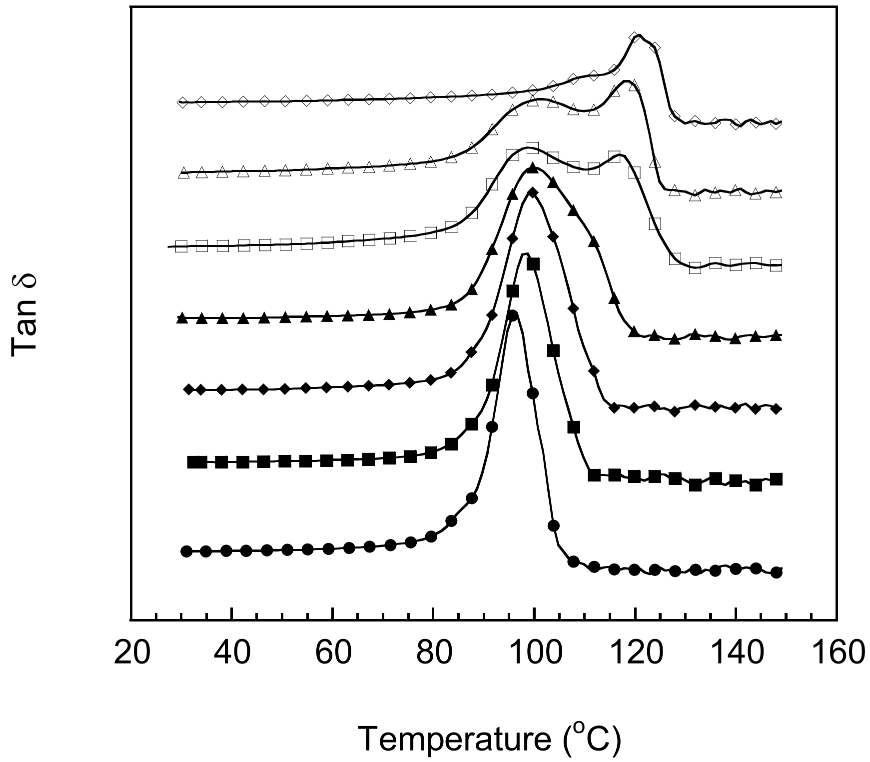


Figure 12.7: Loss tangent of PVC/ASA blends at various mass blending ratios: (●) PVC (◇) ASA (■) PVC/ASA 90:10 (◆) PVC/ASA 80:20 (▲) PVC/ASA 70:30 (□) PVC/ASA 60:40 (△) PVC/ASA 50:50.

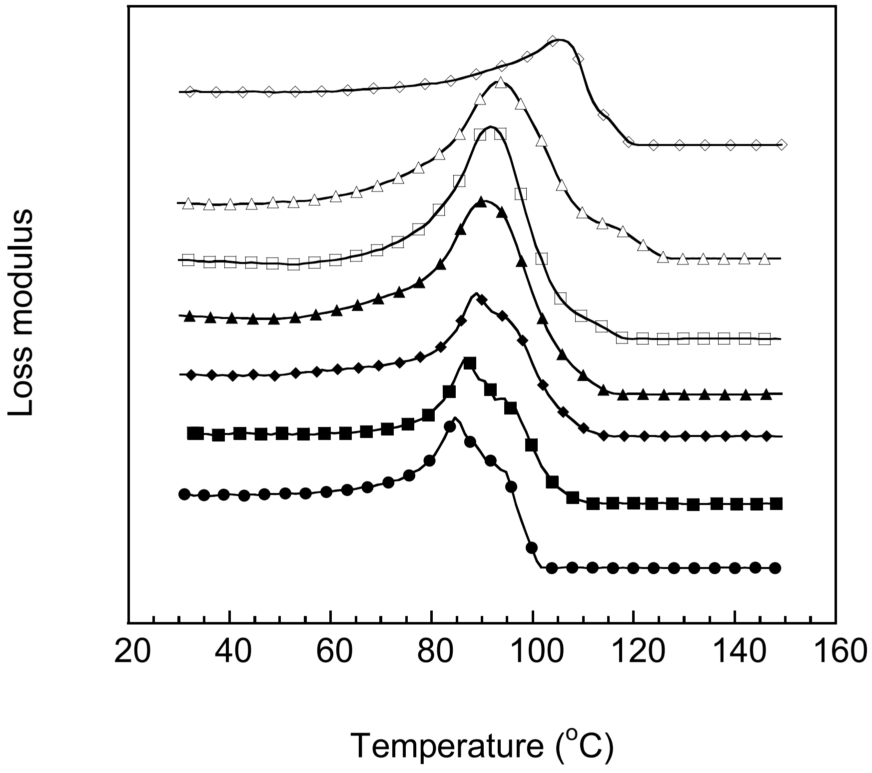


Figure 12.8: Loss modulus of PVC/ASA blends at various mass blending ratios: (●) PVC (◇) ASA (■) PVC/ASA 90:10 (◆) PVC/ASA 80:20 (▲) PVC/ASA 70:30 (□) PVC/ASA 60:40 (△) PVC/ASA 50:50.

12.1.2.3 Heat Distortion Temperature and Vicat Softening Temperature

The effects of ASA contents ranging from 0 wt% to 50 wt% on heat distortion temperature (HDT) and vicat softening temperature of PVC/ASA blends were also measured and are shown in Figure 12.9. From the results, the HDT of the neat PVC and ASA were determined to be 64°C and 77°C, respectively while the vicat softening temperatures of the neat PVC was approximately 77°C and of ASA was about 91°C. In addition, the PVA/ASA blends showed HDT and vicat softening temperatures between the values of the two starting polymers and a linear relationship with the amount of ASA added. The results imply improved thermal stability of the blend with the presence of the ASA in the PVC. A similar study and trend on HDT and vicat softening temperatures in this blend system was also reported by DeArmitt [90].

Due to higher T_g of SAN (ca. 100°C) in ASA matrix, diffusion of the SAN component into the PVC domain can improve thermal properties of the blends and provided the blends with wider service temperature than that of the PVC alone. The addition the ASA, having greater T_g than the PVC, as an impact modifier for PVC thus provided further improvement on the HDT and vicat softening temperature of the blend following the rule of mixture. However, in the opposite case such as those using impact modifier with lower T_g, the HDT was found to decrease substantially with the amount of the modifier i.e. poly(phenylene sulfide)/ nylon66 blends [105].

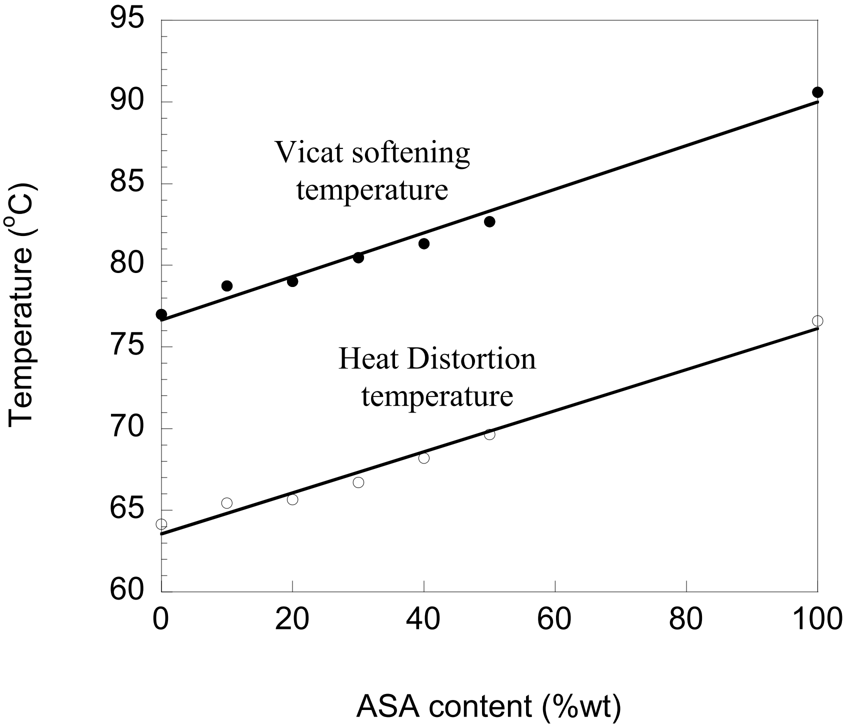


Figure 12.9: HDT and vicat softening temperature of PVC/ASA blends at various mass blending ratios: (●) vicat softening temperature (○) HDT.

12.1.3 Physical Properties

12.1.3.1 Density

Density of PVC blended with ASA as a function of the ASA content is shown in Figure 12.10. The density of the PVC/ASA blends tended to decrease with an increase of the ASA fraction. The density of the PVC/ASA blend at 10 wt% ASA content was determined to be 1.33 g cm^{-3}. As increasing ASA content to 50 wt%, the density was found to be 1.19 g cm^{-3}. These results were also well predicted by a rule of mixture calculated based on the measured density of the PVC of 1.36 g cm^{-3} and the density of the ASA of 1.07 g cm^{-3}. This good agreement between the measured and the theoretical density values suggested negligible amount of void in the blend samples implying suitable blending condition used in this investigation. The measurement is highly crucial for screening qualified specimen before further tests as several tests particularly mechanical tests are highly sensitive to void or defects present in the samples.

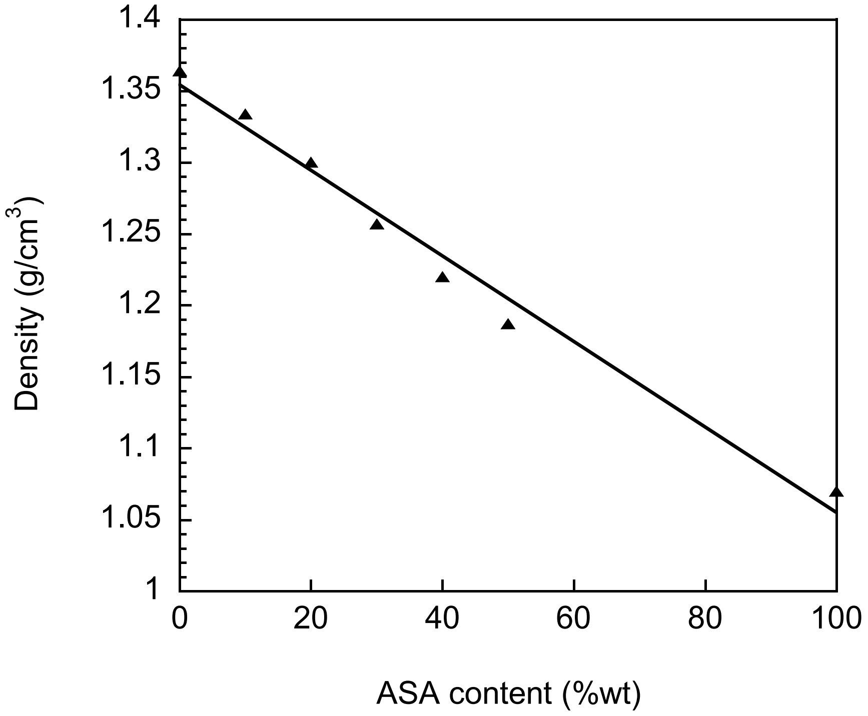


Figure 12.10: Densities of PVC/ASA blends at various mass blending ratios.

12.1.3.2 Water Absorption

It is well known to many researchers that water absorption, the tendency of plastics to absorb moisture, can significantly alter some key mechanical, electrical, or optical property. After water absorption, materials result in dissolving, leaching, plasticizing, swelling, and deterioration in mechanical properties. As shown in Figure 12.11, water absorption of PVC, ASA, and their blends at varied contents of 10 wt% to 50 wt% of ASA was performed up to the saturation state. Table 12.4 listed the water absorption of all specimens at 2 hours, 24 hours, and long-term immersion. The water absorption at 24 hours of PVC was only about 0.06 wt% while that of the blends was found to increase from 0.09 wt% to 0.18 wt% with the increasing of ASA content. The neat ASA exhibited higher value at 24 hours immersion about 0.40 wt% than PVC and its blends with PVC due to the presence of a highly polar moiety of an acrylonitrile component in ASA.

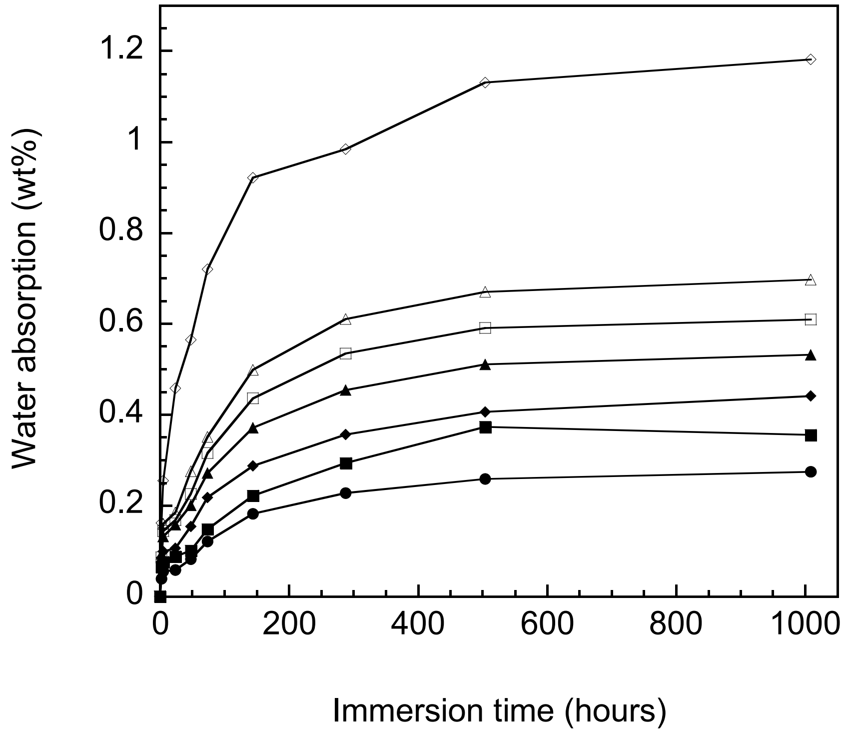


Figure 12.11: Water absorption of PVC/ASA blends at various mass blending ratios: (●) PVC (◇) ASA (■) PVC/ASA 90:10 (◆) PVC/ASA 80:20 (▲) PVC/ASA 70:30 (□) PVC/ASA 60:40 (△) PVC/ASA 50:50.

Table 12.4 Average water absorptions of PVC, ASA and PVC/ASA blends at various mass blending ratios.

Samples	Average water absorption*		
	at 2 hour immersion (wt%)	**at 24 hour immersion (wt%)**	**long-term (51 days) immersion (wt%)**
PVC	0.04	0.06	0.27
PVC/ASA 90:10	0.06	0.09	0.36
PVC/ASA 80:20	0.08	0.10	0.44
PVC/ASA 70:30	0.09	0.16	0.53
PVC/ASA 60:40	0.09	0.17	0.61
PVC/ASA 50:50	0.09	0.18	0.70
ASA	0.16	0.46	1.18

* The deviation of the average value is very small (less than 0.01 wt%).

5.1.3.3 Weatherability

PVC without an aid of suitable UV stabilizers is rather sensitive to the weathering action. Its mechanical properties and color are usually changed as a result of ultraviolet irradiation [1,19]. Especially in the presence of oxygen and moisture, it undergoes a very fast dehydrochlorination and a peroxidation process with the formation of polyenes and subsequent scission of the chains, with the formation of water "washable" products as well as cross-linking [19, 106]. In this work, the blend formulation with ASA content of 50 wt%, which also provides maximum impact strength as discussed earlier, was selected for natural weathering study in comparison with the neat PVC sample. The test was performed in Rayong Province, Thailand, for a time period of up to 120 days (i.e. during December 18th 2010 to April 25th 2011), and the variation of color difference of the specimens as a function of time was recorded as shown in Figure 12.12. From the figure, we can see that the incorporation of ASA into PVC greatly imparted substantial color retention of PVC. The reduction in color changing was reported quantitatively by measuring color difference ($\triangle E^*$) as calculated by measuring changes in L*, a*, and b* color values relative to unexposed controls of the PVC and the

PVC/ASA blend (50/50). Furthermore, △E* value of the neat PVC significantly increased with increasing exposed times while that of the PVC/ASA = 50:50wt% was relatively unchanged as a function of the exposure time.

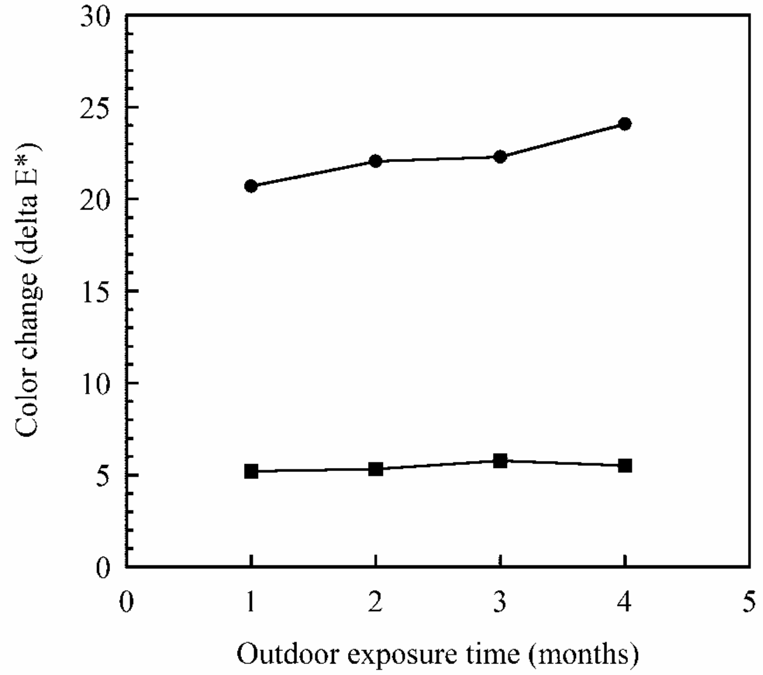


Figure 12.12: Color change after weathering at various outdoor exposure times: (●) PVC, (■)PVC/ASA 50:50wt%.

Figure 12.13a: Visual appearance of the sample surfaces after weathering at various outdoor exposure time: a) PVC b) PVC/ASA 50:50 wt%.

An effect of natural weathering on visual appearance of the sample surfaces, i.e. PVC and PVC/ASA (50:50) is also illustrated in Figure 12.13a. At the end of weathering test (up to 4 months), the neat and un-stabilized PVC suffered a greater change in the color from white to dark grey color possibly owing to the chromophoric group formation of conjugated double bonds i.e., alkene and polyene linkages which can absorb light readily. Photo-degradation might also convert the surface of the neat PVC to dark-colored surface of lower extensibility owing to polymer chain scission [19]. For the PVC/ASA blend system, the sample surface under the effect of the natural weathering showed negligible change in color compared to that of the neat PVC. Therefore, the color retention performance of the neat PVC can be conveniently obtained by incorporation ASA into PVC to form blends. This is also due to the much lower △E* of the neat ASA than that of the neat PVC [93]. Additionally, no surface crack was observed after this period of natural weathering for both the neat PVC and the PVC/ASA blend. In terms of impact retention, the impact strengths of the neat PVC and PVC/ASA blends at ASA content of 30 wt% and 50 wt% was compared after 4 months outdoor exposure. The impact strength of PVC was remarkably decreased by 25% after 4 months of natural aging. For the PVC/ASA blends, ASA was found to significantly improve the impact retention of the blends at ASA content of 50 wt%. After aging PVC/ASA blend at 50 wt% of ASA for 4 months, no change in impact strength was observed. These evidences indicated that ASA can help improve weatherability of PVC/ASA blends.

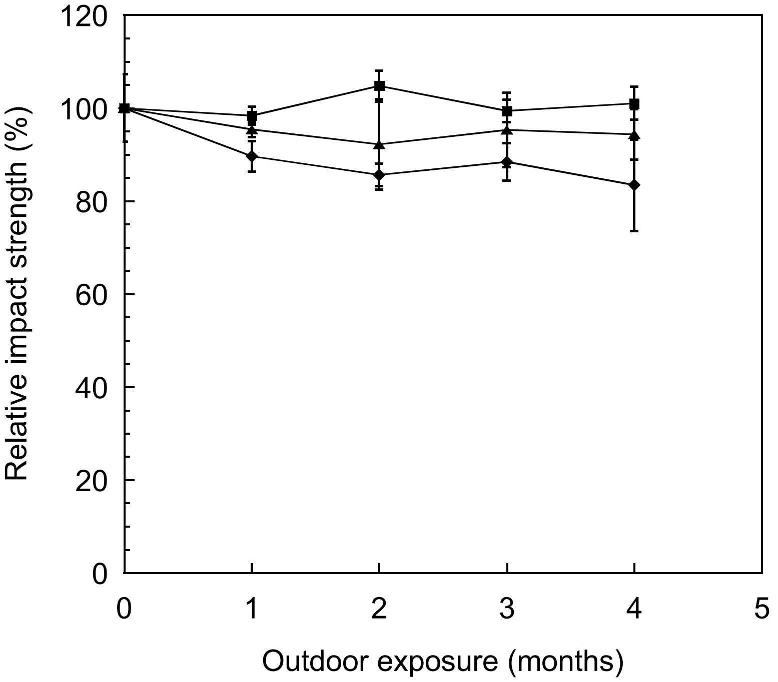


Figure 12.13b: Impact retention after weathering at various outdoor exposure times: (◆) PVC, (▲) PVC/ASA 70:30wt%, (■) PVC/ASA 50:50wt%.

In the following section, we selected PVC/ASA at a mass ratio of 50/50 for further investigation as a matrix for wood composite preparation since it provided the highest impact strength with suitable thermal and mechanical characteristics for wood composites.

12.2 Effects of Processing Temperature on the Mechanical Properties of PVC/ASA Blends

In polymer blend systems, factors which affect the toughness of materials include the presence of rubber particle in the rigid matrix, ability to craze, shear banding and debonding or cavitation, interfacial adhesion between the polymers, and anisotropy. Benson and Burford suggested that these factors are all affected by processing conditions and their effect can be investigated by mechanical testing [91]. In order to obtain the high impact performance matrix for wood composites, PVC/ASA blend with 50 wt% of ASA content that exhibited the greatest impact strength from previous section was used to study in this section. The PVC/ASA blend was compounded by two-roll mills at different processing temperature at 160^{o}C, 170^{o}C, and 180^{o}C.

12.2.1 Impact Properties

The impact behavior of PVC/ASA blend with 50 wt% of ASA content was studied and shown in Figure 12.14. It was suggested that the processing temperature has a significant effect on the impact strength. At the processing temperature of 160 ^{o}C, the impact strength of the blend was found to be 42.1 kJ/m^2 and this value clearly increased to be 72.5 kJ/m^2 when the blend was mixed at the temperature of 170 ^{o}C. Further increase in impact strength was negligible at the processing temperature of 180 ^{o}C. The blend of ASA with other polymer such as poly(butylene terephthalate) (PBT) and poly(ethylene terephthalate) (PET) were studied by Benson and Burford [91,36]. In ASA/PBT blend system, the processing temperature which was used in the study and resulted in optimum mechanical properties to the blends was in a range of 230 ^{o}C. As high as the processing temperature of ASA/PBT system was also appropriate in ASA/PET blend, 210-220 ^{o}C. The poor impact strength at a processing temperature of 160 ^{o}C in our study was possibly due to the lack in flow ability of the blend that resulted in incomplete dispersion of rubber particles of ASA component throughout the PVC matrix.

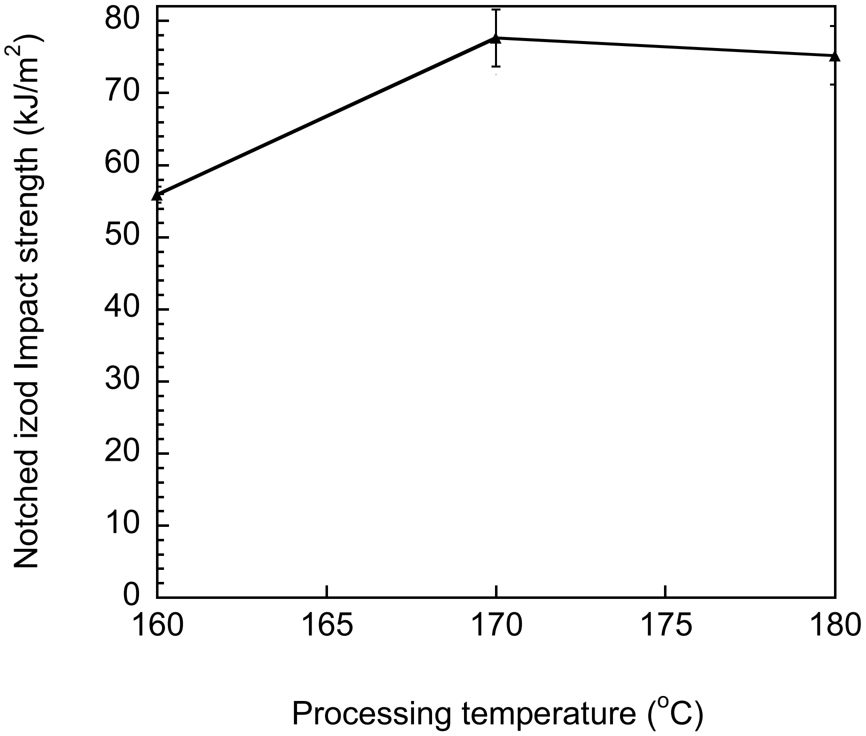


Figure 12.14: Impact strength of PVC/ASA 50:50 blend at processing temperature of 160°C, 170°C, and 180 °C.

12.2.2 Tensile Properties

Tensile properties of PVC/ASA blends with 50 wt% of ASA content were evaluated in Figure 12.15 and Table 12.5. The effect of processing condition at the temperature of 160 °C, 170 °C, and 180 °C on tensile properties was also investigated. As seen in Figure 12.15, processing condition has little influence on tensile properties of PVC/ASA blends. The tensile modulus of PVC/ASA blend at a processing condition of 160 °C, 170 °C, and 180 °C were determined to be 1.7 GPa, 1.9 GPa, and 1.7 GPa, respectively. Tensile strength values were found to correspond to modulus values. Tensile strength of the PVC/ASA blend at a processing condition of 160 °C was 42 MPa. As increasing of processing temperature from 170 °C to 180 °C, the tensile strength of the blend decreased from 45 MPa to 43 MPa; this implied a little effect of processing temperature on tensile properties of the blend. As discussed in previous section, Benson and Burford have studied the effects of processing condition and blending ratio not only on impact strength but also on tensile properties of ASA/PBT blend and ASA/PET blend

[90,107]. The negligible effect of processing temperature on tensile properties was also observed in ASA/PBT blends and ASA/PET blends.

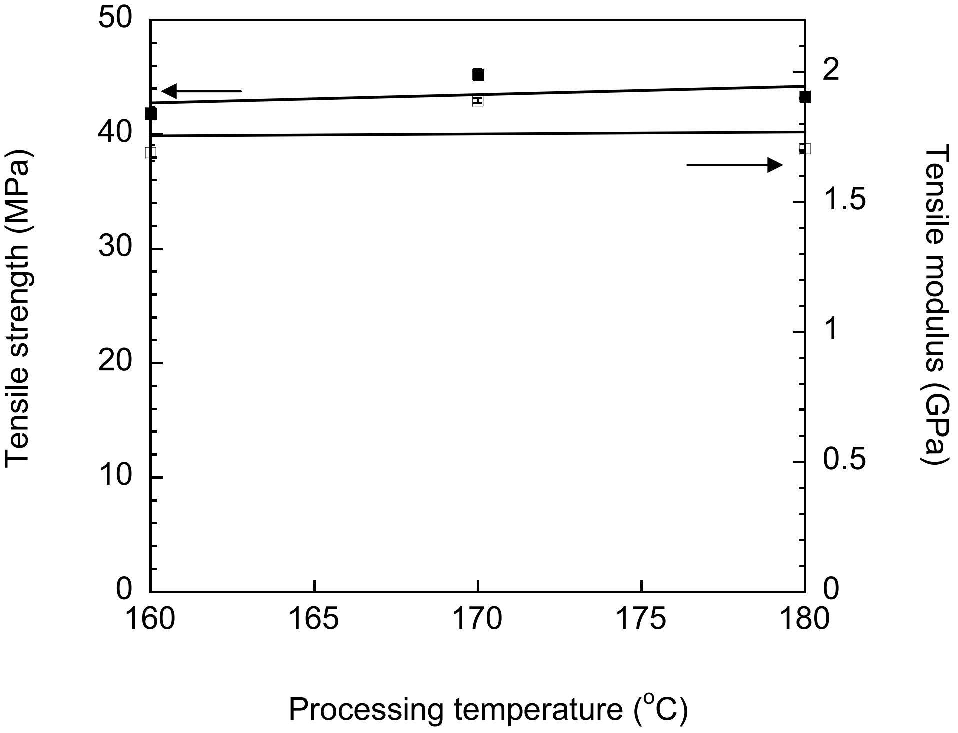


Figure 12.15: Tensile properties of PVC/ASA 50:50 blend at processing temperature of 160°C, 170°C, and 180°C: (■) tensile strength (□) tensile modulus.

Table 12.5 Tensile properties of PVC/ASA 50:50 blends at various processing temperature.

Samples	Tensile modulus (GPa)	Tensile strength (MPa)
160°C	1.69 ± 0.03	42 ± 0.5
170°C	1.89 ± 0.01	45 ± 0.4
180°C	1.70 ± 0.02	43 ± 0.2

5.2.3 Flexural Properties

The effect of processing condition on flexural properties of PVC/ASA blend with 50 wt% of ASA content was also observed and shown in Figure 12.16. The flexural modulus of the blend was found to be 2.59 GPa, 2.65 GPa, and 2.69 GPa, respectively as the processing temperature increased from 160 °C to 180 °C. In addition flexural strength, the flexural strength of PVC/ASA blend at a processing temperature of 160 °C was determined to be 70 GPa. When the processing temperature was increased from 170 °C to 180 °C, the blend exhibited flexural strength at 69 GPa and 72 GPa, respectively. This confirmed negligible effect of processing temperature on tensile properties and flexural properties in the range of temperature between 160 °C and 180 °C. Furthermore, the processing condition which resulted in optimum mechanical properties to the blend was suggested to be 170 °C.

Table 12.6 Flexural properties of PVC/ASA 50:50 blends at various processing temperature.

Samples	Tensile modulus (GPa)	Tensile strength (MPa)
160°C	2.59 ± 0.06	70 ± 1.7
170°C	2.65 ± 0.05	69 ± 0.3
180°C	2.69 ± 0.04	72 ± 1.7

12.3 Effects of Coconut Fiber Content on the Properties of PVC/ASA/Coconut fiber Composites

In recent years, fiber-filled composites have been employed extensively to improve mechanical properties to the polymer matrix. In this research, PVC/ASA blend as composite material was used to explore the effect of coconut fiber contents on characteristics of PVC/ASA/wood composites. Convergent flow or extensional flow gives a high level of fiber orientation parallel to the direction of flow. Moreover near the surface of a flow channel, fiber orient parallel to the surface. In the blending process by two-roll mills, a uniaxially oriented fibrous composite was obtained by vary small gap of two-roll mills.

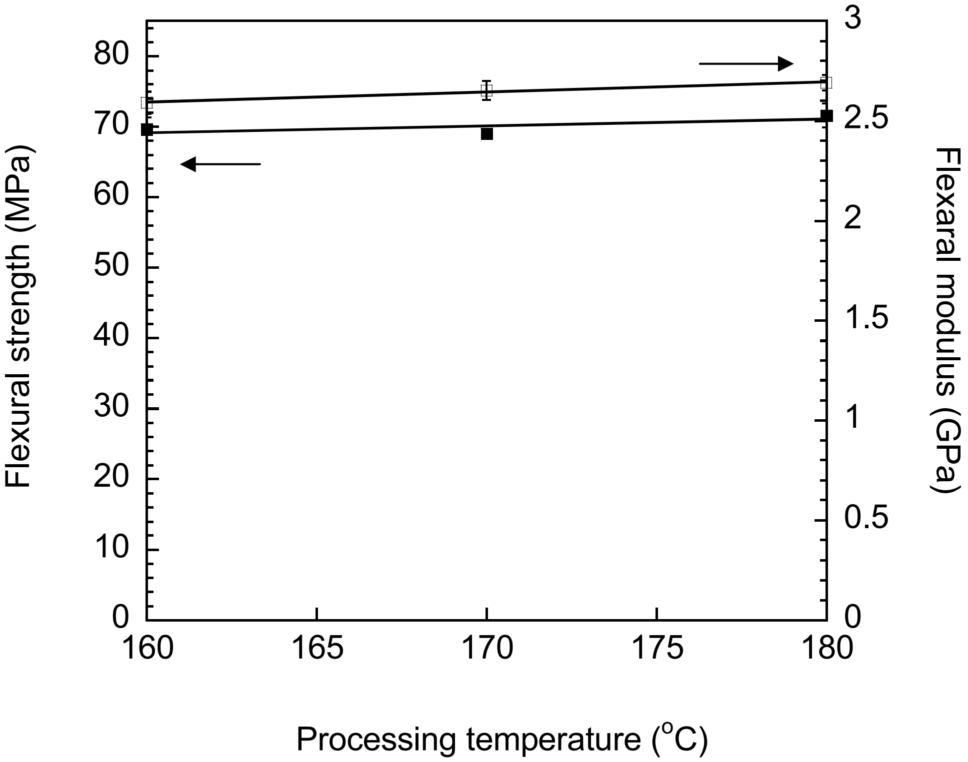


Figure 12.16: Flexural properties of PVC/ASA 50:50 blend at processing temperature of 160°C, 170°C, and 180°C: (■) tensile strength (□) tensile modulus.

12.3.1 Mechanical Properties

12.3.1.1 Impact Properties

Figure 12.18 shows the effect of coconut fiber content on notched Izod impact strength of our PVC/ASA/wood composites**.** From the figure, it can be noticed that the impact strength of composites tended to decrease with increasing coconut fiber content. The impact strength of our wood composite containing 10 wt% of coconut fiber exhibited the value as high as 195 J/m. The value was found to decrease with an increase of coconut fiber content to approximately 111 J/m at 50 wt% of the coconut fiber. A similar trend was also observed in other wood composite systems such as PVC/ABS/wood, PE/wood and PP/wood composites [108-109]. In general, the reduction in impact strength of fiber-filled composite maybe caused by an association of the following two mechanisms: (1) fibers practically drastically reduce the elongation to break and may reduce the area under the stress-strain curve, and (2) stress concentrations occur at regions around fiber ends, portion of poor adhesion, and regions where fibers contact one another. This is why the composite at high level of fiber content exhibits lower impact performance than that with lower level of fiber content [36].

In comparison with other fiber-filled composites, the impact strength of our PVC/ASA/wood composites was found to provide substantially higher value. For examples, Ishizaki *et al.* [108] studied the impact strength of PP/coconut fiber composites and reported the notched Izod impact strength value (at 50 wt% of coconut fiber) to be about 16 J/m. Yuan *et al.* [49] studied the mechanical properties of wood fiber reinforced PE and PP composites and reported that the impact strength value (at 50 wt% of wood fiber) was about 22-30 J/m and 18-22 J/m, respectively. In the case of PVC/pulp fiber composites reported by Ashori et al., the notched Izod impact strength of the composite at 50 wt% of the pulp fiber exhibited the value of 16 J/m [110]. Favaro *et al.* [111] investigated on the properties of sisal fiber-reinforced HDPE composites and reported the highest impact strength value (at 10 wt% of sisal fiber) was only about 65 J/m. The reason of this outstanding impact strength in wood composites from PVC/ASA matrix might be due to the very high inherent impact strength of the PVC/ASA blend matrix comparing with the other matrices i.e. PVC/ASA (50/50) = 778 J/m, PVC/ABS (50/50) = 650 J/m, PP = 15 J/m [49], HDPE = 154 J/m [49] etc. In addition, the suitable level of interfacial interaction between the fiber and the matrix is one key factor to contribute to the enhancement in impact strength of the composite by promoting energy dissipation through fiber pull-out or debonding [36]. An addition of ASA into PVC is believed to help improve this interfacial interaction with the coconut fiber thus a higher degree of energy dissipation. Similar phenomenon was also observed in the PVC/ABS/wood composite system.

Figure 12.17: Fracture surface of PVC/ASA/wood composites at a fixed PVC/ASA mass ratio of 50:50 after notched Izod impact tests at various coconut fiber contents

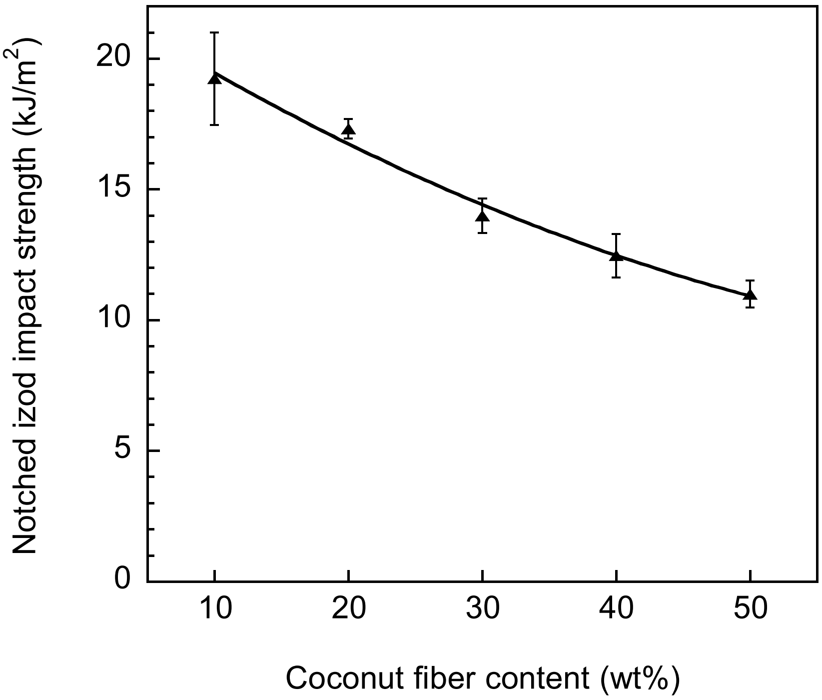


Figure 12.18: Impact strength of PVC/ASA/wood composites at a fixed PVC/ASA mass ratio of 50:50 at various coconut fiber contents.

12.3.1.2 Tensile Properties

In Figure 12.19, the effects of coconut fiber content ranging from 10-50 wt% on tensile properties of the PVC/ASA/coconut fiber composites were illustrated. It can be observed that the tensile modulus of the composites was found to systematically increase with increasing coconut fiber content. The similar behavior was also found in other wood composites system such as Polyester/wood and PP/wood composites [112, 113]. Abdul Khalil *et al.* [112] examined the chemical modification and the effect of fiber type on properties of fiber reinforced polyester composites. The addition of all fiber types (0-55 wt%) improved the tensile modulus of the composites up to 50-60%. Lai *et al.* [113] investigated the mechanical properties of PP/coconut fiber composites at up to 25 wt% of coconut fiber loading. The obtained tensile modulus of the composites was about 15% higher than that of the unfilled PP at the maximum fiber content. This is clear that the addition of rigid coconut fiber filler (having modulus in the range of 4-6 GPa)

[69] could have an effect on the mobility restriction of polymer molecular chains and same observation has also been reported in various wood composite systems [49, 76, 111-115].

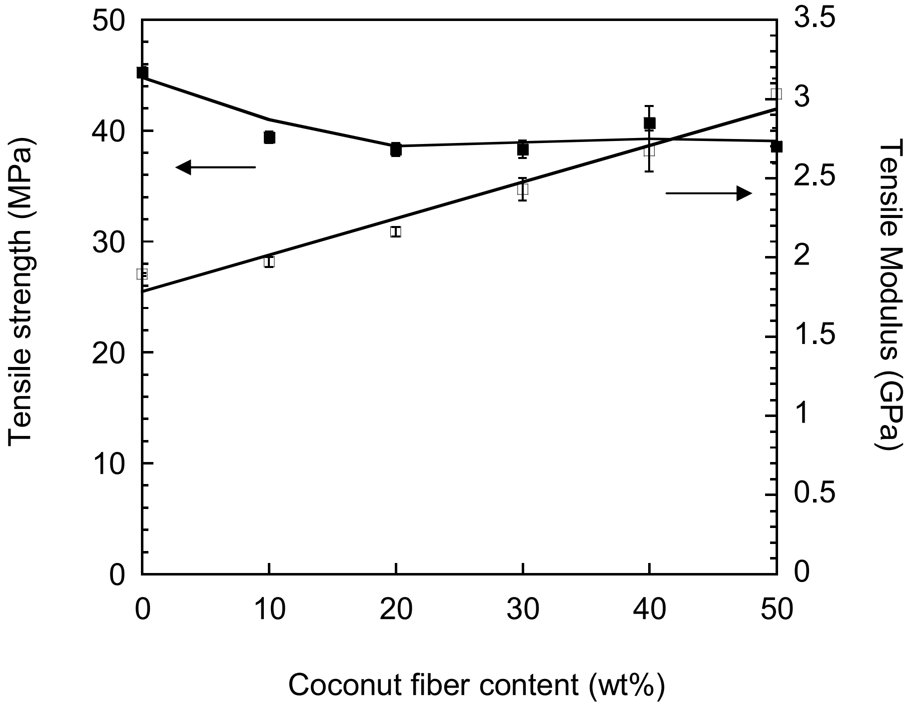


Figure 12.19: Tensile properties of PVC/ASA/wood composites at a fixed PVC/ASA mass ratio of 50:50 at various coconut fiber contents.

Tensile strength of short fiber reinforced WPCs has been observed to mainly decrease with an addition of the short fiber (as opposite to long fiber) such as that observed in PP/coconut fiber [112], HDPE/sisal fiber [111], PP/maple wood fiber [49], PE/maple wood fiber [49]. Neilsen and Landel discussed the tensile strength of composites to be greatly affected by such factors as the perfection of packing and alignment of fibers, and by imperfection such as voids in the material [36]. The decrease in tensile strength in presence of short fiber could be attributed to 1) appreciable distances between each end of different fibers are ineffective in transmitting load from the matrix to the fibers; 2) the fiber ends tend to act as a stress concentrators and thus as crack initiators; 3) fibers that do not overlap one another substantially cannot contribute the composite strengthening; and 4) it is impossible to achieve perfect fiber orientation in short fibers as with continuous fibers. With increasing the content of the short coconut fiber in PVC/ASA matrix, the strength tended to be level off and not show a steady decreasing trend thus due to the shorter distances between fiber ends, the higher degree of fiber overlapping as well as greater fiber orientation from two roll mill processing. Tensile strength of PE/wood fiber composites was found to decrease as fiber content increased i.e. from a value of 24 MPa for unfilled PE to 14.2 MPa for the composite with 50 wt% fiber content [49]. Furthermore, in PP/coconut fiber composites, tensile strength was also found to decrease as fiber content increased i.e. from 30 MPa for unfilled PP to 20 MPa for the composite with 50 wt% fiber content [113]. As compared to the polyolefin/woodfiber systems, PVC/ASA/coconut fiber composites, without any surface treatment, was observed to show an ability to maintain relatively higher tensile strength even with high coconut fiber contents (i.e. 38 MPa at 50% wt% of coconut fiber).

Table 12.7 Tensile properties of PVC/ASA/wood composites at a fixed PVC/ASA mass ratio of 50:50 at various coconut fiber contents.

Samples	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PVC/ASA coconut fiber 0%	1.89 ± 0.01	45.2 ± 0.5	12.6 ± 3.6
PVC/ASA coconut fiber 10%	1.97 ± 0.03	39.4 ± 0.5	3.1 ± 0.7
PVC/ASA coconut fiber 20%	2.16 ± 0.03	38.3 ± 0.6	2.6 ± 0.2
PVC/ASA coconut fiber 30%	2.43 ± 0.07	38.32 ± 0.8	2.1 ± 0.2
PVC/ASA coconut fiber 40%	2.67 ± 0.13	40.7 ± 1.5	1.9 ± 0.1
PVC/ASA coconut fiber 50%	3.03 ± 0.10	38.6 ± 1.6	1.5 ± 0.2

5.3.1.3 Flexural Properties

Figure 12.20 presents the effect of coconut fiber content on flexural properties of PVC/ASA/coconut fiber composites. With increasing the coconut fiber content, flexural modulus of the composites also increased systematically from 3.25 GPa at 10 wt% fiber to 5.06 GPa at 50 wt% fiber. This significant increase in the flexural modulus of the PVC/ASA/coconut fiber composites is primarily attributed to the reinforcing effect imparted by the presence of the coconut fiber in the polymeric matrix as described in the tensile properties of the composites. The similar improvement in flexural modulus was also reported in the systems of PP/wood fiber composites [108, 113]. Besides, the flexural strength of PVC/ASA/coconut fiber composites is also depicted in Figure 3. From the results, the flexural strength of the unfilled PVC/ASA at 50/50 mass ratio was determined to be 66 MPa and the strength of the composite showed an increasing trend up to 40 wt% of the fiber i.e. 83 MPa. Above 40 wt%, the flexural strength of the composite decreased from 83 MPa to 73 MPa (at 50 wt%). When the content of the polymer matrix decreased, the area of fiber for reinforcing was reduced, making the fiber easily slip off after applying stress [113].

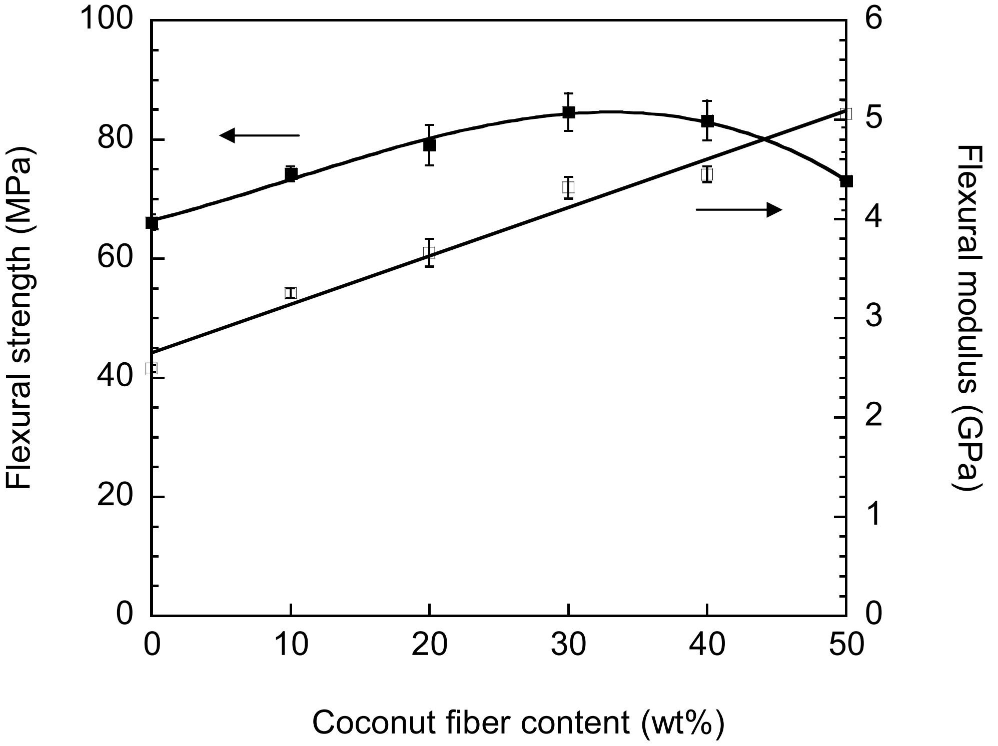


Figure 12.20: Flexural properties of PVC/ASA/wood composites at a fixed PVC/ASA mass ratio of 50:50 at various coconut fiber contents.

Table 12.8 Flexural properties of PVC/ASA/wood composites at a fixed PVC/ASA mass ratio of 50:50 at various coconut fiber contents.

Samples	Flexural modulus (GPa)	Flexural strength (MPa)
PVC/ASA coconut fiber 0%	2.49 ± 0.03	66.1 ± 1.3
PVC/ASA coconut fiber 10%	3.25 ± 0.05	74.2 ± 1.3
PVC/ASA coconut fiber 20%	3.66 ± 0.14	79.0 ± 3.4
PVC/ASA coconut fiber 30%	4.31 ± 0.11	84.6 ± 3.2

PVC/ASA coconut fiber 40%	4.45 ± 0.08	83.1 ± 3.4
PVC/ASA coconut fiber 50%	5.06 ± 0.14	73.0 ± 4.9

12.3.2 Thermal Properties

12.3.2.1 Differential scanning calorimetry

The glass transition behavior of the PVC/ASA/coconut fiber composites at a fixed PVC/ASA mass ratio of 50/50 was examined by DSC as a function of the coconut fiber content (10 wt%-50 wt%). As illustrated in Figure 12.21, the DSC scan was repeated twice in order to eliminate absorbed moisture in all samples. The T_g listed in Table 12.9 was determined by the repeated DSC thermographs. Unfilled PVC/ASA blend showed two T_g's at 84°C and 107°C, but for its composites with coconut fiber, their T_g's slightly increased. The first T_g of composites was in a range of 83°C-84°C, while the second T_g of composites was in a range of 107°C-110°C. DSC analysis indicated that coconut fiber contents influenced on thermal behavior of PVC/ASA/coconut fiber composites by increasing T_g's of PVC and ASA. In addition, it was found that coconut fiber had the same effect on both PVC and ASA phase due to the same difference in the two T_g's with increasing in coconut fiber content.

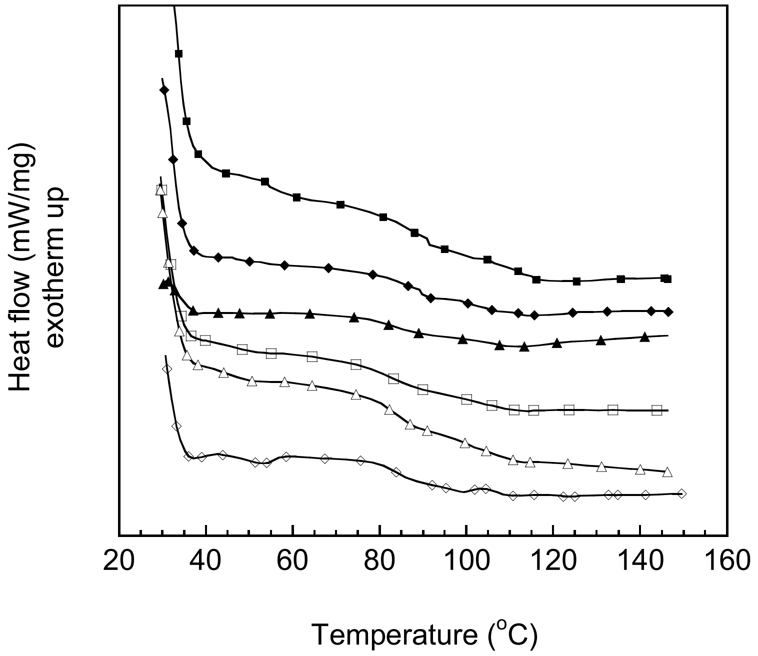


Figure 12.21: DSC thermograms of PVC/ASA/wood composites at a fixed PVC/ASA

mass ratio of 50:50 at various coconut fiber contents: (◇) PVC/ASA coconut fiber 0% (△) PVC/ASA coconut fiber 10% (□) PVC/ASA coconut fiber 20% (▲) PVC/ASA coconut fiber 30% (◆) PVC/ASA coconut fiber 40% (■) PVC/ASA coconut fiber 50%.

12.3.2.2 Dynamic Mechanical Analysis

From DMA analysis, the effects of coconut fiber content on storage modulus and glass transition temperature (obtained from the peak of loss modulus) of the composites are illustrated in Figures 12.22-12.24 and also summarized in Table 12.9. From Figure 12.22, the storage modulus in glassy state of the PVC/ASA/coconut fiber composites was found to increase with increasing coconut fiber contents from the reinforcing effect of the more rigid coconut fiber to the PVC/ASA matrix. The trend was in good agreement with the tensile and flexural modulus as previously discussed. Furthermore, two glass transition temperatures of the composites were clearly observed from the two loss modulus peaks in each thermogram of the composite in Figure 12.23. It can be seen that T_{g1} of the composites continuously increased from about 95°C (at 10 wt% fiber) to 100°C (at 50 wt% fiber) while T_{g2} of the composites also increased from 113°C to 115°C at the same fiber contents. A similar behavior was also observed in the system of PVC/ENR/oil palm empty fruit bunch composites reported by Ratnam *et al*. [116] and PP/natural fiber composites reported by Tajvidi *et al*. [117]. The observed enhancement in T_g was attributed to a restriction effect on the motion of molecular chains of the polymer matrix due to impediment of a more rigid coconut fiber. This also implied some interfacial interaction to exist between the fiber and the matrix.

Table 12.9 Glass transition temperatures of PVC/ASA/wood composites at various coconut fiber contents from loss modulus

Fiber content (wt%)	Storage modulus (GPa)	T_{g1} (°C)	T_{g2} (°C)
10	2.63	94.8	113.4
20	3.00	95.0	114.0
30	3.68	95.8	114.0
40	4.29	96.8	114.3

50	4.85	100.1	114.5

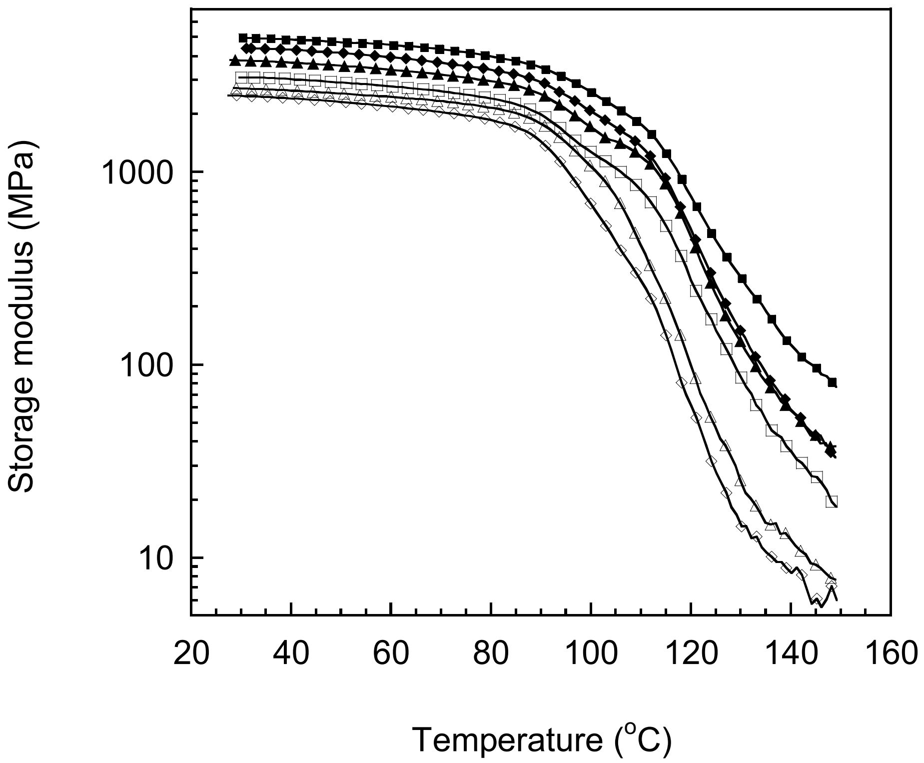


Figure 12.22: Storage modulus of PVC/ASA/wood composites at a fixed PVC/ASA mass ratio of 50:50 at various coconut fiber contents:
(◇) PVC/ASA coconut fiber 0% (△) PVC/ASA coconut fiber 10%
(□) PVC/ASA coconut fiber 20% (▲) PVC/ASA coconut fiber 30%
(◆) PVC/ASA coconut fiber 40% (■) PVC/ASA coconut fiber 50%.

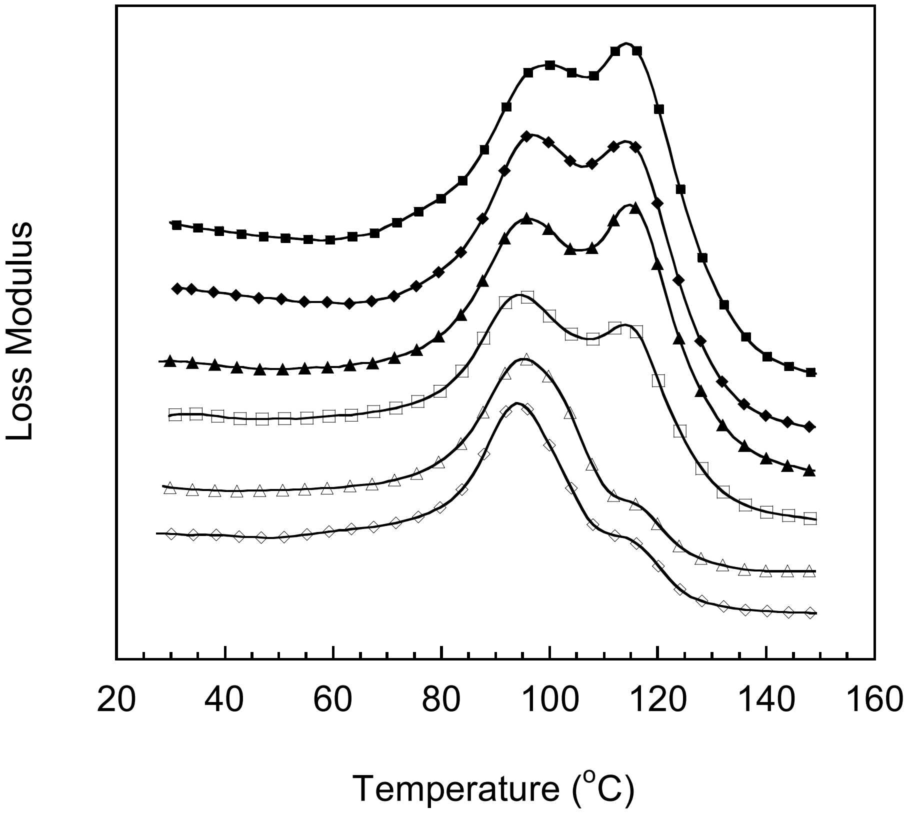


Figure 12.23: Loss moduli of PVC/ASA/wood composites at a fixed PVC/ASA mass ratio of 50:50 at various coconut fiber contents:
(◇) PVC/ASA coconut fiber 0% (△) PVC/ASA coconut fiber 10%
(□) PVC/ASA coconut fiber 20% (▲) PVC/ASA coconut fiber 30%
(◆) PVC/ASA coconut fiber 40% (■) PVC/ASA coconut fiber 50%.

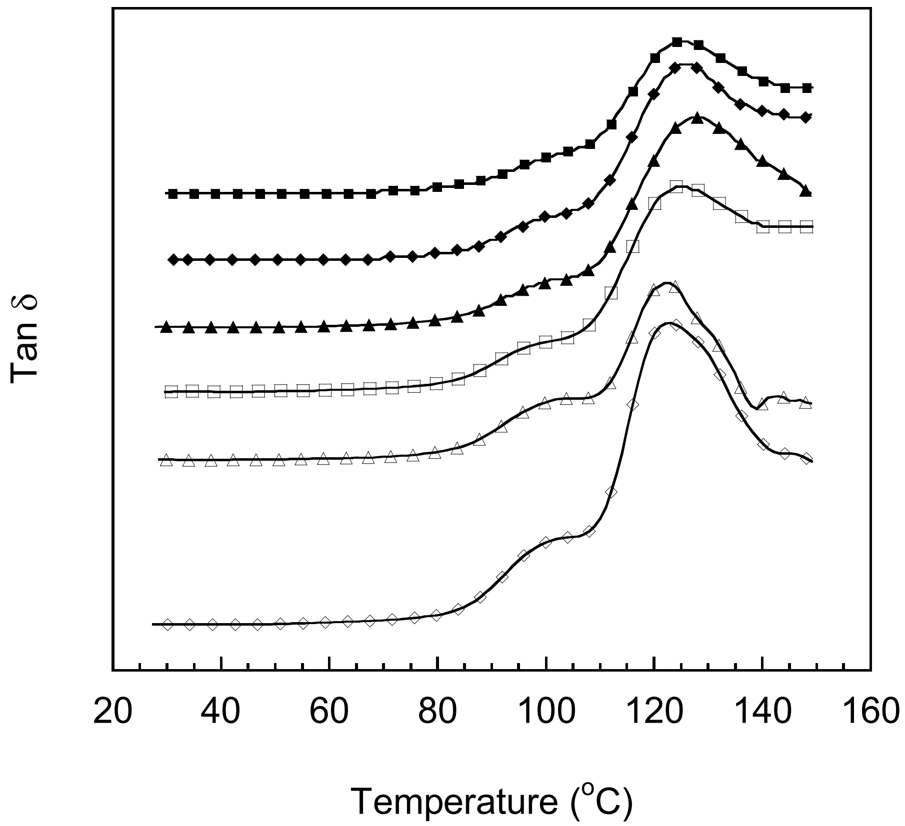


Figure 12.24: Loss tangent of PVC/ASA/wood composites at a fixed PVC/ASA mass ratio of 50:50 at various coconut fiber contents:
(◇) PVC/ASA coconut fiber 0% (△) PVC/ASA coconut fiber 10%
(□) PVC/ASA coconut fiber 20% (▲) PVC/ASA coconut fiber 30%
(◆) PVC/ASA coconut fiber 40% (■) PVC/ASA coconut fiber 50%.

Additionally, the temperature dependence of tan δ of PVC/ASA/wood composite is illustrated in Figure 12.24. For the unfilled PVC/ASA, the broad transition zone was visible in the temperature range from 90 to 130 °C, corresponding to α relaxations of the PVC and ASA. Addition of coconut fiber resulted in a lowering of the tan δ peaks. As same as in many composite systems, the damping of polymer matrix is always greater than that of reinforced composites [36, 117]. With increasing coconut fiber content, loss tangent peaks of PVC/ASA matrix was flatten and shifted to higher temperature. The decrease in tan δ peak suggested the addition of the fiber contribute to the more elastic nature of the wood composites.

12.3.2.3 Heat Distortion Temperature and Vicat Softening Temperature

The effects of coconut fiber contents on vicat softening temperature and heat distortion temperature (HDT) of PVC/ASA/coconut fiber composites are shown in Figure 12.25. From this figure, the vicat softening temperature of the unfilled PVC/ASA was determined to be about 83°C. It is evident that the vicat softening temperature and HDT of the composites increase with increasing coconut fiber contents i.e. vicat softening temperature increased from 85°C (at 10 wt% fiber) to 96°C (at 50 wt% fiber). For HDT, the unfilled PVC/ASA showed HDT to be 70°C and this value was also found to systematically increase with the coconut fiber content i.e. the HDT increased from 73°C (at 10 wt% fiber) to 82°C (at 50 wt% fiber). As compared with polyolefins wood composites, the thermal stability of our PVC/ASA/wood composites exhibited a substantially higher value thus allowed an application of these wood composites at significantly higher temperature [109].

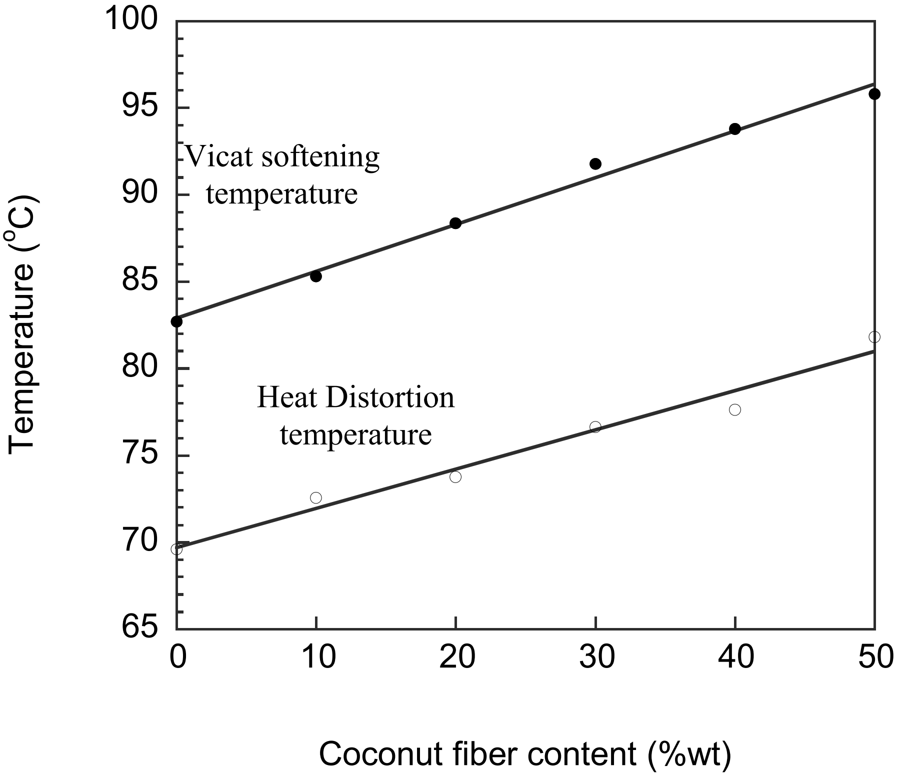


Figure 12.25: HDT and vicat softening temperature of PVC/ASA/wood composites at a fixed PVC/ASA mass ratio of 50:50 at various coconut fiber contents: (●) vicat softening temperature (○) HDT.

12.3.3 Physical Properties

12.3.3.1 Density

The values of density of the PVC/ASA/coconut fiber composites at various coconut fiber contents at 10-50 wt% are shown in Figure 12.26. The density of the unfilled PVC/ASA was determined to be 1.19 g/cm^3. The density of PVC/ASA/coconut fiber at 10 wt% coconut fiber content was determined to be 1.20 g/cm^3. As increasing coconut fiber content to 50 wt%, the density systematically increased to 1.27 g/cm^3.

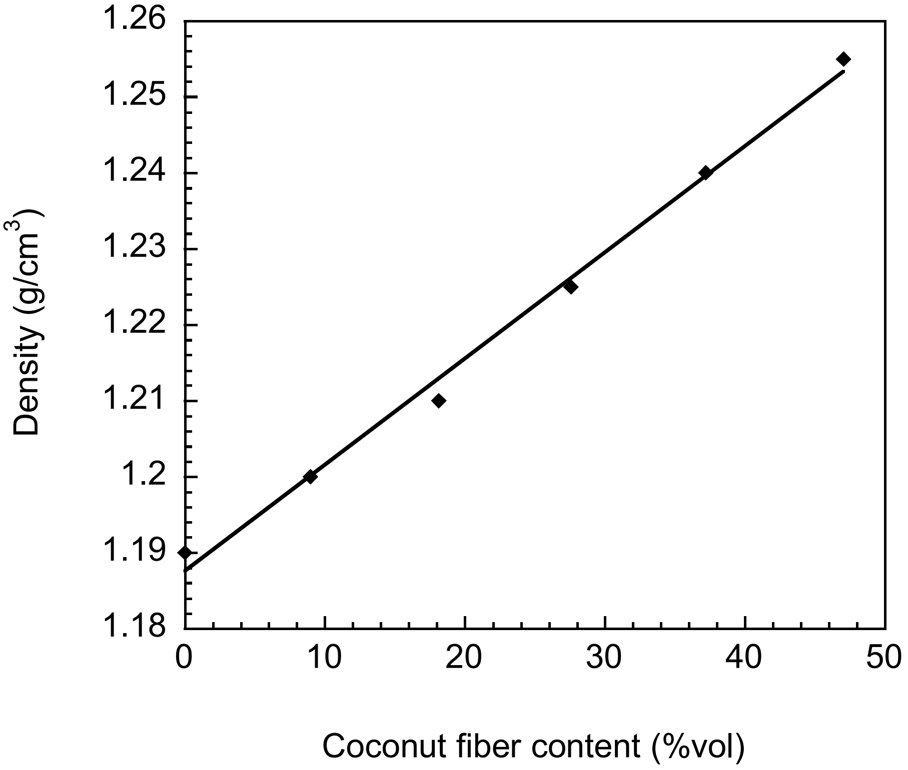


Figure 12.26: Densities of PVC/ASA/wood composites at a fixed PVC/ASA mass ratio of 50:50 at various coconut fiber contents.

12.3.3.2 Water Absorption and Thickness Swelling

The percentage of the water uptake as a function of time of the unfilled PVC/ASA and PVC/ASA/coconut fiber composites at different coconut fiber contents is shown in Figure

12.27. After 24 hours immersion, water absorption of the unfilled PVC/ASA was very low i.e. 0.18 w%, due to its relatively hydrophobic nature compared to natural fiber. Water uptake of the composites expectedly increased with an increase of the coconut fiber content as seen in the figure. With an addition of 10 wt% of coconut fiber, the water absorption value was raised to about 0.65 wt% and at up to 50 wt% fiber, the water absorption of the composites increased to 4.03 w%. These values are considered to be much lower than that of natural wood with the reported water absorption value as high as 39-70% [118].

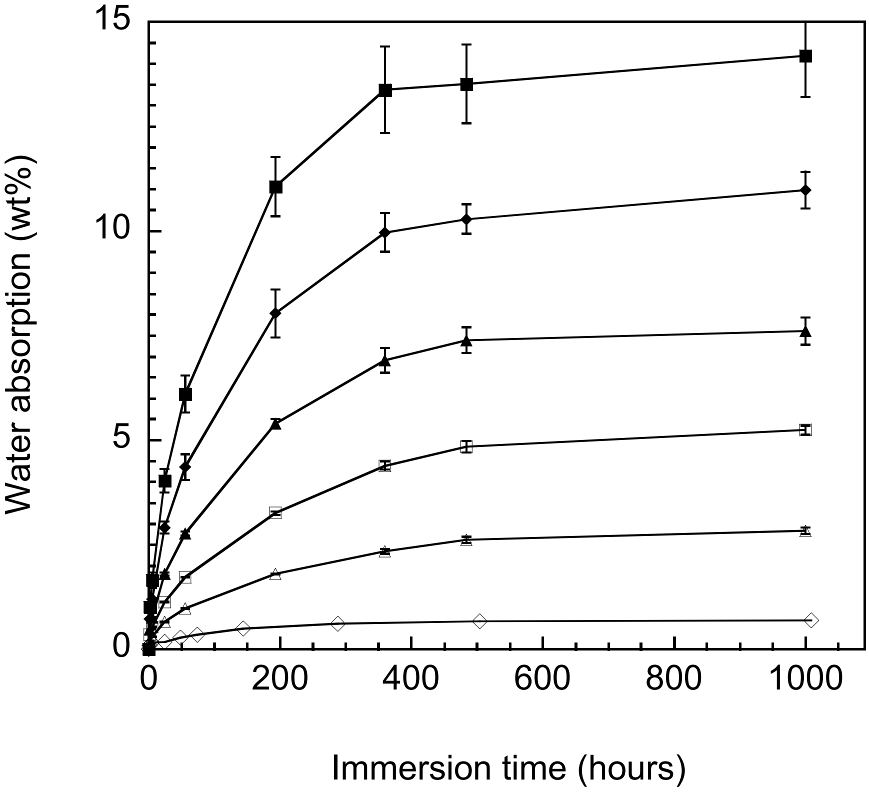


Figure 12.27: Water absorption of PVC/ASA/wood composites at a fixed PVC/ASA mass ratio of 50:50 at various coconut fiber contents:
(◇) PVC/ASA coconut fiber 0% (△) PVC/ASA coconut fiber 10%
(□) PVC/ASA coconut fiber 20% (▲) PVC/ASA coconut fiber 30%
(◆) PVC/ASA coconut fiber 40% (■) PVC/ASA coconut fiber 50%.

In a previous study, Ayrilmis and Jarusombuti [119] reported that the wood plastic composites containing a compatibilizer such as maleated polypropylene (MAPP) had significantly lower thickness swelling and water absorption than those without the MAPP.

According to their research, the interfacial bonding between the wood fiber and the polymer matrix was an important factor influencing the water absorption and the thickness swelling of the wood plastic composites. High water absorption of the composite at high fiber content may be due to the hydrogen bonding between water molecule and free hydroxyl groups present in the coconut fiber and the diffusion of water molecule into the interface between fiber and matrix. In addition, larger amount of voids might exist between the hydrophilic filler and the hydrophobic polymer matrix thus further contributed to the much greater water uptake of the composites with very high fiber loading [120]. The relatively low water absorption value of our wood composites thus suggested good matrix and fiber wetting with substantial interaction interaction between to two components. Moreover, the thickness swelling values (Figure 12.28) of the composite samples showed similar trend as water absorption experiment. For the 24 hours immersion, the thickness swelling of PVC/ASA/coconut fiber at 50 wt% fiber loading was observed to be 2.5%.

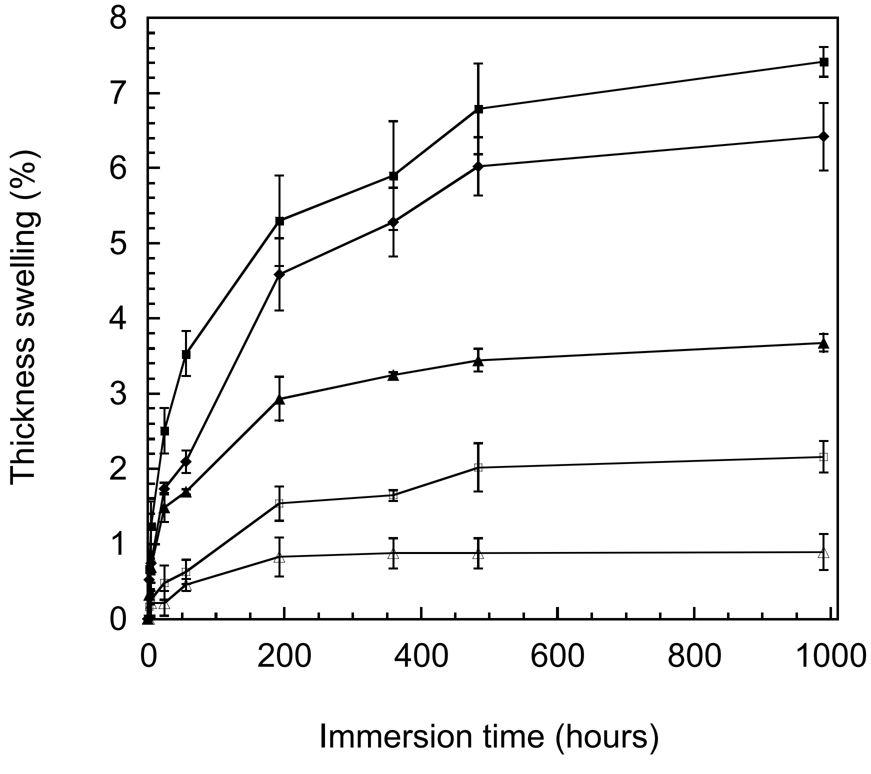


Figure 12.28: Thickness swelling of PVC/ASA/wood composites at a fixed PVC/ASA mass ratio of 50:50 at various coconut fiber contents: (△) PVC/ASA coconut fiber 10% (□) PVC/ASA coconut fiber 20% (▲) PVC/ASA coconut fiber 30% (◆) PVC/ASA coconut fiber 40%

(■) PVC/ASA coconut fiber 50%.

Table 12.10 The average water absorption and thickness swelling of PVC/ASA/wood composites at a fixed PVC/ASA mass ratio of 50/50 at various coconut fiber contents.

Fiber content (wt%)	**Average water absorption**		**Thickness swelling**	
	at 2 hour immersion (wt%)	**at 24 hour immersion (wt%)**	**at 2 hour immersion (wt%)**	**at 24 hour immersion (wt%)**
0	0.09 ± 0.00	0.18 ± 0.01	-	-
10	0.19 ± 0.07	0.65 ± 0.01	0.00 ± 0.00	0.20 ± 0.16
20	0.34 ± 0.01	1.12 ± 0.02	0.16± 0.23	0.48 ± 0.23
30	0.46 ± 0.01	1.79 ± 0.04	0.32± 0.01	1.48 ± 0.19
40	0.72 ± 0.00	2.90 ± 0.14	0.52± 0.16	1.73 ± 0.08
50	1.01 ± 0.13	4.03 ± 0.28	0.66± 0.05	2.50 ± 0.30

12.3.3.3 Weatherability

Natural weathering up to 3 months of unfilled PVC/ASA blend and PVC/ASA/coconut fiber at various coconut fiber contents ranging in 0 to 50 wt% fiber was investigated and the measured color change of the samples as a function of time is shown in Figure 12.29. From this figure, the unfilled PVC/ASA blends exhibited very little change in color whereas its composites showed higher degree of color change with increasing coconut fiber content. Moreover it was noticed that the lightness difference was a major influence to the total color change i.e. the composites showed a fading in color under weathering. The addition of ASA into PVC was reported in our recent work to significantly reduce color change of the neat PVC. Figure 12.30 shows SEM micrographs of the unweathered and the 3-month naturally weathered composites. Interface cracking was observed at the surface of the weathered composites. With increasing coconut fiber content, greater and larger cracks between fiber and polymer matrix were observed. The phenomenon helps explain the fading behavior of the composites due to outdoor exposure. The gaps or cracks between the matrix and the fiber induce light scattering on the composite surface thus the observed whitening of the surface. From the research by Fabiyi *et al.* [121-122], PVC and pine wood erosion was observed at the surface of weathered PVC composites by SEM. Crazing on the composite surface may be caused by differentially contact (resulting from wetting and drying) between wood and plastic interface during natural weathering, resulting in color fading [122].

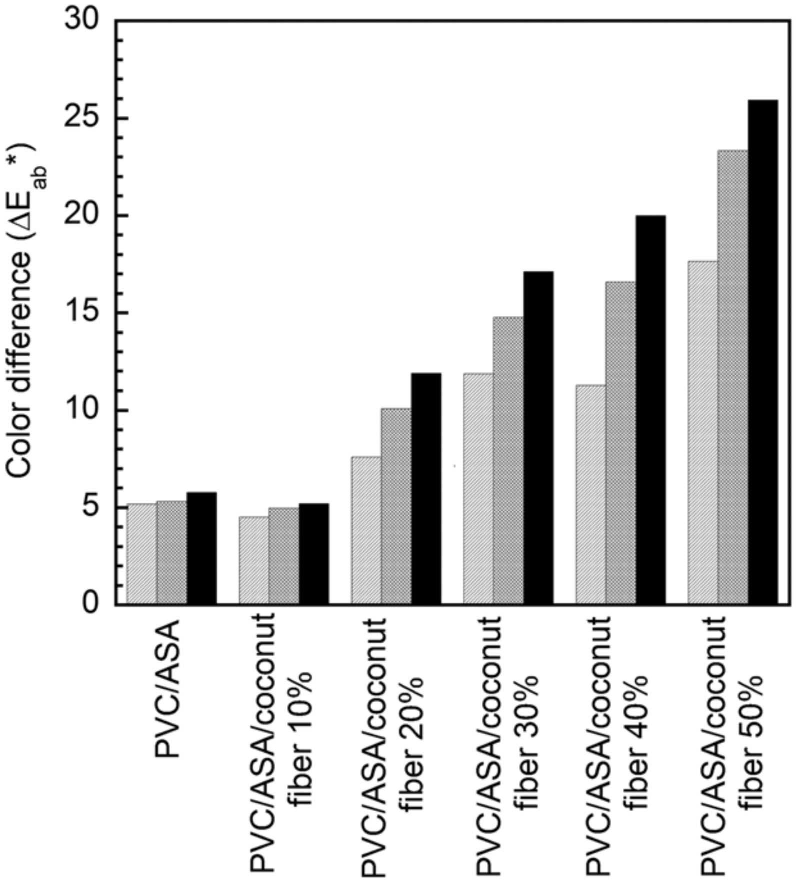


Figure 12.29: Color difference after weathering of PVC/ASA composite at various coconut fiber contents: ▨ 1 month, ▩ 2 months, ■ 3 months

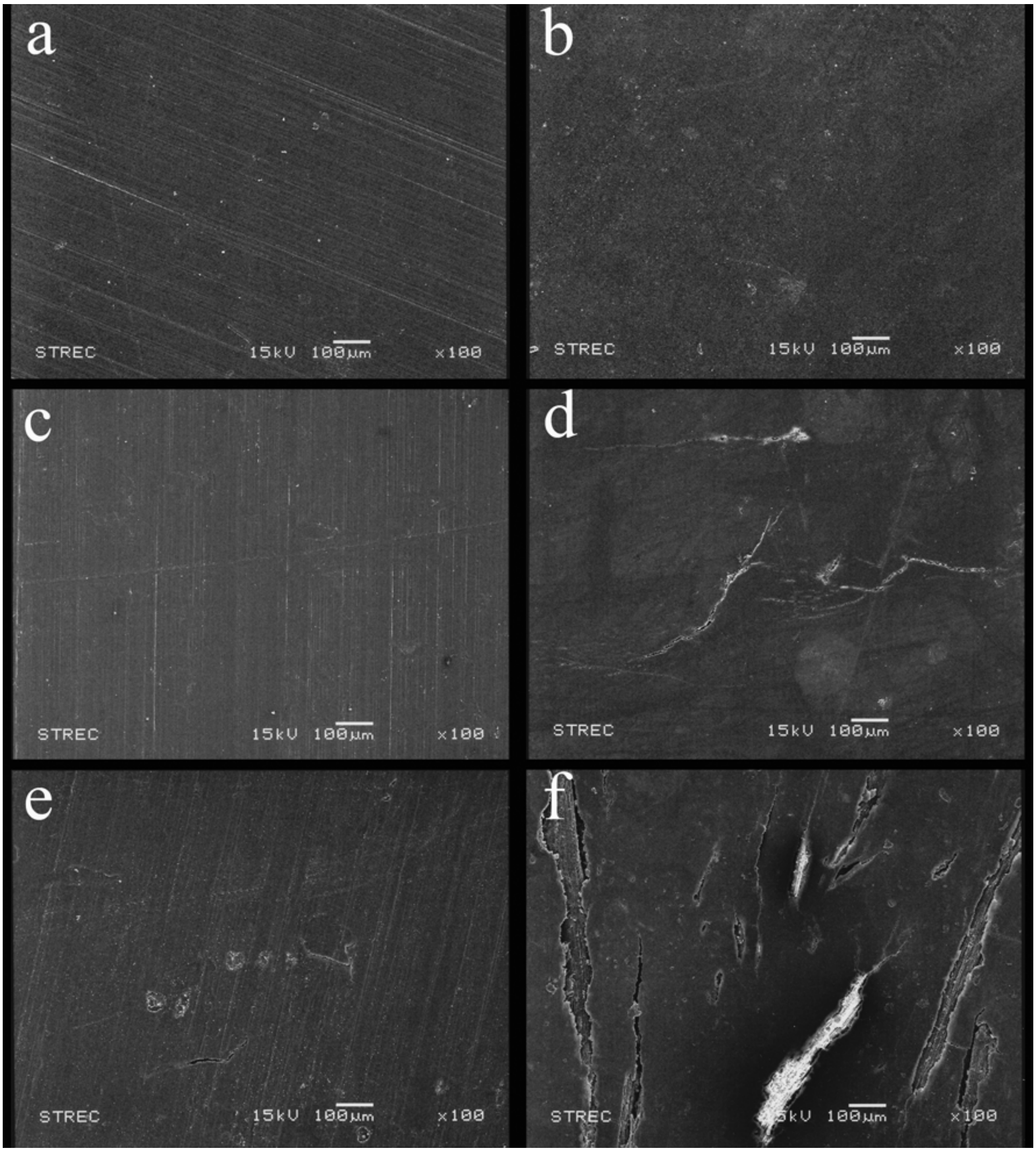


Figure 12.30: Scanning electron micrographs (x100) of PVC/ASA/coconut fiber composites; (a) un-weathered PVC/ASA matrix, (b) 3-months exterior-weathered PVC/ASA matrix, (c) un-weathered composite with 10% of coconut fiber, (d) 3-months exterior-weathered composite with 10% of coconut fiber, (e) un-weathered composite with 50% of coconut fiber, (f) 3-months exterior-weathered composite with 50% of coconut fiber,

In comparison on the impact retention, the impact strength of unfilled PVC/ASA and its composites at different coconut fiber content was investigated after natural exposure for 3 months. After weathering for 3 months, unfilled PVC/ASA showed the impact strength varied from 100-103% compared to control sample. For the PVC/ASA/coconut fiber composites, the impact strength after weathering was found in the range of 95-105% compared to control samples. That means no significant change in impact strength of weathered composites, which suggested that coconut fiber had no effect on the impact retention of PVC/ASA/coconut fiber composites upon natural aging for 3 months. On the other hand, after weathering for 3 months, ASA nicely maintained the impact strength of PVC/ASA/coconut fiber composites.

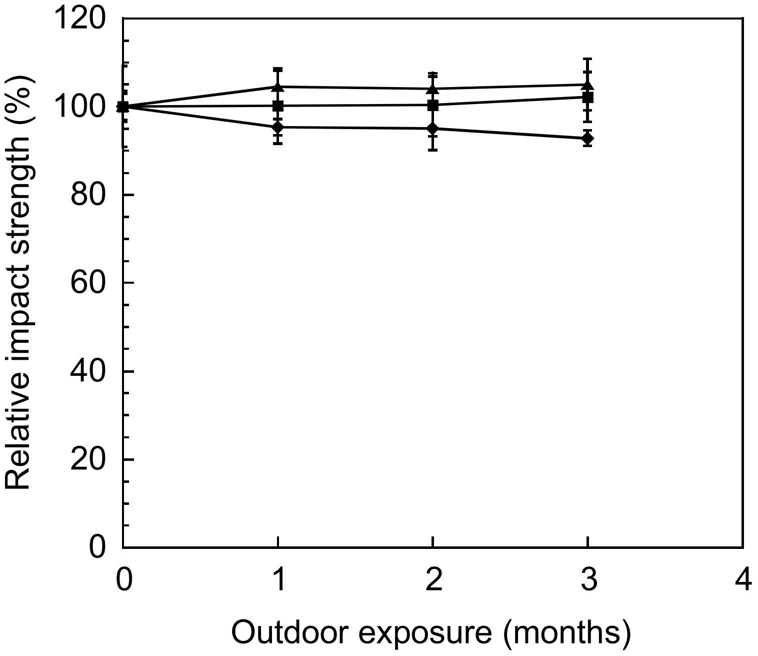


Figure 12.31: Impact retention after weathering at various outdoor exposure times: (■) PVC/ASA coconut fiber 10%, (▲) PVC/ASA coconut fiber 30%, (◆) PVC/ASA coconut fiber 50%.

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ACTIVITIES

13.1 International publications

- Rimdusit, S., Damrongsakkul, S., Atthakorn, D., Saramas, D. and Tiptipakorn, S. (2011). Mechanical, Thermal, and Water Uptake Characteristics of Woodflour-Filled Polyvinyl Chloride (PVC)/ Acrylonitrile Butadiene Styrene (ABS) Blends, Journal of Applied Polymer Science (in press).
- Rimdusit, S., Damrongsakkul, S., Wongmanit, P., Saramas, D. and Tiptipakorn, S. Characterization of coconut fiber-reinforced polyvinyl chloride (PVC)/acrylonitrile styrene acrylate (ASA) blends, (Submitted to Journal of Reinforced Plastics and Composites).
- Rimdusit, S., Wongmanit, P., Damrongsakkul, S., Saramas, D. and Jubsilp, D. High Impact Strength and Thermomechanical Characteristics of Poly(vinyl chloride) /Acrylonitrile Styrene Acrylate Blends (Submitted to Journal of Polymer Research).

13.2 Proceedings (International and National)

- Atthakorn, D.; Damrongsakkul, S.; Saramas, D.; and Rimdusit, S. Proceeding of the 19th TICHE conference, pp. 408-409. Kanchanaburi, Thailand, Oct. 26-27, 2009.
- Atthakorn, D.; Damrongsakkul, S.; Saramas, D.; and Rimdusit, S. Proceeding of the 2nd TJIA (Thailand-Japanese International Academic conference, pp.39-40. Kyoto, Japan, Nov. 20, 2009.
- Wongmanit, P.; Damrongsakkul, S.; Saramas, D.; and Rimdusit, S. Proceeding of the 1st PCT (1st Polymer Conference of Thailand), pp. 63. Bangkok, Thailand, Oct. 7-8, 2010.
- Wongmanit, P.; Damrongsakkul, S.; Saramas, D.; and Rimdusit, S. TJIA (Thailand-Japan International Academic Conference) 2010 Conference proceeding, pp. 68-69. Nagoya, Japan, Nov. 19, 2010.

13.3 Master Degree Graduates

Ms. Dolhathai Atthakorn, M.Eng. Chulalongkorn University.

Ms. Patima Wongmanit, M.Eng. Chulalongkorn University.

13.4 Academic and Research Network Connections (Domestic)

- Dr. Chanchira Jubsilp, Department of Chemical Engineering, Faculty of Engineering, Srinakharinwirot University, Nakhonnayok, Thailand.
- Dr. Sunan Tiptipakorn, Department of Chemistry, Faculty of Liberal Arts and Science, Kasetsart University, Kamphaeng Saen, Nakorn Pathom, Thailand.

13.5 Academic and Research Network Connections (International)

- Prof. Dr. Salim Hiziroglu, Department of Natural Resource Ecology and Management, Oklahoma State University, Oklahoma, USA.
- Prof. Dr. Tsutomu Takeichi, Department of Materials Science, Toyohashi University of Technology, Toyohashi, Japan.

Outputs		ในกรณีล่าช้า (ผลสำเร็จไม่ถึง 100%) ให้ท่านระบุสาเหตุและการแก้ไขที่ท่านดำเนินการ
กิจกรรมในข้อเสนอโครงการ/ หรือจากการปรับแผน	ผลสำเร็จ(%)	
วัสดุทดแทนไม้จากพีวีซีที่ทนแรงกระแทก	100%	
ผลงานวิจัยตีพิมพ์ระดับนานาชาติ	85%	อยู่ระหว่างรอผลการพิจารณาบทความที่ส่งไปตีพิมพ์ในวารสารนานาชาติ จำนวน 2 ฉบับ
ผลงานวิจัยตีพิมพ์ในที่ประชุมนานาชาติ	100%	
ผลงานวิจัยตีพิมพ์ในที่ประชุมระดับชาติ	100%	

ลงนาม...
(หัวหน้าโครงการวิจัยผู้รับทุน)

วันที่..

APPENDICES

Appendix A International Publication

Journal of Applied Polymer Science Journal

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Mechanical, Thermal, and Water Uptake Characteristics of Woodflour-Filled Polyvinyl Chloride/Acrylonitrile Butadiene Styrene Blends

Sarawut Rimdusit,[1] Dolhathai Atthakorn,[1] Siriporn Damrongsakkul,[1] Duangporn Saramas,[2] Sunan Tiptipakorn[3]

[1] *Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand*
[2] *Vinythai PLC., Bangkok 10110, Thailand*
[3] *Department of Chemistry, Faculty of Liberal Arts and Science, Kasetsart University, Kamphaeng Saen, Nakorn Pathom 73140, Thailand*

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ABSTRACT: Woodflour-filled composites based on polymeric blends of polyvinyl chloride (PVC) and super high-impact grade ABS were developed. Mechanical, thermal, and water uptake characteristics of the PVC/ABS matrix and their wood composites were evaluated. In the case of PVC/ABS matrix, the blend at a mass ratio of 50/50 rendered the impact strength with a very high value of up to 65 kJ/m^2, noticeably higher than those of the parent resins, that is, 6 kJ/m^2 of PVC and 35 kJ/m^2 of ABS. Dynamic mechanical analysis thermograms showed two distinct glass transition temperatures (T_gs) that shifted toward each other indicating partial miscibility of the blends. Water absorption of the blends after 24 h immersion was low, that is, within the range of 0.04–0.2 wt % and exhibits a behavior closed to pseudo-Fickian type. The obtained PVC/ABS wood composites exhibited an increase of flexural modulus as well as T_gs with an increase of woodflour content. Finally, impact strength of the PVC/ABS composites was significantly higher than those of PVC composites or polyethylene composites comparing at the same woodflour content. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2011

Key words: blends; composites; impact resistance; mechanical properties; reinforcement

INTRODUCTION

In the recent years, wood plastic composites (WPCs) have made significant contributions to various applications such as buildings and constructions, automotives, gardening, and outdoor products due to their ease of processing and recyclability.[1,2] Polyvinyl chloride (PVC) is one of thermoplastics widely used as a matrix in WPC production, because this polymer can fit into the respective pricing category and at the same time having properties necessary for the WPC materials to pass the building standard. It provides high strength and modulus when compared with polyolefin. Furthermore, it is an inherent flame retardance polymer, which possesses a limiting oxygen index (LOI) as high as 50, while the materials with LOI of more than 26 can be classified as self-extinguishable.[3]

The applications of the PVC wood composites are recently reported to dramatically increase in various forms of construction parts such as window and door profiles, decking, railing, and siding.[1,4] From several literatures,[5–8] the WPC composites containing various matrix types experience critical problems of impact properties. At present, the practical and popular ways to toughen PVC wood composites are the use of impact modifiers. There are some impact modifiers that are widely used in PVC industries, that is, chlorinated polyethylene (CPE), methyl methacrylate butadiene styrene (MBS), and acrylic-based (ACR) impact modifiers. From the previous reports,[9–11] the impact properties of PVC wood composites were improved by adding these impact modifiers, while the other mechanical and particularly thermal properties of the modified PVC and its composites were significantly decreased. That is because the glass transition temperatures of those impact modifiers are low (i.e., −16°C for CPE, −70°C for MBS, and −40 to −50°C for ACR).[12]

In this research, the blend of PVC and ABS was proposed as an alternative matrix for an enhancement of impact properties of its WPC without sacrificing its thermal properties. It was reported that PVC/ABS blends could reduce maximum overall rate of thermal

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Correspondence to: S. Rimdusit (sarawut.r@chula.ac.th).

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decomposition process when ABS was incorporated in PVC.[13,14] PVC/ABS blends were first commercially introduced in 1960.[15,16] The outstanding commercial success of PVC/ABS blends has been gained from cost dilution and high performance characteristics with an addition of ABS particularly on its impact property. In these blending systems, PVC contributes to good flame retardancy and high tensile and flexural properties, whereas ABS can enhance processability, impact, and chemical resistance of the products. Property profiles of these blends are superior to those of component homopolymers, which makes them economically attractive for special markets, for example, automotive engineering plastics.[17,18]

Pavan et al.[19] studied the impact performance of PVC/ABS blends; they found that the impact behavior varied extensively over the composition range and related to the blends composition and structure. Additionally, Sharma et al.[15] discussed about the development of PVC/ABS blends in various properties such as mechanical properties and thermal properties. About the application of PVC/ABS as a matrix in composite system, Qin et al.[20] developed clay-filled PVC/ABS blends and found that an incorporation of appropriate amount of clay could enhance the mechanical properties such as yield strength without impairing the impact strength.

Although the PVC/ABS blends have been well known for its outstanding impact properties, the application of the blend in high-impact wood polymer composites has received little attention. In this study, PVC/ABS blend is proposed to be used as a matrix in WPC to use its outstanding impact property and high thermal stability. Some other essential properties such as water uptake will also be investigated.

EXPERIMENTAL

Raw materials

PVC Siamvic 258RB used in the study possesses the characteristics as presented in Table I. Kane Ace PA 20 was used as processing aid additive, while SAK-WP-08-NP and calcium stearate were applied as heat stabilizers and external lubricants, respectively. PVC resin and the additives were supported by Vinythai Public Co., Thailand. The internal lubricants, Loxiol P1141, were supported by the Siam Chemicals Solutions Co., ABS (SP200 superhigh impact grade), which was supplied by IRPC Public Co., Thailand, possesses the characteristics as shown in Table II. The woodflour of Redwood (*Xylia xylocarpa*) as a waste material from a saw-mill factory in Thailand was used as filler and had an average particle size of 280 μm. It was crushed by Fritsch pulverisette cutting mill 15 and dried in an oven at 105°C for 24 h before use.

TABLE I
Characteristics of PVC Suspension Resin (Siamvic 258RB)

Characteristic	Standard	Value
Viscosity index (mL/g)	ISO 1628-2	82
K-value (cyclohexanone)	DIN 53726	58
Polymerization degree	JIS K6721	680
Bulk density-compaction (kg/L)	ISO 1068	0.56
Volatile matter (%)	ISO 1269	≤0.3
Particle size (sieve analysis) (μm)	ISO 1624	120–150

TABLE II
Characteristics of ABS (Injection Grade)

Property	ABS (SP200) injection grade
Melt flow index (g/10 min) at 220°C/10 kg	17
Notched Izod impact strength (kJ/m^2) at 6 mm thickness at 23°C	35
HDT (6 mm thickness at 0.45 MPa)	90
Flexural strength (MPa)	56
Tensile strength (MPa)	41
Flexural modulus (GPa)	2.0

Composite preparation

PVC resin and its additives were blended using a high speed mixer (Plasmec Turbomixer 100L equipped with cooler) at a mixing speed of 1200 rpm. The PVC/ABS blends were prepared by two-roll mills at 160°C for 6 min to yield a homogeneous mixture. ABS contents were varied from 0 to 50 wt %. In the composite systems, the woodflour content was varied from 0 to 50 wt %. The obtained PVC/ABS blends and composites sheet were then compression-molded at 170°C and 15 MPa for 4 min. The compression-molded sheets were then cut into pieces for further property evaluations.

Sample characterizations

Flexural properties of the wood composite specimens were determined following ASTM D790-M93, using a universal testing machine (Instron 5567). The test was carried out in three-point bending mode with a support span of 48 mm at the crosshead speed of 1.2 mm/min. The dimension of the each specimen was 12.7 × 60 × 3.2 mm^3.

Notched Izod impact strength of the specimens was obtained by an impact tester (Yasuda) according to ASTM D256-04. The dimension of the test specimen was 12.7 × 60 × 3.2 mm^3 while the depth under notch of the specimen was 10 mm. The average values were calculated from 10 tests on each material.

Interfacial adhesion of the composites were studied using a scanning electron microscope (JSM-5800LV, JEOL) with an acceleration voltage of 15 kV. The surface of each impact fracture specimen was coated with thin gold film prior to testing.

Thermal characteristics of the blends and composite specimens were examined by a dynamic mechanical analyzer (DMA: NETZSCH-DMA242). The dimension of the test specimen was 50 × 10 × 2 mm^3. Three-point bending mode of deformation was used under a test temperature range from 30 to 150°C at the heating rate of 2°C/min. The test amplitude and frequency were 30 μm and 1 Hz, respectively. Glass transition temperature was obtained from the peak of loss tangent of the thermogram.

Water absorption measurement was conducted following ASTM D570, using disk-shape specimens with a diameter of 50.8 mm and a thickness of 3.2 mm. Three specimens were placed in an oven at 50°C for 24 h, cooled in a desiccator, and then weighted. The specimens were then immediately immersed in distilled water and weighed periodically. Based on the initial mass of each specimen, the amount of water absorbed was calculated from the following equation.

$$\mathrm{WA}(\%) = \left(\frac{M_e - M_o}{M_o}\right) \times 100$$

where WA (%) is the percentage of water absorption and M_o and M_e are the values of specimen mass before and after immersion, respectively.

RESULTS AND DISCUSSION

Impact properties of PVC/ABS matrix

The effect of ABS content on impact strength of F1 PVC/ABS blends is exhibited in Figure 1. It could be noticed that the impact strength of the blend gradually increased at ABS content of less than 30 wt %. The drastic increase in the impact strength was observed when the ABS content was ranging from 30 to 50 wt % and reached the maximum of 65 $\mathrm{kJ/m}^2$ at 50 wt % of ABS. Additionally, the impact strength remained unchanged at 50–70 wt % of the ABS. The impact strength of blend, however, started to decrease when ABS was greater than 70 wt % to the value of about 35 $\mathrm{kJ/m}^2$ of the neat ABS. This transition behavior in impact strength of our PVC/ABS blend was also observed in other particle toughened polymers.[15,19,21,22] As suggested by Sharma and coworkers, the maximum impact strength can be achieved in this kind of polymer blend when critical volume fraction of elastomer phase is attained. However, when this critical elastomer content is exceeded, impact strength drops. At the peak value of impact strength, optimum balance between sufficient elastomer content and the preferred combination of toughening mechanisms such as multiple crazing with interacting shear deformation might be obtained.[15]

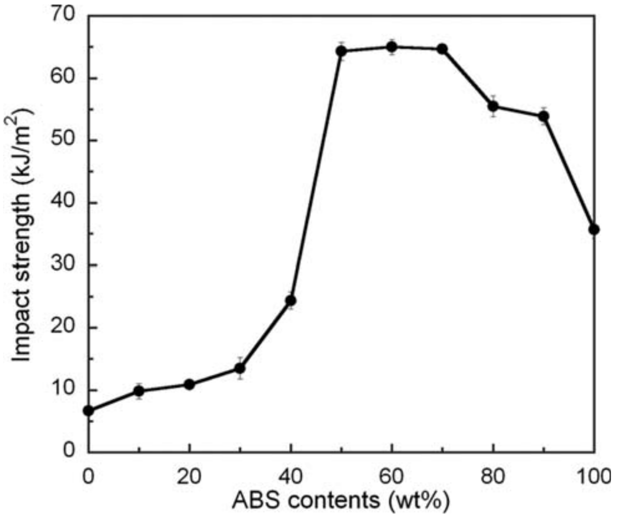

Figure 1 Impact properties of the PVC/ABS blends at various mass blending ratios.

In addition, impact strength of our PVC/ABS blends not only revealed synergistic behavior but also rendered much higher values than those from previously reported PVC/ABS blends.[15,23] The use of novel super high-impact grade ABS from IRPC IRPC Public Co. to form alloys with PVC was found to provide such a high impact strength value with the rigid PVC used.

From the visual appearance observation of the tested samples under impact loading, the fracture surface of the neat PVC revealed a mirror-like surface of brittle failure nature, whereas that of ABS showed a rough surface due to plastic deformation of ductile failure with obvious stress whitening phenomenon. The PVC/ABS blends exhibited systematic variation in the fracture surface from rather brittle to highly ductile failure with increasing ABS content in the blends. In addition, a stress whitening zone (resulting from the mismatch in refractive index in the area of stress concentration) was observed to be more pronounced with the amount of ABS added to the PVC. This phenomenon is associated with the formation of many microcracks in the specimen, which arises from drawing the cavitations of the rubber phase in ABS.[24]

Thermomechanical properties of PVC/ABS matrix

Figure 2 is DMA thermograms showing the relationship F2 between storage modulus of the blends and temperature. The results provide useful information on rigidity or stiffness of the specimens. At glassy state of the samples (i.e., at 40°C), storage moduli of neat PVC and ABS were determined to be ∼ 3.08 and 2.23 GPa, respectively. The PVC/ABS blend at 10 wt % of ABS provided the storage modulus of 2.94 GPa, and the modulus systematically decreased

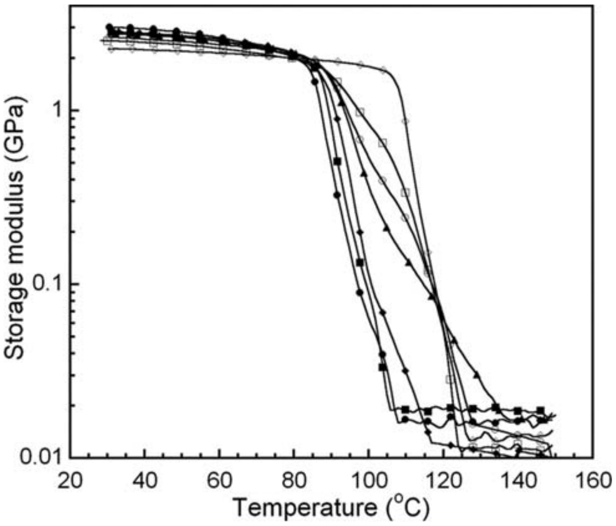

Figure 2 Storage moduli of PVC/ABS blends at various mass blending ratios: (●) PVC, (■) PVC/ABS 90/10, (◆) PVC/ABS 80/20, (▲) PVC/ABS 70/30, (○) PVC/ABS 60/40, (□) PVC/ABS 50/50, and (◇) ABS.

to 2.46 GPa at 50 wt % of ABS. The effect of ABS on modulus of PVC was also found to follow a rule of mixture as seen in the inset of Figure 2.

DMA thermograms can also provide some useful information on miscibility of the blend specimens. The loss tangent of the PVC, the ABS, and the blends at various ABS contents ranging from 0 to 50 wt % is exhibited in Figure 3. The peak of the loss tangent was used to indicate the glass transition temperature of each sample. From the figure, PVC and ABS showed single loss tangent peak corresponding to their T_gs. In the case of the blends, two peaks of glass transition temperatures (T_gs) were clearly observed. It was found experimentally that the T_g values of the PVC and ABS were 94 and 120°C, respectively, whereas two T_g values of the blend at, for example, 50 wt % of ABS were located at 96 and 116°C. The shifting of the T_g values toward each other was an important characteristic suggesting partial miscibility of the blending systems. Moreover, the blend with 10 wt % of ABS showed an overlapping peak, whereas the blends with more than 20 wt % of ABS clearly exhibited two separate peaks. The height of those two peaks evidently varied systematically with the amount of each blend component, that is, the peak at higher T_g increases with the amount of the ABS and vice versa. Although the type of ABS used in this study was different from that reported in Jin et al.'s[25] research, similar results in partially miscible nature of PVC/ABS blend were observed.

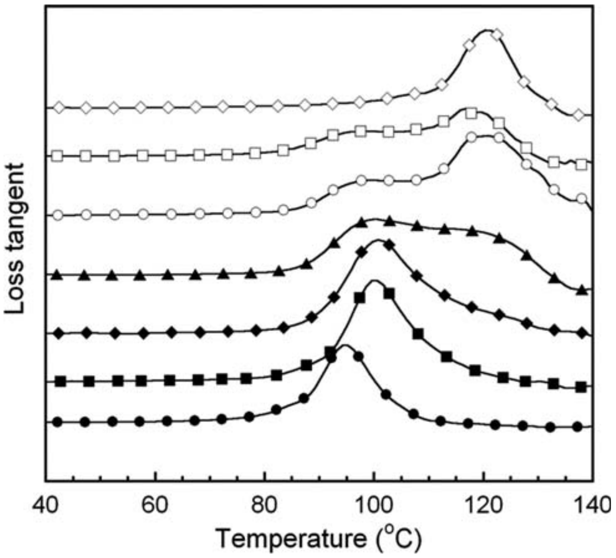

Figure 3 Loss tangent of PVC/ABS blends at various mass blending ratios: (●) PVC (■) PVC/ABS 90/10, (◆) PVC/ABS 80/20, (▲) PVC/ABS 70/30, (○) PVC/ABS 60/40, (□) PVC/ABS 50/50, and (◇) ABS.

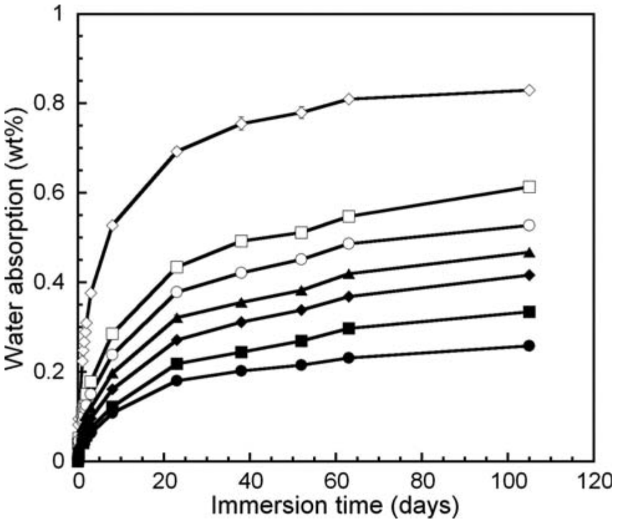

Figure 4 Water absorption of PVC/ABS blends at various mass blending ratios: (●) PVC, (■) PVC/ABS 90/10, (◆) PVC/ABS 80/20, (▲) PVC/ABS 70/30, (○) PVC/ABS 60/40, (□) PVC/ABS 50/50, and (◇) ABS.

Water absorption of PVC/ABS matrix

Water absorption experiment of PVC/ABS blends at various blend contents was performed until the saturation state was reached. The results are presented in Figure 4. After water immersion for 24 h, the neat PVC and pure ABS specimens absorbed water only up to 0.04 and 0.2 wt %, respectively. For PVC/ABS blends, the water uptake was found to increase with increasing of ABS content likely due to the presence of highly polar moiety of acrylonitrile component in ABS. In other words, the ABS is more polar than the PVC. The addition of ABS into PVC thus might contribute to the better wetting or greater interfacial interaction with the relatively highly polar woodflour filler.

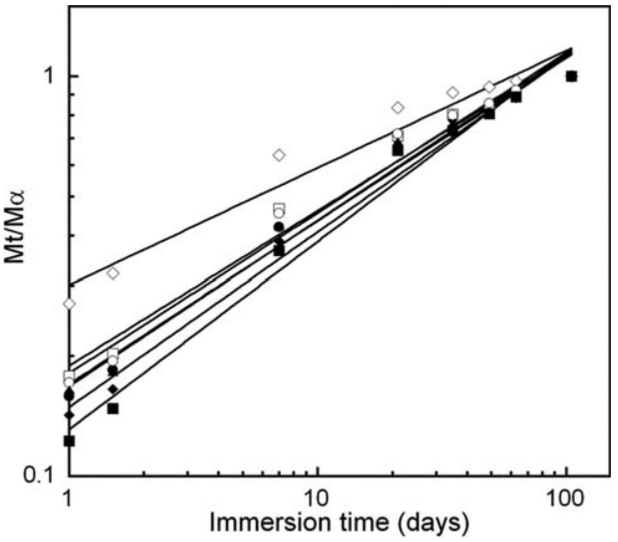

Figure 5 Plots between log M_t/M_α and time to determine the diffusion exponents in eq. (2) (●) PVC, (■) PVC/ABS 90/10, (◆) PVC/ABS 80/20, (▲) PVC/ABS 70/30, (○) PVC/ABS 60/40, (□) PVC/ABS 50/50, and (◇) ABS.

In addition, the values of water uptake up to 24 h at room temperature of the blends were also very low level, that is, <0.2%, which is desirable in most wood-substituted products. Furthermore, from the curves, it could be noticed that the water absorption for over 105 day-immersion of all blend specimens was less than 0.8 wt %, which is considered to be very low. The generalized equation to explain mass diffusion in materials can be expressed as:

$$M_t = M_\alpha k_n t^n \tag{2}$$

where M_t is the mass of a sample at time t and M_α the mass of the sample at saturation or infinite time. The diffusion behaviors can be classified as follows: supercase II ($n > 1$), case II ($n = 1$), anomalous ($1/2 < n < 1$), classical/Fickian ($n = 1/2$), and pseudo-Fickian ($n < 1/2$).[26]

F5 Figure 5 illustrates log (M_t/M_α) versus log(t) plots, which show the slopes ranging from 0.29 to 0.47. Thus, it could be concluded that these blending systems exhibited the diffusion behavior close to pseudo-Fickian type. According to Rogers[27] and Pritchard,[28] the pseudo-Fickian behavior is similar to Fickian one in the early stage of diffusion, but the rate of approaching equilibrium is delayed possibly due to the effects of concurrent diffusion and sorption behavior.

Mechanical properties of woodflour-filled PVC/ABS blends

The PVC/ABS blend at a mass ratio of 50/50 was selected for further investigation as a matrix of wood composite, because this blend composition provided the greatest impact strength as discussed in the previous section. Figure 6 reveals that flexural modulus of F6 the PVC/ABS wood composites systematically increased with increasing the woodflour content while their flexural strength tended to decrease with the amount of woodflour. The enhancement of flexural modulus of the wood composites could be attributed to the fact that the addition of rigid woodflour filler (having modulus in the range of 10–15 GPa)[29] could have an effect on the mobility restriction of polymer molecular chains.[30]

In contrast to the flexural modulus of the composites shown in Figure 6, flexural strength of the composites tended to decrease with the amount of woodflour. The unfilled-PVC/ABS (50/50 mass ratio) provided the flexural strength of 75 MPa while an addition of woodflour into the matrix resulted in a decrease in flexural strength to 64.2 MPa (at 10 wt % of woodflour) and to 49.6 MPa (at 50 wt % of woodflour). The decrease in flexural strength of the PVC/ABS/wood composite with the woodflour content is attributed to a formation of a weak interfacial bonding between the woodflour and the PVC/ABS matrix or from some defect formation due to imperfect fiber-matrix wetting.[5,31] The increase in modulus and decrease in strength due to the incorporation of woodflour or natural fiber into polymeric matrices imply the strength of the material is more sensitive to matrix properties and interfacial interaction formed in the composites than modulus.[31] The behaviors are commonly observed such as in PE wood, PP wood, PVC wood, or ABS wood.[32–37] However, the flexural properties of our PVC/ABS wood composites were observed to be superior to those wood composites comparing at the same wood flour content possibly from substantial

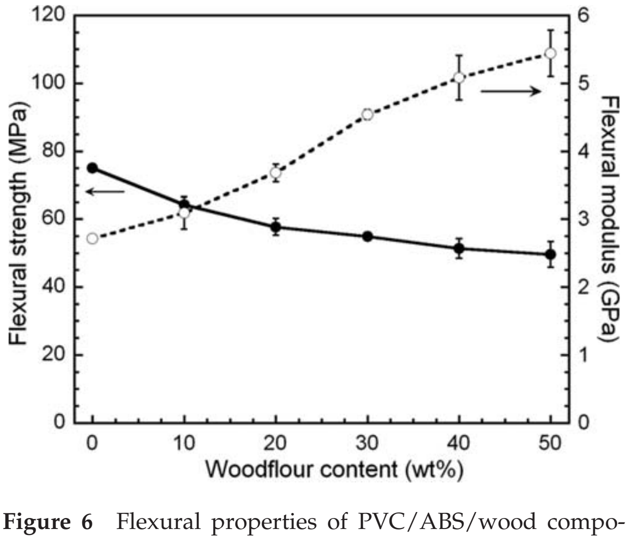

Figure 6 Flexural properties of PVC/ABS/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents.

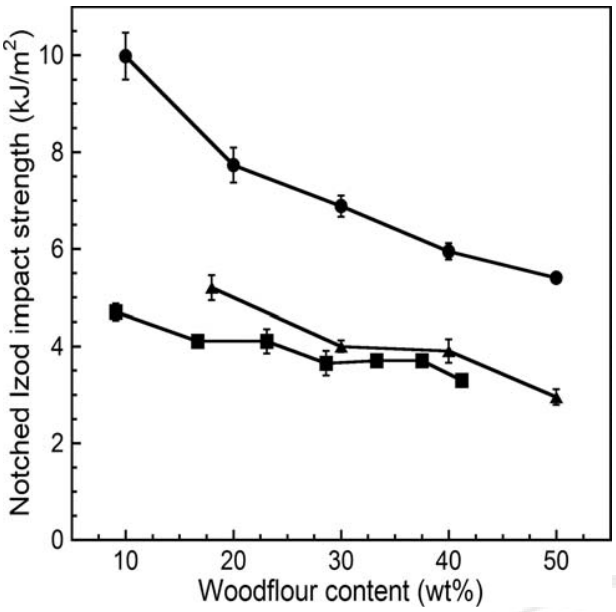

Figure 7 Impact properties of PVC/ABS/wood composites at a fixed PVC/ABS mass ratio of 50/50 at various woodflour contents comparing with PVC/wood and PE/wood composites. (●) PVC/ABS/Wood composites, (■) PVC/Wood composites,[9] and (▲) PE/Wood composites.[33]

interfacial interaction and better wetting of the matrix and the woodflour.

F7 In Figure 7, the effect of woodflour content on notched Izod impact strength of the PVC/ABS/wood composites is illustrated. It can be observed that the impact strength of the composites was found to decrease with increasing woodflour content. The PVC/ABS/wood composite at 10 wt % of woodflour showed the impact strength of 9.98 kJ/m^2; and the value was found to decrease with an increase of woodflour content to ~ 5.40 kJ/m^2 at 50 wt % of woodflour. A similar behavior was also found in various wood composites systems such as PVC wood, PE wood, and PP wood composites.[32–34]

In comparison with PVC/wood composite at 50 wt % of woodflour, the notched Izod impact strength of the PVC/wood composite was reported to be 4.53 kJ/m^2, which was ~ 20% lower than that of the PVC/ABS/wood composite in our study. The differences in the impact strengths of the composites are mainly attributed to the inherent impact strength of the matrix and to some contribution from the interfacial interaction between the matrix and the woodflour. In comparison, the impact strength of PVC, PE, and PVC/ABS matrices are 4.7, 9.5, and 65 kJ/m^2, respectively.[8,29]

In general, a decrease of impact strength of natural fiber/polymer composites was usually derived from debonding and friction effects, especially when no fiber surface treatments were applied. As the woodflour content was increased, the ductile portion (PVC/ABS matrix) automatically reduced, thus decreasing the composites toughness.[38]

In comparison with polyolefin wood composites, the impact strength of PVC/ABS wood composites was found to provide substantially higher value. Selke and Wichman[32] reported an impact strength value of PE wood (at 40 wt % of woodflour) to be about 4 kJ/m^2. In addition, Oskman and Clemons[34] studied the mechanical properties of PP/wood composites and reported that the impact strength value (at 40 wt % of woodflour) was only about 2.6 kJ/m^2.

The fracture surface micrographs of PVC wood composite and PVC/ABS wood composite under impact load are shown in Figure 8(a,b). It could be noticed that the rougher surface of PVC/ABS matrix in Figure 8(b) might explain the higher impact strength of its wood composite than the smoother surface of PVC matrix. That means that the use of an inherently high impact strength PVC/ABS blend F8

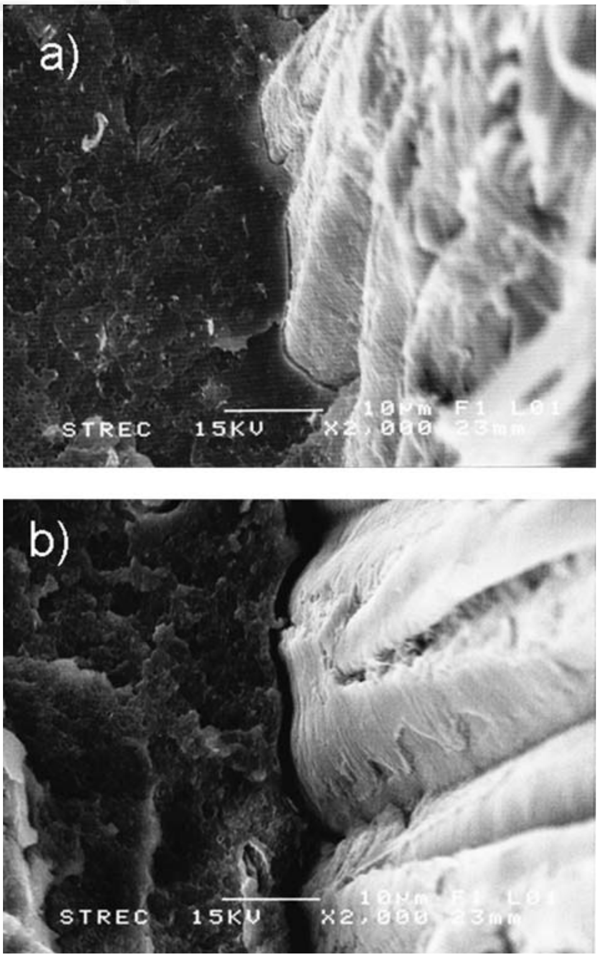

Figure 8 Scanning electron microscope micrographs of fracture surface under impact load of wood composites: (a) PVC with woodflour 30 wt %; (b) PVC/ABS 70/30 with woodflour 30 wt %.

as a matrix in WPC could dissipate greater impact energy thus provided greater impact strength wood composite than the PVC matrix. The effect is evidently more pronounced when the amount of woodflour was reduced.

Thermal properties of woodflour-filled PVC/ABS blends

F9 From DMA analysis in Figure 9, the effects of adding 50 wt % of woodflour on storage modulus and glass transition temperature (obtained from the peak of loss tangent) of the composites are depicted. From the figure, the storage modulus at room temperature of the PVC/ABS wood composites substantially increased from 2.46 GPa of the unfilled PVC/ABS to the value of 5.98 GPa with an addition of the woodflour. This phenomenon could be attributed to the reinforcing effect due to the higher modulus value of the natural filler than that of the polymer matrix. Furthermore, two glass transition temperatures of the composites as obtained from the two loss tangent peaks were also observed due to the use of the partially miscible PVC/ABS at 50/50 mass ratio as the composite matrix. In addition, we also observed that T_{g1} of PVC/ABS increased from about 95–98°C with an addition of 50 wt % of woodflour, whereas T_{g2} slightly increased from 116 to 122°C. The phenomenon suggested an existence of some interfacial interaction between the PVC/ABS and the woodflour that might have a restriction effect on the motion of molecular chains of the polymer matrix due to impediment of a more rigid woodflour particle.[30] The similar increase in T_g with an addition of woodflour was also observed in the system of PVC/sawdust composites reported by Sombatsompop et al.[8]

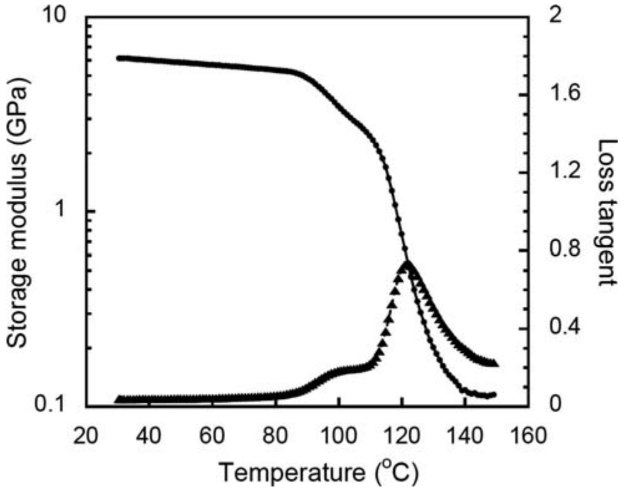

Figure 9 DMA thermograms of PVC/ABS 50/50 with wood flour 50 wt %.

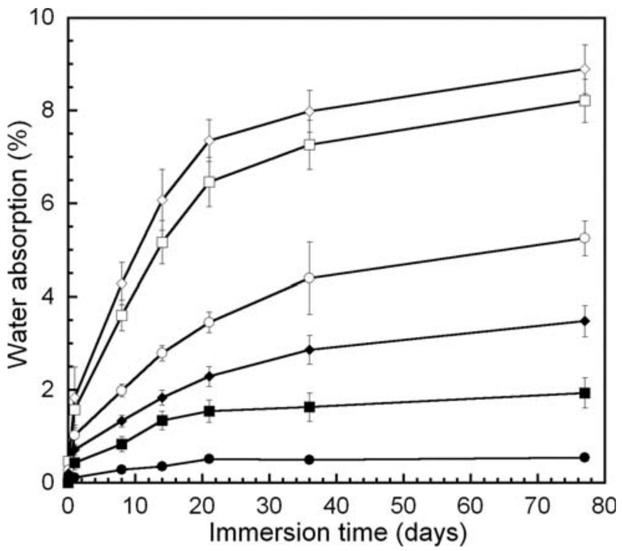

Figure 10 Water absorption of PVC/ABS/wood composites at a fixed PVC/ABS mass ratio of 50/50 and at various woodflour contents: (●) 0%, (■) 10%, (◆) 20%, (○) 30%, (□) 40%, and (◇) 50%.

Water absorption of woodflour-filled PVC/ABS blends

F10 The effects of woodflour contents in the range of 0–50 wt % on water absorption of PVC/ABS wood composites are shown in Figure 10. At 24-h immersion, the water absorption of the unfilled PVC/ABS matrix was only about 0.1%. With an addition of 10 wt % of woodflour, the absorption behavior at 24 h provided insignificant change in its value. This is attributed to the ability of the PVC/ABS to cover or encapsulate most of woodflour particles, so that water cannot interact with the woodflour. At higher woodflour content, water absorption of PVC/ABS/wood composites was found to increase with increasing woodflour content, that is, the water absorption of the composite at 50 wt % of woodflour at 24-h immersion was ~ 1.8%. For the long-term immersion, the PVC/ABS wood composite at 50 wt % of woodflour rendered the water absorption value of up to 7.34 wt %. However, this value was still significantly lower than the water absorption in real wood, that is, in the range of 24–100%.[39] This was likely due to the hydroxyl groups in the structure of cellulose and hemicellulose of woodflour, which is higher hydrophilicity in nature than our PVC/ABS matrix.[6]

Consequently, the degree of water absorption of the composite increased with the woodflour loading. In principle, there are three main regions where the absorbed water in the composites can reside, that is, (1) gaps between woodflour and matrix, (2) lumen, and (3) cell wall. To develop composites with better mechanical properties and to decrease their moisture uptake, it is necessary to make the woodflour more hydrophobic possibly by suitable treatment to strengthen interfacial interaction with the polymer matrix used. From the calculation based on eq. (2), the diffusion behaviors of our wood composites can also be classified as pseudo-Fickian type with the exponents ranging from 0.35 to 0.43.

CONCLUSIONS

Woodflour-filled composites based on the polymeric blends of PVC and super high-impact grade ABS were developed. The results revealed that the PVC/ABS matrix at a mass ratio of 50/50 rendered the highest impact strength that was noticeably higher than those of the parent polymers. Two distinct glass transition temperatures (T_gs) were observed, which indicated partial miscibility of the blends. The water absorption of the blends after immersion for 24 h was in the range of 0.04–0.2 wt %. Furthermore, the woodflour-filled PVC/ABS composites exhibited a systematic increase of flexural modulus and glass transition temperature with an increase of woodflour content, whereas flexural strength slightly decreased with the amount of the woodflour. In addition, the impact strength of the PVC/ABS composites was significantly higher than those of PVC composites and polyethylene composites at the same filler content. Finally, water absorption experiment revealed that water diffusion behavior of PVC/ABS and its wood composites was closed to pseudo-Fickian type.

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Corresponding Author: Sarawut Rimdusit, Ph.D.

Corresponding Author's Institution: Chulalongkorn University

First Author: Sarawut Rimdusit, Ph.D.

Order of Authors: Sarawut Rimdusit, Ph.D.;Patima Wongmanit, M.Eng.;Siriporn Damrongsakkul, Ph.D.;Duangporn Saramas, M.S.;Chanchira Jubsilp, D.Eng.

Abstract: Substantial enhancement in impact property of poly(vinyl chloride)/acrylonitrile styrene acrylate (PVC/ASA) blends were observed. The effect of ASA content on mechanical characteristics, including impact, tensile, and flexural properties were investigated. The results suggested that the impact strength of the PVC/ASA blends increased drastically at the ASA content of about 30-40 wt% and at the ASA content of 50 wt%, the very high impact strength of up to 77.6 kJ m-2 was obtained. The modulus and strength under tensile and flexural loads of PVC/ASA blendswere fo un to increase with the PVC fraction while glass transition temperature and heat deflection temperature systematically increased with increasing ASA content. The blends are partially miscible in nature as evidenced from the two glass transition temperatures observed in dynamic mechanical analysis. The obtained PVC/ASA blends clearly showed a potential use as high impact plastic products for outdoor application.

High Impact Strength and Thermomechanical Characteristics of Poly(vinyl chloride) / Acrylonitrile Styrene Acrylate Blends

Sarawut Rimdusit[1], Patima Wongmanit[1], Siriporn Damrongsakkul[1],
Duangporn Saramas[2], Chanchira Jubsilp[3]

[1] Polymer Engineering Laboratory, Department of Chemical Engineering,
Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand.

[2] Vinythai PLC., Map Ta Phut Industrial Estate No. 2, I-3 Road, Rayong 21150, Thailand

[3] Department of Chemical Engineering, Faculty of Engineering, Srinakharinwirot
University,Nakhonnayok, 26120, Thailand.

ABSTRACT

Substantial enhancement in impact property of poly(vinyl chloride)/acrylonitrile styrene acrylate (PVC/ASA) blends were observed. The effect of ASA content on mechanical characteristics, including impact, tensile, and flexural properties were investigated. The results suggested that the impact strength of the PVC/ASA blends increased drastically at the ASA content of about 30-40 wt% and at the ASA content of 50 wt%, the very high impact strength of up to 77.6 kJ m^{-2} was obtained. The modulus and strength under tensile and flexural loads of PVC/ASA blends were found to increase with the PVC fraction while glass transition temperature and heat deflection temperature systematically increased with increasing ASA content. The blends are partially miscible in nature as evidenced from the two glass transition temperatures observed in dynamic mechanical analysis. The obtained PVC/ASA blends clearly showed a potential use as high impact plastic products for outdoor application.

Keywords: PVC/ASA blend; impact strength; natural weathering; partially miscible blend.

* Corresponding author. Tel: +66 2 218 6862; Fax: +66 2 218 6877.

E-mail address: sarawut.r@chula.ac.th (S. Rimdusit).

INTRODUCTION

Currently, poly(vinyl chloride) (PVC) belongs to the widely used commodity polymers, especially in house construction, medical, food packaging, housekeeping, sewer system, electrical wires and cables as well as automotive industries. PVC has been utilized extensively due to a relatively low price, widely developed processing, mechanical property modification and environmental resistance by incorporation of varied additives [1-3]. This is the reason for standing growing production and application of this polymer. Recently, PVC becomes highly attractive for products in building and construction market by an incorporation of natural fibers to form PVC wood composites [4-7]. However, compared to other commodity thermoplastics, PVC has a disadvantage of being inclined to occasional brittleness and is notch sensitive [8, 9].

To gain more flexibility with enhanced impact strength of PVC, impact modifiers are used as additives for various applications. Operations such as chemical modification, compounding or blending with conventional polymers have been generally regarded as the means of adjusting or producing a desired property balance of PVC. If properly directed, these methods can be a convenient way of developing materials with novel or selectively enhanced properties which are possibly superior to those of the starting components [10, 11]. By blending an elastomeric component into PVC, it is possible not only to toughen the PVC but also enhance other properties of the polymer according to the type and quantity of modifier used. One notable example is blends of PVC with stryrenic polymer such as acrylonitrile-butadiene styrene (ABS) terpolymer which is a compound with highly balanced properties of impact strength, stiffness, and processability [12-14] or with methacrylate-butadiene-styrene (MBS) copolymers [12, 15] as well as with poly(butylene adipate-co-terephthalate) [9]. In case of the PVC blended with ABS [16, 17], the result is a material having remarkable enhancement in impact strength and toughness with inherent flame resistance. The obtained impact property was also reported to be superior to those of the individual components [10, 11, 16, 18]. Furthermore, the inherent flame retardancy of PVC, due to the presence of chlorine in large quantities in the polymers, makes it suitable for applications where the more expensive flame retarded ABS could not be employed [19]. This blend has recently been reported to show substantial affinity with natural fiber and is a good candidate for a matrix of natural fiber composites with outstanding impact strength [16].

However, an addition ABS into PVC tends to cause lower weathering durability of the PVC [20, 21]. When the PVC-based polymer blend is used for long period in outdoor applications or under fluorescent light, photo-yellowing or deterioration of properties will occur. Discovering weathering resistant impact modifiers for PVC becomes a more significant research field. Ethylene propylene diene monomer (EPDM) and acrylic modifiers are weathering resistant impact modifiers for PVC, while MBS and ABS are not because the major drawback for these polymers is that the residual double bond in the butadiene is readily attacked by ultraviolet light, so these polymers cannot be used for outdoor applications [22]. Although acrylic modifiers are durable to weathering, they impart low thermal stability to PVC. Therefore, in this study, a more preferable impact modifier of PVC for an outdoor application is acrylonitrile styrene acrylate copolymer (ASA) which has a two-phase material, comprising a styrene acrylonitrile (SAN) matrix with acrylate rubber particles dispersed with SAN inclusions. The presence of the rubber particles help enhance fracture toughness by fracturing after crazing and yielding [6, 7, 23]. The rubber component of ASA is far more thermally stable than the polybutadiene in ABS. This is a significant characteristic particularly for the blend system that might experience high processing temperatures. Additional advantage of ASA copolymer compared to ABS terpolymer is its enhanced weatherability compared to ABS [24-26].

As a consequent, the aim of this paper is to investigate the effect of ASA contents on PVC/ASA blend properties. It is expected that blends of PVC with ASA might provide similar enhancement on impact strength as ABS with minimized color change of the sample due to superior weathering durability of the ASA to ABS. Major properties include dynamic mechanical properties, flexural and tensile properties, and water absorption of the PVC/ASA blends will also be characterized as the information on these properties of the blends is very scarce and receives little attention. The blend is expected to replace PVC/ABS matrix recently reported to impart outstanding impact strength to its composite with natural fiber.

EXPERIMENTAL

Materials

Poly(vinyl chloride), PVC, grade 258RB with *K*-value = 58, degree of polymerization about 680 and bulk density-compaction of 0.56 kg/l compounded with stabilizer, processing aid, and external lubricant was obtained from Vinythai Public Co. Ltd., Thailand. Internal lubricant (Loxiol P1141) was supported by Siam Chemical Solutions Co., Ltd. Extrusion grade acrylonitrile styrene acrylate (ASA) resin as an impact modifier for PVC, KIBILAC PW-997S, was purchased from Global Connections Co., Ltd., Thailand. It was suitable for extrusion application with high impact performance including construction and automobiles.

Preparation of PVC/ASA blends

PVC dry blend powder was blended with ASA pellet ranging from 0-50 wt% of ASA content by two-roll mills with 0.125 mm gap at 170ºC for 6 min to yield a homogeneous mixture. The obtained PVC/ASA compound was then preheated for 3 min and pressed into sheet by compression molding at 170ºC and pressure of 15 MPa for 4 min. The compression-molded sheet was then cut into desired shapes for further property evaluations.

Characterizations of PVC/ASA blends

Density of PVC/ASA blends was measured by a water displacement method, ASTM D792. The samples were rectangular shape with a 3 mm thickness. Notched Izod impact test was performed on an impact tester (Yasuda Seiki Seisakusho, Ltd.) following ASTM D256. Tensile and flexural properties of the composites were measured using a universal testing machine, Instron, model 5567 according to ASTM D638 and ASTM D790. Five replicated samples of each composition were tested for tensile and flexural properties while the impact strength value of twelve replicated samples was determined. The resulting average data as well as their standard deviation were reported. Dynamic mechanical analysis (DMA) was conducted on NETZSCH, model DMA242 in the tensile geometry at 1 Hz with a strain amplitude of 30 μm and at a heating rate of 2°C min^{-1} from 30 to 150°C using a sample size of 10 mm×50 mm×2 mm.

Heat distortion temperature (HDT) determined according to ASTM D648 is the temperature at which the sample has a specified bending. The samples with the dimension of 13mm×127mm×3mm are heated at a constant heating rate of 120°C hr^{-1} while a bending load is applied until they deflect to 0.25 mm. In this test the temperature at which a sample has a specified bending under influence of a constant load of 0.45 N mm^{-2} is determined. The vicat softening temperature is the temperature at which a flat-ended needle penetrates the sample to the depth of 1 mm under a specific load. A test sample was placed in the testing apparatus so that the penetrating needle rested on its surface at least 1 mm from the edge. A load of 50 N was applied to the sample. The samples having dimension of 20mm×20mm×3mm are heated up at a constant heating rate of 50°C hr^{-1} while a bending load is applied until the needle penetrated 1 mm following ASTM D1525.

Color change measurement originally resulted from the consolidation of separately published methods for instrumental evaluation of color differences. The total difference,

$\Delta E_{ab}*$, between two colors each given in terms of lightness (L*) and chromaticity coordinate (a* and b*) is calculated following ASTM D 2244 by Ultrascan Pro spectrometer (Hunter Lab, USA) which measures both reflected and transmitted color and meets CIE (International Commission on Illumination) standard.

Water absorption test was conducted in accordance with ASTM D 570. Before testing, the weight of each sample was measured. Three samples in a form of disk having a 50.8 mm diameter and a 3.2 mm thickness of each blend were submerged in distilled water at 25°C. Samples were removed at certain periods of time, blotted to remove the excess water on the surface and immediately weighed. Based on the initial mass and the dimension of each sample, the mass and the dimension of the samples after immersed in water was calculated.

Contact angle measurement was performed at room temperature using a contact angle meter model Cam-Plus Micro equipped with an optical microscope from Tantec. The measured liquid was deionized water with a droplet radius of 10 µm. Contact angle of each sample was averaged from 10 measured values.

RESULTS AND DISCUSSION

Density measurement of PVC/ASA blends

Density of PVC blended with ASA as a function of the ASA content is shown in Fig. 1. The density of the PVC/ASA blends tended to decrease with an increase of the ASA fraction. The density of the PVC/ASA blend at 10 wt% ASA content was determined to be 1.33 g cm^{-3}. As increasing ASA content to 50 wt%, the density was found to be 1.19 g cm^{-3}. These results were also well predicted by a rule of mixture calculated based on the measured density of the PVC of 1.36 g cm^{-3} and the density of the ASA of 1.07 g cm^{-3}. This good agreement between the measured and the theoretical density values suggested negligible amount of void in the blend samples implying suitable blending condition used in this investigation. The measurement is highly crucial for screening qualified specimen before further tests as several tests particularly mechanical tests are highly sensitive to void or defects present in the samples.

Impact strength of PVC/ASA blends

The effects of ASA content ranging from 0 wt% to 50 wt% on notched Izod impact strength at room temperature of PVC/ASA blends are presented in Fig. 2. From the figure, we can see that the neat PVC exhibited a notched Izod impact strength value of 6.8±0.5 kJm^{-2} whereas that of ASA was around 47.0±3.1 kJ m^{-2}. Interestingly in PVC/ASA blend systems, the impact strength of the blends with a maximum value as high as 77.6±4.0 kJ m^{-2} was obtained at ASA content of 50 wt%. The strength was observed to increase with an increase of ASA content up to 50 wt% and then decreased. The remarkable improvement of impact strength of the PVC/ASA blends was possibly due to an ability of ASA to form optimal energy dissipation phase morphology i.e. co-continuous phase, with the PVC in the polymer blend [27]. When the polymer blend was subjected to an external stress, the elastomeric phase in ASA might be able to effectively initiate and terminate crazes. With this crazing, energy was transformed into deformation of the rubber particles in the ASA followed by the formation of voids in the rubber phase itself. However, further deformation can effectively be stopped by other rubber particles [26]. As also seen in the figure, the impact strength increased slightly when ASA content was less than 30 wt% and the sharp increase in impact strength was observed with ASA content greater than 30 wt%. The point of drastic change in impact strength of the PVC/ASA blend systems is called a brittle-ductile transition.

In this case, ASA content is a major factor that induces the brittle-ductile transition. At the ASA content of 0-30 wt%, the impact strength was low and brittle fracture was observed with little stress whitening zone as shown in Fig. 3. Beyond 30 wt% of the ASA, ductile fracture with a pronounced stress whitening zone can be clearly seen. Stress whitening is the phenomenon possibly resulted from crazing in the matrix, internal cavitation of the rubber particles or debonding at the matrix-particle interface [28]. This transition behavior in impact strength of our PVC/ASA blend was also observed in other particle toughened polymers [28-32] Sharma and coworkers [29] reported that the maximum impact strength can be achieved in this kind of polymer blend at the critical volume fraction of the elastomer phase. However, when this critical elastomer content is exceeded, impact strength drops. At the peak value of impact strength, optimum balance between sufficient elastomer content and the preferred combination of toughening mechanisms such as multiple crazing with interacting shear deformation might be attained.

Tensile and flexural properties of PVC/ASA blends

In general, mechanical properties particularly strength of polymer blend were reported to be largely dependent on good interfacial adhesion between the component polymers of the blend [33]. In this work, the tensile and flexural properties of PVC/ASA blends with various ASA contents are reported in Table 1. In the case of tensile properties, we can see that the tensile modulus of PVC was found to be 2.18 GPa whereas that of ASA was 1.57 GPa. As the PVC content increased, tensile modulus of PVC/ASA blends was found to systematically increase suggesting that PVC contributed to an improved stiffness of the blend.The behavior was found to follow a rule of mixture. Similar observation was also reported in PC/ABS blend [27, 31], PVC/ABS blend [34] and PVC/PBAT blend [9].

Our PVC exhibits tensile strength of 53.0±0.3 MPa which is substantially higher than that of ASA (38.0±0.9 MPa). Moreover, the tensile strength of the PVC/ASA blends rendered the values between that of neat PVC and neat ASA as also being predicted by a rule of mixture, indicating substantial interfacial interaction between the two polymers. Similar behavior was also observed in the PVC/ABS blend [16], PC/ABS blend [24, 31], PC/ASA/SAN blends [32] and HDPE/UHMWPE blends [35]. However, negative deviation in tensile strength was observed in PET/ASA system which was reported to be rather incompatible (poor interfacial interaction) in nature [36]. Lastly, the tensile elongation of the ASA was found to be lower than that of PVC. With increasing the ASA fraction in the PVC/ASA blend, a decrease in the elongation at break was observed. This is due to the fact that the PVC possesses a greater elongation at break than the ASA used.

The flexural properties of the PVC/ASA blend systems at varied ASA content is also reported in Table 1. From the table, the modulus and strength of the blend samples under flexural load of the PVC/ASA blends showed a similar trend to that of tensile modulus and strength. The flexural modulus of the blend systems was found to increase from 2.73 GPa at 50 wt% PVC content to 3.00 GPa at 90 wt% PVC content due to the higher rigidity of the PVC while those of the neat PVC and the neat ASA were determined to be 3.20 GPa and 2.23 GPa, respectively. In case of flexural strength, the PVC/ASA blends at various blending ratios exhibited the flexural strength at 79 MPa for the blend containing 10 wt% ASA. With increasing ASA content, the flexural strength decreased to 69 MPa for the blend containing 50 wt% of the ASA while the flexural strength of the PVC and the ASA was determined to be 87 MPa and 63 MPa, respectively. This behavior is similar to that of ABS/SAN blends [37]. From the result, the effect of the ASA content on PVC/ASA blends tended to follow the additivity rule confirming good interfacial interaction between the two phases as described in the tensile test.

Thermomechanical properties of PVC/ASA blends

Fig. 4 exhibits storage modulus (E′) as a function of temperature of the PVC/ASA blends. From this figure, storage modulus at room temperature of PVC was determined to be 2.9 GPa while that of ASA was about 2.0 GPa. The higher storage modulus at room temperature of the neat PVC compared to that of the ASA is consistent with those of tensile and flexural test discussed in the previous section. Furthermore increasing the amount of ASA in PVC from 0 wt% to 50 wt% led to a systematic decrease in storage modulus of the blends from 2.9 GPa to 2.3 GPa. However, as heating continued in the DMA test, PVC was observed to lose their rigidity at elevated temperature more readily than ASA and their blends. The greater change in slope of the modulus curve vs. temperature of PVC compared to ASA is one parameter indicating better thermal stability of the latter. The enhancement in thermal stability of the blends was thus obtained due to the superior thermal stability of ASA to PVC.

The temperature dependence of the tan δ peak of PVC/ASA blends at different ASA content is illustrated in Fig. 5. Glass transition temperature (T_g), determined from the peak of the tan δ, of the neat PVC and the neat ASA were found to be 96°C and 121°C respectively. For the PVC/ASA blends, heavily overlapped with only one dominant peak was observed when ASA content in the blends is less than 30 wt%. However, when the ASA content was greater than 30 wt%, two clearly separated peaks of the PVC-rich phase (T_g1) and of the ASA-rich phase (T_g2) existed. Furthermore, the positions of both peaks tended to shift towards each other in the obtained polymer blends [9]. For example, T_g1 of the PVC-rich phase was found to increase from 98°C to 102°C with the increase of ASA content while T_g2 of the ASA-rich phase was found to shift to lower temperature from 119°C to 117°C at the blend composition of 30 wt% of ASA. This behavior suggested the partially miscible nature of the ASA with PVC. Normally, the shifting of T_gs of two individual components towards each other means the improved compatibilization while the final single broad relaxation denotes the complete compatibilization. In our work, the incorporation of ASA chains into PVC chains might provide an enhanced interfacial adhesion between the PVC and ASA domains from the partial miscibility of the blends observed. The similar shifting in T_g has also been reported in PVC/ABS [16] and PC/ABS systems [27, 31].

Heat resistance measurement of PVC/ASA blends

The effects of ASA contents ranging from 0 wt% to 50 wt% on heat distortion temperature (HDT) and vicat softening temperature of PVC/ASA blends were also measured and are shown in Fig. 6. From the results, the HDT of the neat PVC and ASA were determined to be 64°C and 77°C, respectively while the vicat softening temperatures of the neat PVC was approximately 77^{o}C and of ASA was about 91°C. In addition, the PVA/ASA blends showed HDT and vicat softening temperatures between the values of the two starting polymers and a linear relationship with the amount of ASA added. The results imply improved thermal stability of the blend with the presence of the ASA in the PVC. A similar study and trend on HDT and vicat softening temperatures in this blend system was also reported by DeArmitt [38].

Due to higher T_g of SAN (ca. 100^{o}C) in ASA matrix, diffusion of the SAN component into the PVC domain can improve thermal properties of the blends and provided the blends with wider service temperature than that of the PVC alone. The addition the ASA, having greater T_g than the PVC, as an impact modifier for PVC thus provided further improvement on the HDT and vicat softening temperature of the blend following the rule of mixture. However, in the opposite case such as those using impact modifier with lower T_g, the HDT was found to decrease substantially with the amount of the modifier i.e. poly(phenylene sulfide)/ nylon66 blends [39].

Natural weathering durability of PVC/ASA blends

PVC without an aid of suitable UV stabilizers is rather sensitive to the weathering action. Its mechanical properties and color are usually changed as a result of ultraviolet irradiation [1, 40]. Especially in the presence of oxygen and moisture, it undergoes a very fast dehydrochlorination and a peroxidation process with the formation of polyenes and subsequent scission of the chains, with the formation of water "washable" products as well as cross-linking [1, 41]. In this work, the blend formulation with ASA content of 50 wt%, which also provides maximum impact strength as discussed earlier, was selected for natural weathering study in comparison with the neat PVC sample. The test was performed in Rayong Province, Thailand, for a time period of up to 120 days (i.e. during December 18th 2010 to April 25th 2011), and the variation of color difference of the specimens as a function of time was recorded as shown in Fig. 7. From the figure, we can see that the incorporation of ASA into PVC greatly imparted substantial color retention of PVC. The reduction in color changing was reported quantitatively by measuring color difference (△E*) as calculated by measuring changes in L*, a*, and b* color values relative to unexposed controls of the PVC and the PVC/ASA blend (50/50). Furthermore, △E* value of the neat PVC significantly increased with increasing exposed times while that of the PVC/ASA = 50:50wt% was relatively unchanged as a function of the exposure time.

An effect of natural weathering on visual appearance of the sample surfaces, i.e. PVC and PVC/ASA (50:50) is also illustrated in Fig. 8. At the end of weathering test (up to 4 months), the neat and un-stabilized PVC suffered a greater change in the color from white to dark grey color possibly owing to the chromophoric group formation of conjugated double bonds i.e., alkene and polyene linkages which can absorb light readily. Photo-degradation might also convert the surface of the neat PVC to dark-colored surface of lower extensibility owing to polymer chain scission [1]. For the PVC/ASA blend system, the sample surface under the effect of the natural weathering showed negligible change in color compared to that of the neat PVC. Therefore, the color retention performance of the neat PVC can be conveniently obtained by incorporation ASA into PVC to form blends. This is also due to the much lower △E* of the neat ASA than that of the neat PVC [25]. Additionally, no surface crack was observed after this period of natural weathering for both the neat PVC and the PVC/ASA blend.

Water absorption and density measurement

It is well known to many researchers that water absorption, the tendency of plastics to absorb moisture, can significantly alter some key mechanical, electrical, or optical properties. After water absorption, materials may be dissolved, leached, plasticized, swelled, or show deterioration in mechanical properties. As shown in Fig. 9, water absorption of PVC, ASA, and their blends at varied contents of 0 wt% to 50 wt% of ASA was performed up to the saturation state. We can see that the water absorption at 24h of PVC was found to be only about 0.06 wt% while that of the blends was found to increase from 0.09 wt% to 0.18 wt% with an increase of ASA. Furthermore, the neat ASA exhibited a higher water uptake value, at 24h immersion, of about 0.40 wt% likely due to the presence of a highly polar moiety of an acrylonitrile component in ASA.

The phenomenon was also confirmed by contact angle measurement as plotted in Fig. 10. The contact angle data of the PVC/ASA blends was very corresponsive to the water absorption value of the blends. From the figure, the neat PVC, having lower water absorption than the neat ASA, showed higher contact angle of about 98^{o} while the neat ASA provided a contact angle of about 88^{o}. Day and Sperry [42] studied the relationship of water absorption and contact angle of laminated plastics. The factor influencing the contact angle is the affinity of the surface for water. If the material is a strongly hydrophilic solid, the water droplet can spread out on the solid surface and the contact angle will approach 0^{o}. Moderate hydrophilic solids have a contact angle up to 90°, while the contact angle of water on the hydrophobic solid is typically larger than 90°. The stronger affinity to water of ASA thus rendered the observed increase in water absorption in the PVC/ASA blends with the amount of the ASA.

CONCLUSIONS

High impact strength polymer blends between PVC and ASA, as an impact modifier, with improved thermal properties and weathering durability were developed. The effects of the ASA content on mechanical, thermal properties and outdoor weathering durability of the PVC/ASA blends may be summarized as follows. PVC/ASA blends exhibited highest impact strength, i.e. 77.6 kJ m^{-2}, when ASA content in the blend is about 50 wt%. Tensile and flexural properties of the blends were found to slightly decrease with the ASA content. Glass transition temperature and thermal stability of the blends could be enhanced by the presence of ASA in the blends. The shifting of the two glass transition temperatures of the PVC domain and ASA domain towards each other in the blend suggesting partially miscible nature of these polymers. Finally, outdoor weathering durability of the blends was substantially enhanced by the ASA addition as confirmed by a negligible color change of the blend samples after outdoor weathering up to 4 months.

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Fig. 5 Loss tangent of PVC/ASA blends at various ASA contents: (●) PVC, (■) PVC/ASA 90:10 wt%, (◆) PVC/ASA 80:20 wt%, (▲) PVC/ASA 70:30 wt% (▼) PVC/ASA 60:40 wt%, (○) PVC/ASA 50:50 wt%, (□) ASA.

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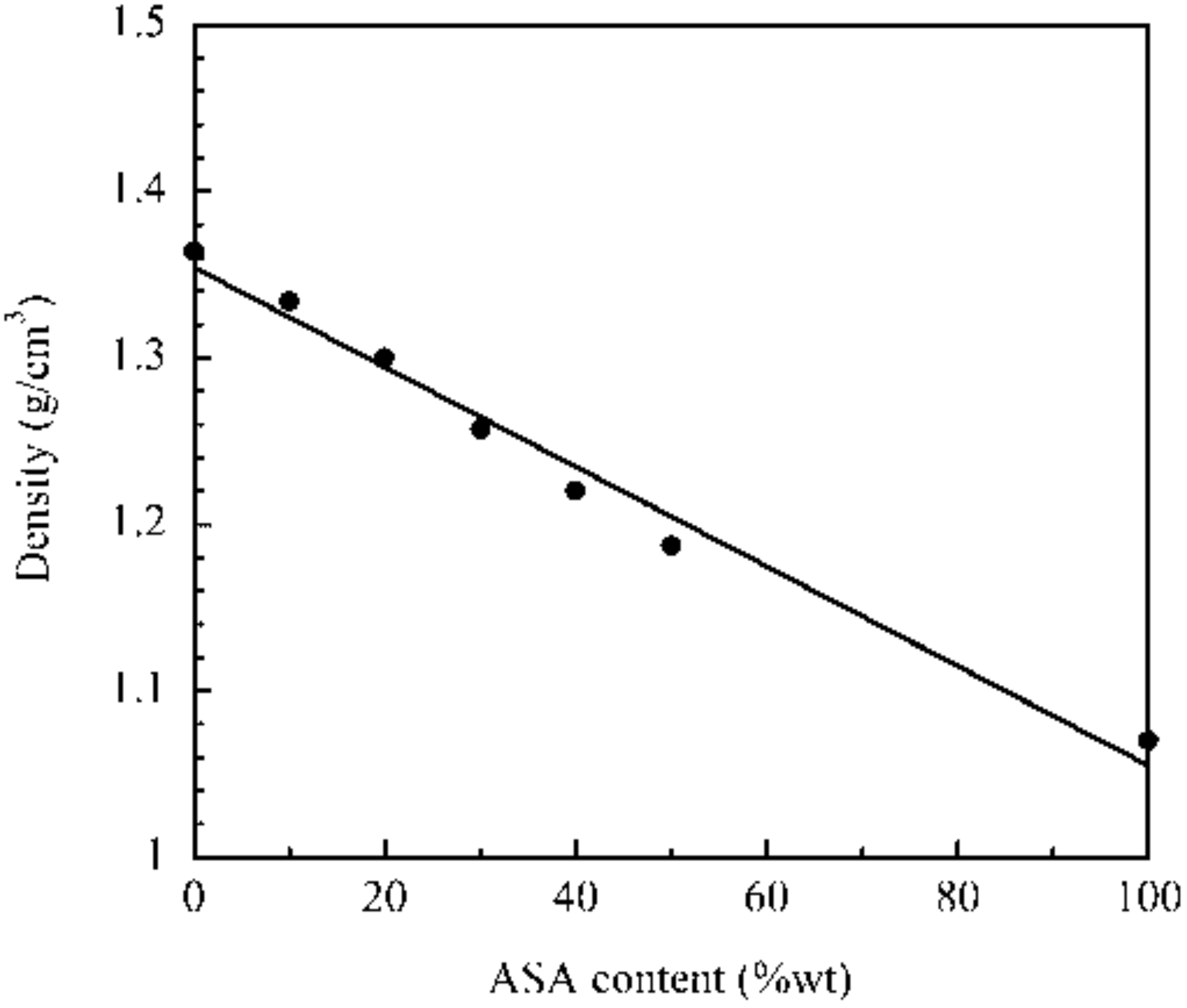
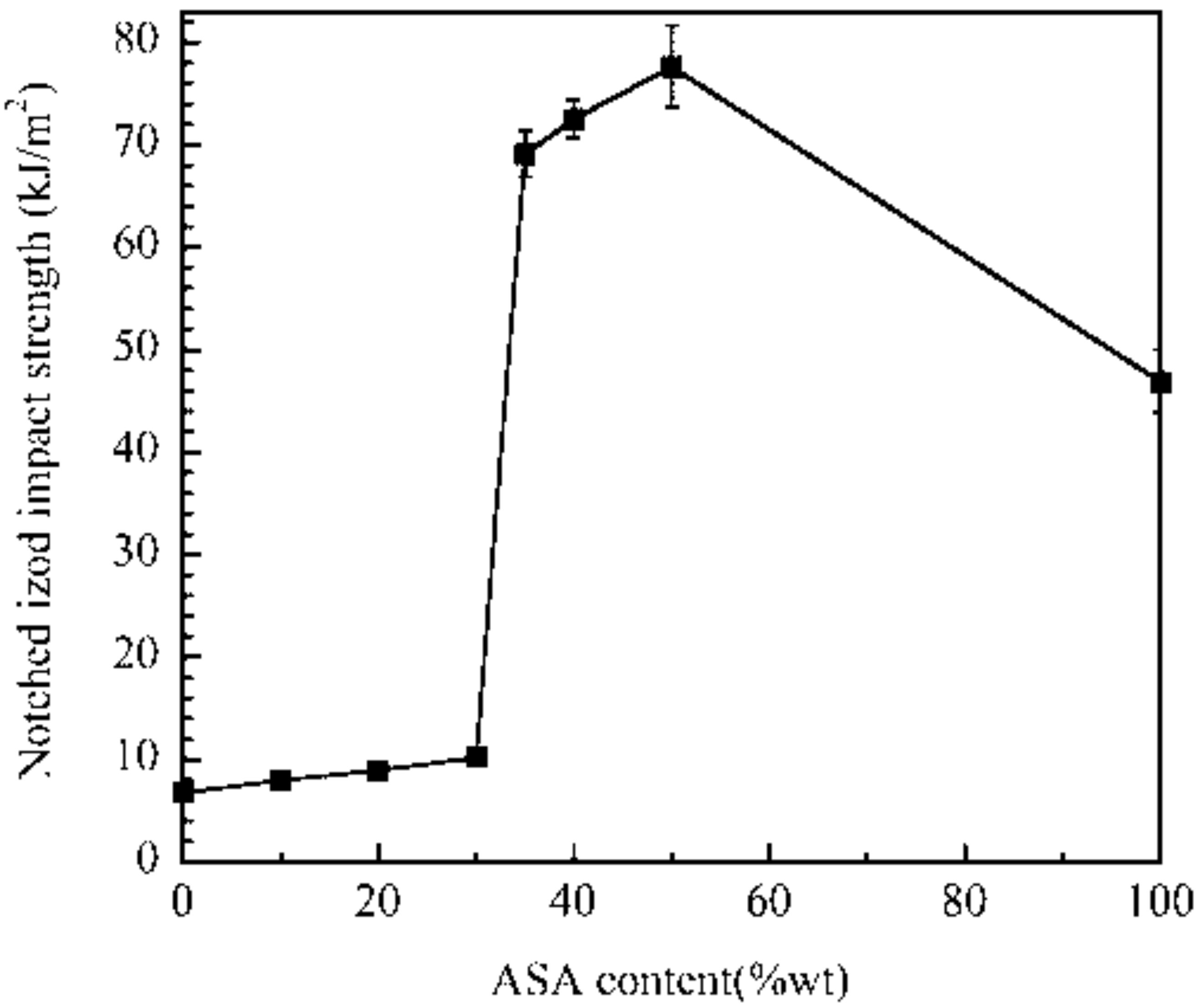
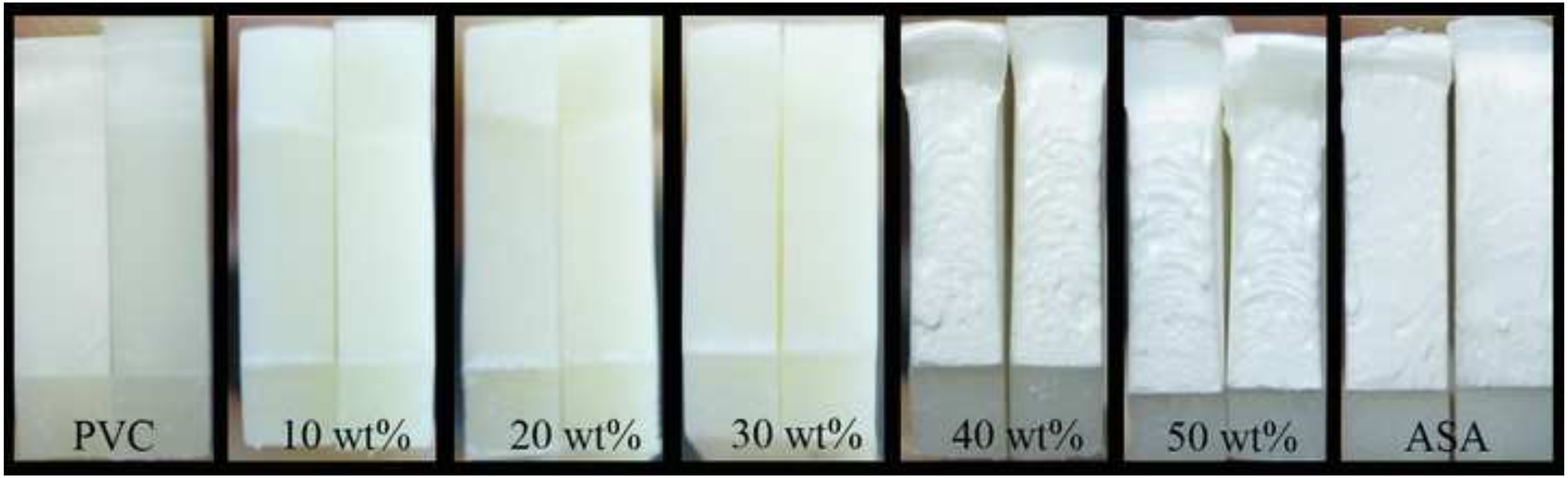
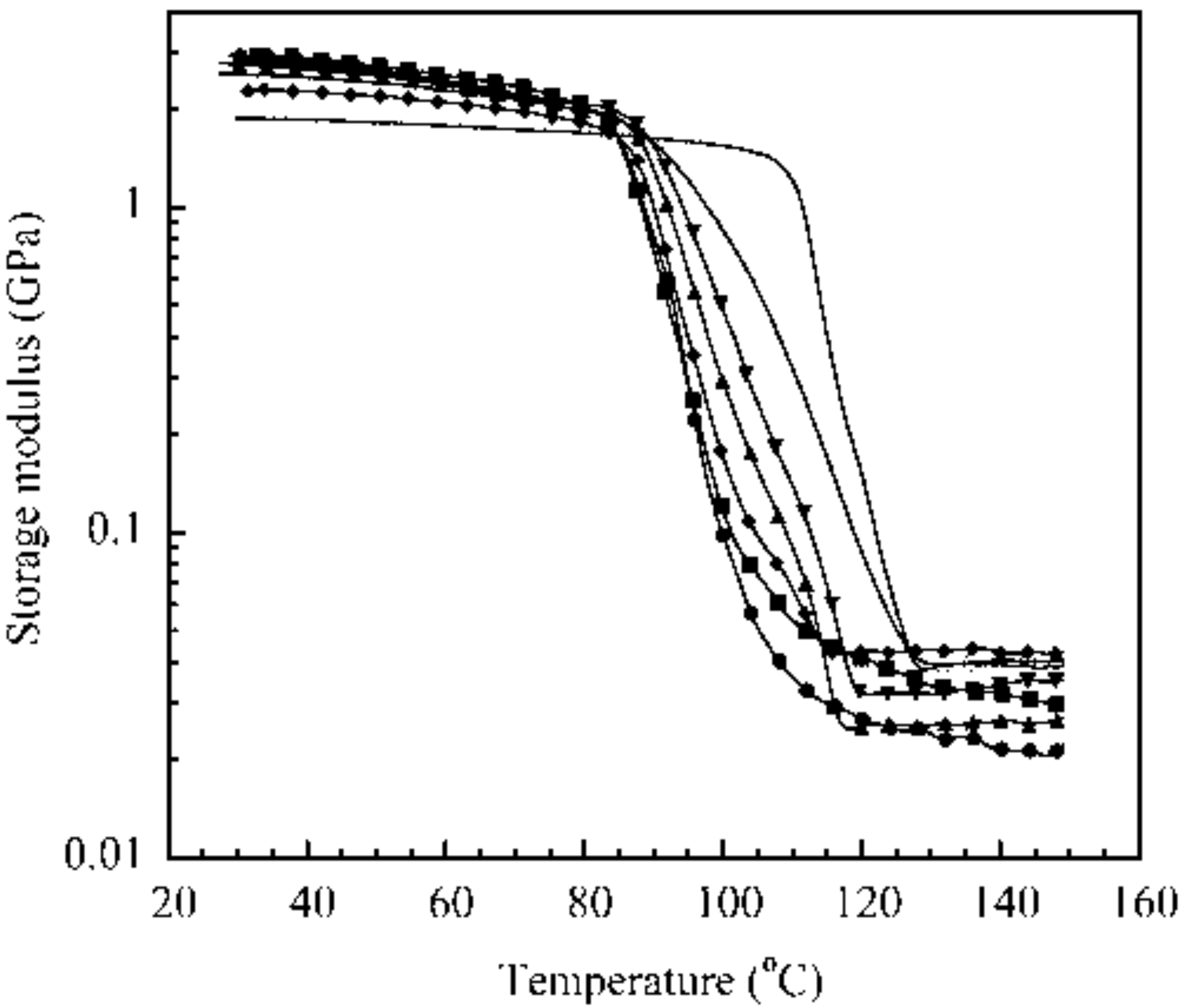
Fig. 10 Contact angle of PVC/ASA blends at different ASA contents.

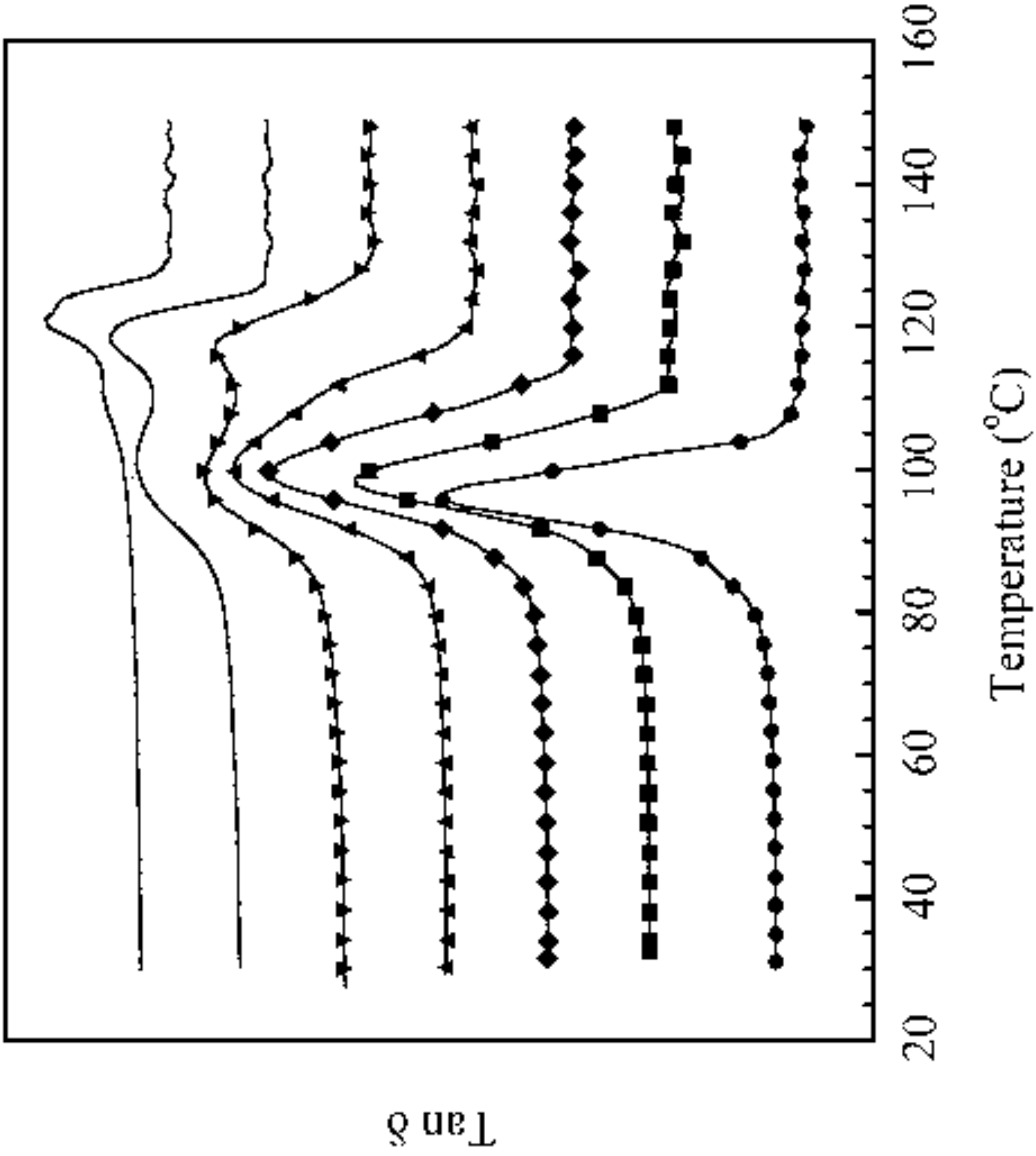

1.5
1.4
1.3
1.2
1.1
1
Density (g/cm^3)
0
20
40
60
80
100
ASA content (%wt)

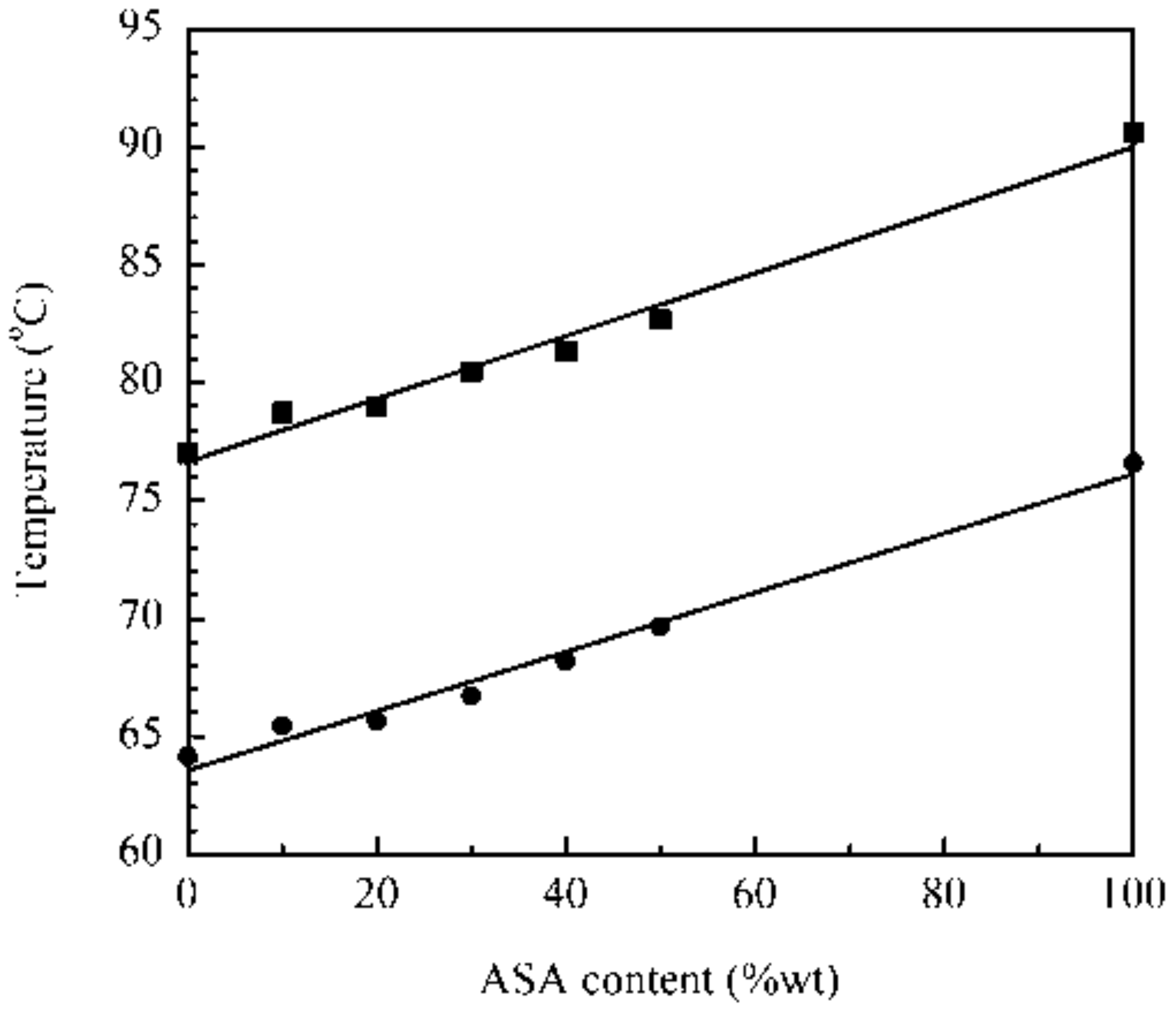

Notched izod impact strength (kJ/m^2)
0
10
20
30
40
50
60
70
80
ASA content(%wt)
0
20
40
60
80
100

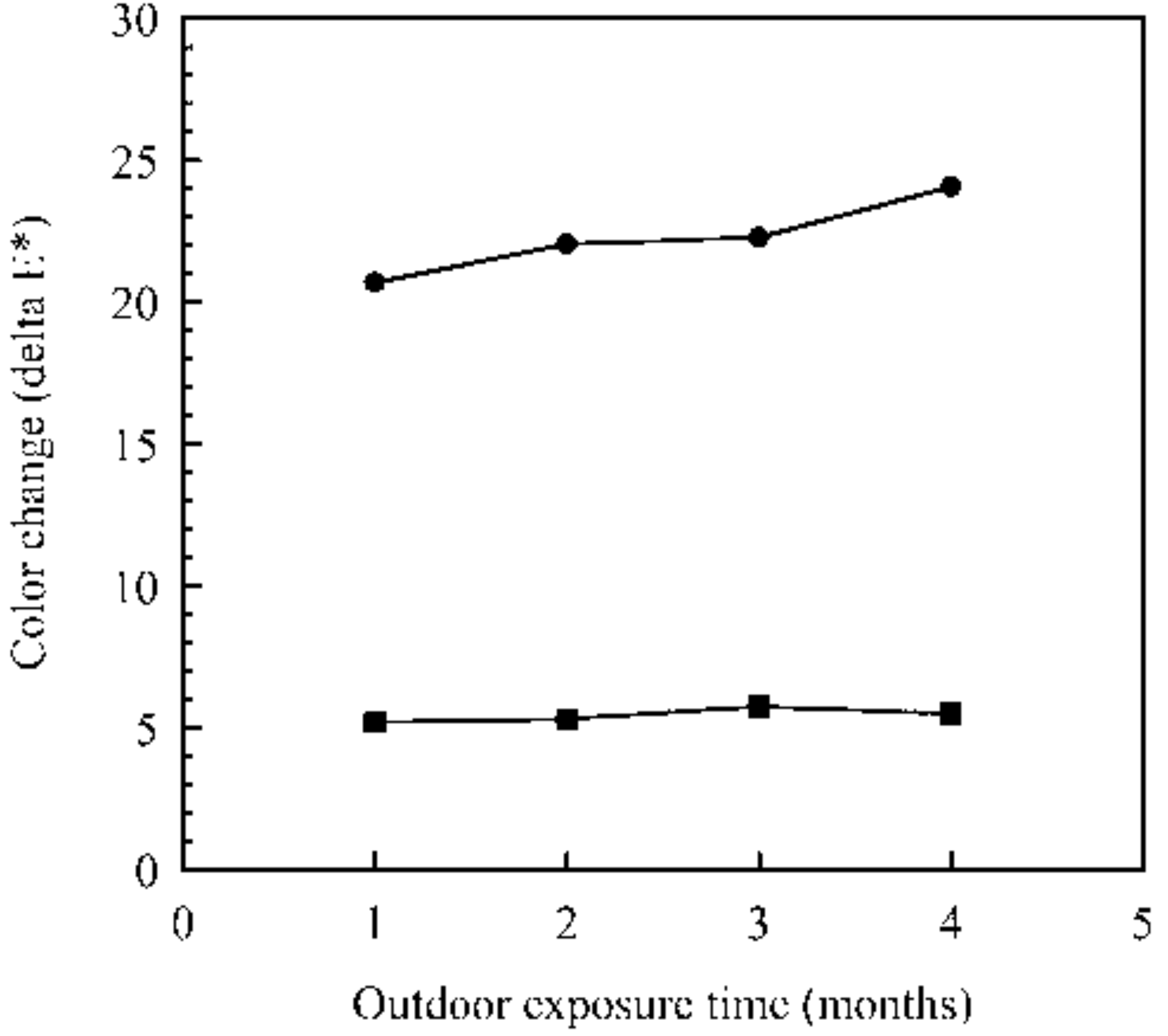

PVC
10 wt%
20 wt%
30 wt%
40 wt%
50 wt%
ASA


Storage modulus (GPa)
1
0.1
0.01
20
40
60
80
100
120
140
160
Temperature (°C)

Line Figure

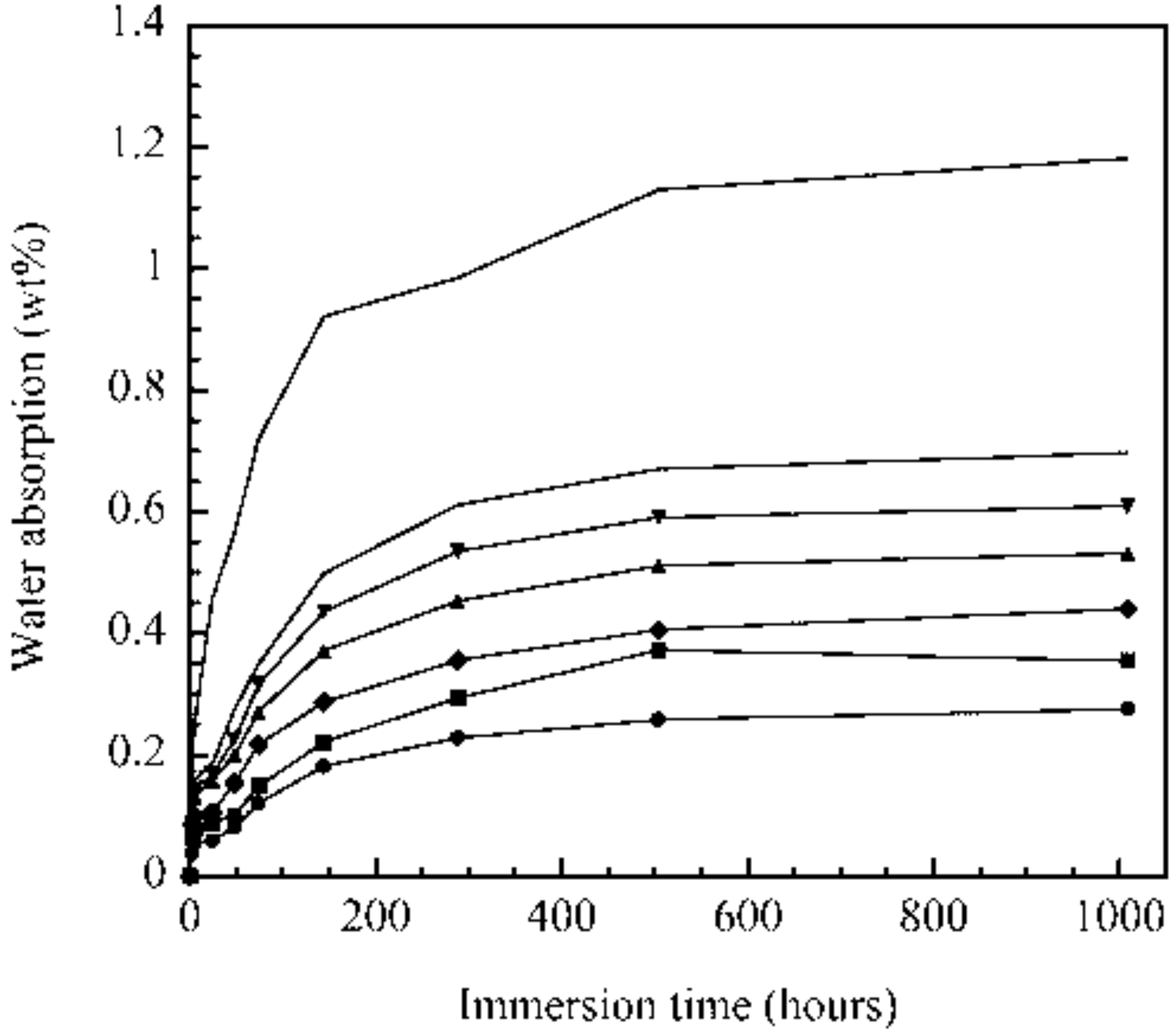



95
90
85
80
75
70
65
60
Temperature (°C)
0
20
40
60
80
100
ASA content (%wt)


30
25
20
15
10
5
0
Color change (delta E*)
0
1
2
3
4
5
Outdoor exposure time (months)


(a)
(b)

Line Figure


Water absorption (wt%)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
200
400
600
800
1000
Immersion time (hours)

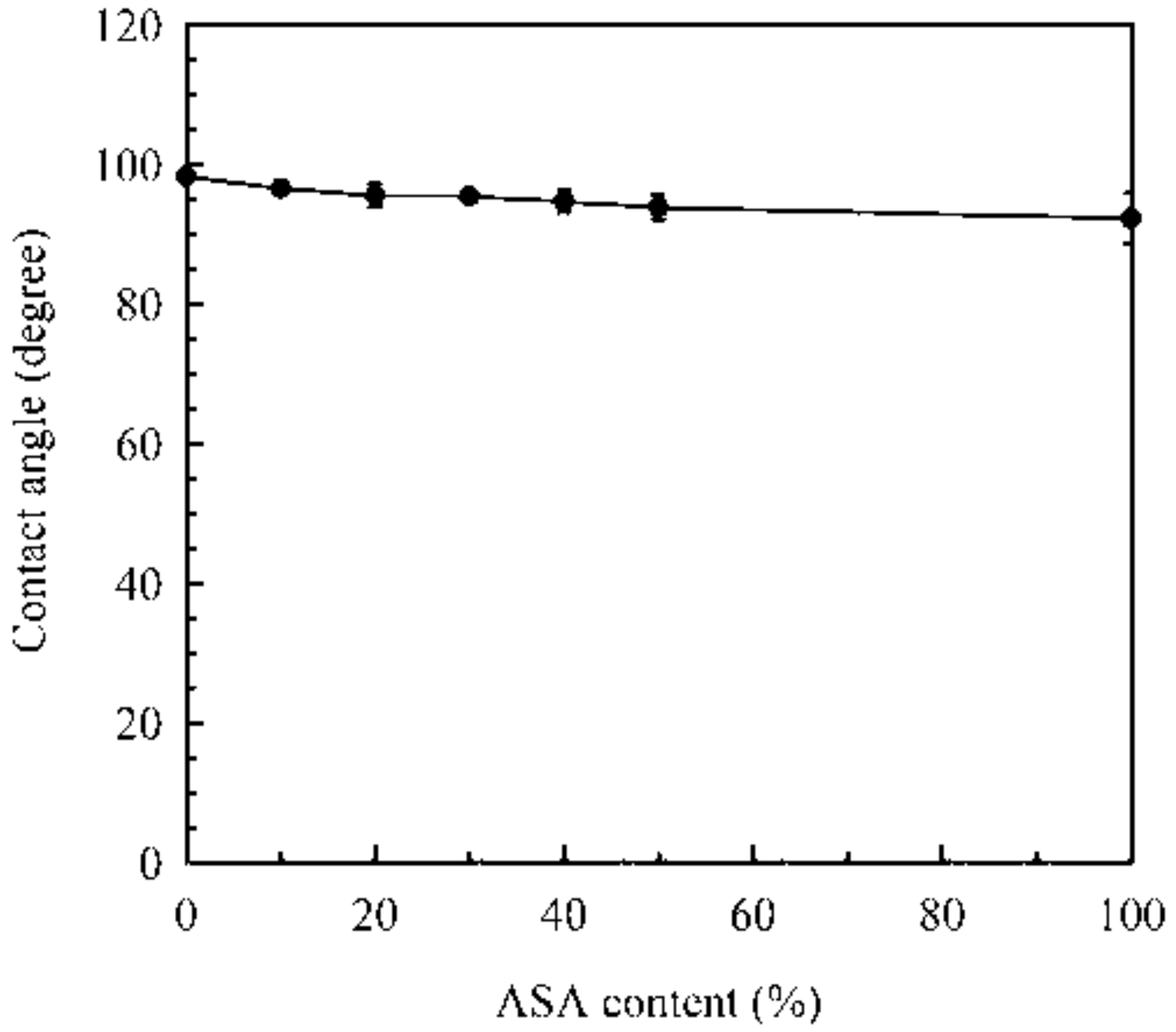

120
100
80
60
40
20
0
Contact angle (degree)
0
20
40
60
80
100
ASA content (%)

Table 1 Tensile and flexural properties of PVC/ASA blends at various ASA contents.

Sample (wt%)	Tensile property			Flexural property	
	Modulus (GPa)	Strength (MPa)	Elongation at break (%)	Modulus (GPa)	Strength (MPa)
PVC	2.18 ± 0.05	53 ± 0.3	113 ± 29	3.20 ± 0.08	87 ± 1.0
PVC/ASA 90:10	2.10 ± 0.05	51 ± 0.4	84 ± 24	3.00 ± 0.06	79 ± 1.6
PVC/ASA 80:20	2.01 ± 0.02	48 ± 0.5	62 ± 31	2.87 ± 0.05	75 ± 1.5
PVC/ASA 70:30	1.93 ± 0.02	46 ± 0.3	42 ± 24	2.76 ± 0.04	71 ± 0.8
PVC/ASA 60:40	1.89 ± 0.03	46 ± 0.2	24 ± 7	2.74 ± 0.10	72 ± 2.2
PVC/ABS 50:50	1.89 ± 0.01	45 ± 0.4	13 ± 4	2.73 ± 0.05	63 ± 0.3
ASA	1.57 ±0.02	38 ± 0.9	6 ± 1	2.23 ± 0.04	63 ± 0.6

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Characterization of coconut fiber-reinforced polyvinyl chloride (PVC)/ acrylonitrile styrene acrylate (ASA) blends

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Keyword:	Polyvinylchlordie, Styrenic copolymer, Blends, Wood plastic composites, Impact strength
Abstract:	Coconut fiber-filled composites based on PVC/ASA blend were developed. The results reveal that impact strength of the PVC/ASA/coconut fiber composites is significantly higher than those of PVC wood composites or polyolefins wood composites comparing at the same fiber content. Dynamic mechanical analysis (DMA) thermograms exhibit two distinct glass transition temperatures (Tgs) of the blend matrix indicating partial miscibility of the blends. The modulus and Tgs of the composites systematically increase with the fiber content. The PVC/ASA blend shows a potential use as a matrix of high impact wood composite products with good thermal stability due to the outstanding impact and thermal properties of the blend.

Characterization of coconut fiber-filled polyvinyl chloride (PVC)/ acrylonitrile styrene acrylate (ASA) blends

Sarawut Rimdusit[1], Siriporn Damrongsakkul[1], Patima Wongmanit[1],
Duangporn Saramas[2] and Sunan Tiptipakorn[3]

Abstract

Coconut fiber-filled composites based on PVC/ASA blend were developed. The results reveal that impact strength of the PVC/ASA/coconut fiber composites is significantly higher than those of PVC wood composites or polyolefins wood composites comparing at the same fiber content. Dynamic mechanical analysis (DMA) thermograms exhibit two distinct glass transition temperatures (T_gs) of the blend matrix indicating partial miscibility of the blends. The modulus and T_gs of the composites systematically increase with the fiber content. The PVC/ASA blend shows a potential use as a matrix of high impact wood composite products with good thermal stability due to the outstanding impact and thermal properties of the blend.

Keywords

PVC/ASA blend, wood plastic composite, impact strength, coconut fiber.

[1]Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Pathumwan, Bangkok, 10330, Thailand.
[2]Vinythai PLC., 14th F., Green Tower, 3656/41 Rama IV Rd., Bangkok 10110, Thailand.
[3]Department of Chemistry, Faculty of Liberal Arts and Science, Kasetsart University, Kamphaeng Saen, Nakorn Pathom, 73140, Thailand.

Corresponding author:
Sarawut Rimdusit, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Pathumwan, Bangkok, 10330, Thailand.
Email: sarawut.r@chula.ac.th

Introduction

Nowadays, wood plastic composites (WPCs) have become a large market volume of building products and one of the most rapidly expansion segments of the building products industry, especially for decking, railing, and related outdoor structures.[1] This is due to its competitive price, the absence of knots and splinters, acceptable mechanical properties, good durability, low maintenance, resistance to termites, and better fire resistance over traditional materials. Major thermoplastics practically used in WPCs including high and low density polyethylene (HDPE and LDPE), polypropylene (PP), polyvinylchloride (PVC), and polystyrene (PS).[2] Although PE is currently the dominant polymer matrix used in WPCs by far, there is movement towards PVC/wood composite due to better compatibility with natural fiber, less cost, less flammability, and better inherent mechanical properties. Because of its versatility, low cost, energy efficiency, and long life cycle, PVC becomes appropriate products in so many applications especially in building and construction market.[3]

PVC-based WPCs offer acceptable mechanical properties, chemical and flame resistance, as well as a relatively long lifetime (UV resistance). However, compared to other WPCs, PVC has some inherent disadvantages. It possesses rather high glass transition temperature which causes PVC to be brittle at ambient temperature thus poor impact properties of its wood composites.[1] To gain more flexibility and improved impact strength of PVC/wood composites, impact modifiers such as chlorinated polyethylene (CPE), methyl methacrylate butadiene styrene copolymer (MBS), acrylic rubber (ACR), and ethylene propylene diene rubber (EPDM) are studied to enhance impact properties of PVC wood composites.[4-6] Although those modifiers effectively impart high impact properties to PVC, they contribute to lowering thermal stability of the matrix due to their low glass transition temperatures.[4-6] In our recent work, styrenic-based copolymer from acrylonitrile butadiene styrene (ABS) has been demonstrated to exhibit remarkable enhancement in impact strength.[7] In this research, another high thermal stability styrenic-based copolymer from acrylonitrile styrene acrylate copolymer (ASA) is proposed as an impact modifier for PVC particularly for outdoor applications as ASA is known for its high impact property with higher weathering resistance than ABS.

Acrylonitrile styrene acrylate (ASA) is a styrene acrylonitrile copolymer (SAN) modified with an acrylate rubber. ASA resins are used in industrial applications, for example, coating, adhesives, and paints. Furthermore, ASA can be blended with many polymers (such as PVC in this study) to make alloys and compounds to gain the benefits from ASA's outstanding impact resistance and excellent weatherability.[8-10] Due to special acrylic ester rubber in the matrix, ASA resin provides resistance to UV radiation and atmospheric oxygen. Furthermore, under long period of exposure to UV, moisture, heat and impact, ASA shows very low level of yellowing and minimal decrease in toughness.[10] Recently ABS copolymers are used as an effective impact modifier for

PVC due to high thermal stability and superior impact resistance of the obtained blend.[7, 11-12] However, for outdoor applications, stabilized ABS still shows a decrease in impact strength after long period of exposure due to the presence of unsaturated structure. This problem might be solved by using ASA copolymer that contains saturated structure in polymer chains.[10] In these PVC/ASA blending systems, PVC contributes to flame retardance, tensile and flexural properties, whereas ASA imparts processability, impact strength, heat resistance, and color retention to the mixtures.

The use of coconut, rice straw, pine, sisal, and oil palm, and other natural fibers as alternative reinforcement in polymeric materials have been the focus of increasing interest of worldwide research due to the need for more environmentally friendly products with renewable characteristic.[13-20] Coconut fiber is resilient, strong, highly durable, rot resistant, and difficult to ignite.[16] It is one of the toughest plant fibers available and is highly abundant in Thailand as waste materials of coconut milk industry. Some research and development efforts are underway to find new areas of application for coconut fiber.[13, 17]

Recently, there is no study discussing the influence of coconut fiber contents on the properties of PVC/ASA/coconut fiber composite. In this research, PVC/ASA blend at an optimal mass ratio of 50:50 is used as a matrix for coconut fiber-reinforced composites. The fabrication of PVC/ASA composites filled with short coconut fiber at various coconut fiber contents are carried out. The effect of the coconut fiber on physical, mechanical, and thermal properties of the obtained composites will be determined.

Experimental

Materials

The characteristics of PVC Siamvic 258RB used in this study were presented in Table 1. The additives used in PVC compound were Kane Ace 20 as processing aid, SAK-WP08-NP as heat stabilizer, and calcium stearate as external lubricant. PVC resin and these additives were kindly supported by Vinythai Public Co., Ltd., Thailand. Loixol P1141, internal lubricant, was supplied by Siam Chemicals Solutions Co., Ltd. ASA resin (KIBILAC PW-997S extrusion grade), which was purchased from Global Connections Co., Ltd., possesses the characteristics as shown in Table 2. The natural fiber used as reinforcing filler for wood plastic composites was derived from the husk of the coconut (*Cocos Nucifera*). In this study, coconut fiber was cut by Fritsch pulverisette cutting mill 15 to reduce the fiber length to 3-8 mm and was dried in an oven at 105°C for 24 hours prior to composite molding compound preparation.

Composite preparation

PVC resin and its additives were blended using a high speed mixer (Plasmec Turbomixer 100L with cooler) with a mixing speed of 1200 rpm. In this study, the coconut fiber content was varied from 10-50 wt%. The mixtures of PVC, ASA and coconut fiber at a fixed PVC/ASA mass ratio of 50:50 were prepared by two-roll mills at 170°C for ca. 6 minutes to yield a homogeneous mixture. The obtained PVC/ASA/coconut fiber composite sheets were then compression-molded at 170°C and 15 MPa for 4 minutes. The compression-molded samples were then cut into desirable shapes for further property evaluations.

Specimen characterizations

Notched Izod impact strength of the specimens was obtained by Impact Tester (Yasuda) according to ASTM D256-04. The dimension of the test specimen was 12.7 × 60 × 3.2 mm^3 while the depth under notch of the specimen was 10 mm. The average impact strength values were calculated from ten tests on each material.

Tensile properties of PVC/ASA wood composites were investigated using a universal testing machine (Instron 5567) according to ASTM D638 with a crosshead speed of 6.0 mm/min. The test specimens are a dumbbell shape with a uniform thickness. The average values from both flexural and tensile analyses were determined from at least five tests on each sample.

Flexural properties of the wood composite specimens were determined following ASTM D790-M93, using a universal testing machine (Instron 5567). The test was carried out in a three-point bending mode with a support span of 48 mm and at a crosshead speed of 1.2 mm/min. The dimension of the each specimen was 12.7 × 60 × 3.2 mm^3.

Surface texture of the wood composites before and after weathering test was studied using a Scanning Electron Microscope (SEM: JSM-5800LV, JEOL) with an acceleration voltage of 15 kV. The weathering surface of each specimen was coated with thin gold film prior to testing.

Thermal characteristics of the composite specimens were examined by a dynamic mechanical analyzer (DMA: NETZSCH-DMA242) over a temperature range from 30°C-150°C with a 2°C/min heating rate. The testing strain amplitude and frequency were 30µm and 1Hz, respectively. Rectangular samples with a 50 mm in length, 10 mm in width, and 2 mm in thickness were tested in a three point bending mode. Glass transition temperature was obtained from a peak of loss modulus curve in the DMA thermogram.

Thermal stability of the composites was also characterized by HDT (heat distortion temperature) and Vicat softening temperature measurements. In the heat distortion temperature test, each specimen was placed under the deformation measuring device with a mean of raising the temperature at 120°C/h or 2 ± 0.2°C/min until the midpoint of the beam deflected to 0.25 mm following ASTM D648. This temperature was recorded as the deflection temperature under flexural load. In the Vicat softening point test the specimen was immersed in a silicon oil bath at 30°C then the sample was heated at a rate of 50°C/h following ASTM D1525. The temperature at which the needle was penetrated to a depth of 1 ± 0.01 mm was recorded as the Vicat softening temperature of each sample.

Water absorption measurement was conducted following ASTM D570, using a specimen in the shape of a disk 50.8 mm in diameter and 3.2 mm in thickness. Three specimens were conditioned in an oven at 50°C for 24h, cooled in a desiccator, and then weighed. The specimens were then immediately immersed in distilled water and were weighed periodically. Based on the initial mass of each specimen, the amount of water absorbed was calculated from the following equation:

$$WA(\%) = \left(\frac{M_t - M_o}{M_o}\right) \times 100 \qquad (1)$$

where WA is water absorption at time t (%); M_t and M_o are the mass values of the specimen after and before immersion, respectively.

In the water immersion tests, thickness at three positions of each specimen was also measured for determination of the thickness swelling (TS) following equation (2):

$$TS(\%) = \left(\frac{T_t - T_o}{T_o}\right) \times 100 \qquad (2)$$

where TS, is thickness swelling at time t (%), T_t and T_o are thicknesses at time t and dried condition mm, respectively.

Contact angle measurement was performed at room temperature using a contact angle meter model Cam-Plus Miccro equipped with an optical microscope from Tantec. The measured liquid was deionized water with a droplet size of 10 µm. Contact angle of each specimen was averaged from 10 measured values.

After 3 months of exposure to natural weathering in Rayong Province, Thailand (during December 18th 2010 to March 21th 2011), color change of composites was recorded in CIELAB system by using Ultrascan Pro spectrometer (Hunter Lab, USA). The color of each sample was an average of five different measurements at various parts of the sample. The total color difference, $\Delta E_{ab}*$, between non-aged samples and aged samples each given in terms of lightness (L*) and chromaticity coordinate (a* and b*) is calculated following ASTM D 2244 by the formula

$$\Delta E_{ab}* = [(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2]^{1/2} \qquad (3)$$

where $\Delta L* = L_1* - L_0*$, $\Delta a* = a_1* - a_0*$, and $\Delta b* = b_1* - b_0*$ are the respective color coordinate differences.

Results and discussion

Mechanical properties of coconut fiber-reinforced PVC/ASA

Figure 1 shows the effect of coconut fiber content on notched Izod impact strength of our PVC/ASA/wood composites**.** From the figure, it can be noticed that the impact strength of composites tended to decrease with increasing coconut fiber content. The impact strength of our wood composite containing 10 wt% of coconut fiber exhibited the value as high as 195 J/m. The value was found to decrease with an increase of coconut fiber content to approximately 111 J/m at 50 wt% of the coconut fiber. A similar trend was also observed in other wood composite systems such as PVC/ABS/wood, PP/wood and PE/wood composites.[7,13,21-23] In general, the reduction in impact strength of fiber-filled composite maybe caused by an association of the following two mechanisms: (1) fibers practically drastically reduce the elongation to break and may reduce the area under the stress-strain curve, and (2) stress concentrations occur at regions around fiber ends, portion of poor adhesion, and regions where fibers contact one another. This is why the composite at high level of fiber content exhibits lower impact performance than that with lower level of fiber content.[24]

In comparison with other fiber-filled composites, the impact strength of our PVC/ASA/wood composites was found to provide substantially higher value. For examples, Ishizaki *et al.*[13] studied the impact strength of PP/coconut fiber composites and reported the notched Izod impact strength value (at 50 wt% of coconut fiber) to be about 16 J/m. Yuan *et al.*[25] studied the mechanical properties of wood fiber reinforced PE and PP composites and reported that the impact strength value (at 50 wt% of wood fiber) was about 22-30 J/m and 18-22 J/m, respectively. In the case of PVC/pulp fiber composites reported by Ashori et al., the notched Izod impact strength of the composite at 50 wt% of the pulp fiber exhibited the value of 16 J/m.[26] Favaro *et al.*[27] investigated on the properties of sisal fiber-reinforced HDPE composites and reported the highest impact strength value (at 10 wt% of sisal fiber) was only about 65 J/m. The reason of this outstanding impact strength in wood composites from PVC/ASA matrix might be due to the very high inherent impact strength of the PVC/ASA blend matrix comparing with the other matrices i.e. PVC/ASA (50/50) = 778 J/m, PVC/ABS (50/50) = 650 J/m [7], PP = 15 J/m [25], HDPE = 154 J/m [25] etc. In addition, the suitable level of interfacial interaction between the fiber and the matrix is one key factor to contribute to the enhancement in impact strength of the composite by promoting energy dissipation through fiber pull-out or debonding.[24] An addition of ASA into PVC is believed to help improve this interfacial interaction with the coconut fiber thus a higher degree of energy dissipation. Similar phenomenon was also observed in the PVC/ABS/wood composite system.[7]

In Figure 2, the effects of coconut fiber content ranging from 10-50 wt% on tensile properties of the PVC/ASA/coconut fiber composites were illustrated. It can be observed that the tensile modulus of the composites was found to systematically increase with increasing coconut fiber content. The similar behavior was also found in other wood composites system such as Polyester/wood, PP/wood and Polycaprolactone/wood composites.[23, 28-30] Abdul Khalil *et al.*[28] examined the chemical modification and the effect of fiber type on properties of fiber reinforced polyester composites. The addition of all fiber types (0-55 wt%) improved the tensile modulus of the composites up to 50-60%. Ashori *et al.*[23] investigated the mechanical properties of PP/wood composites at up to 40 wt% of aspen fiber loading. The obtained tensile modulus of the composites was about 60% higher than that of the unfilled PP at the maximum fiber content. Sun *et al.*[29] examined the formulation and compounding processes on properties of PP/sisal composites. The addition of sisal fibers (0-30 wt%) improved the tensile modulus of the composites up to 120%. Ibrahim *et al.*[30] investigated the mechanical properties of Polycaprolactone/oil palm composites at up to 50 wt% of oil palm fiber loading. The obtained tensile modulus of the composites was about 100% higher than that of the unfilled Polycaprolactone at 50% of oil palm fiber content. This is clear that the addition of rigid coconut fiber filler (having modulus in the range of 4-6 GPa)[16] could have an effect on the mobility restriction of polymer molecular chains and same observation has also been reported in various wood composite systems.[18, 23, 25, 27-30, 34-35]

Tensile strength of short fiber reinforced WPCs has been observed to mainly decrease with an addition of the short fiber (as opposite to long fiber) such as that observed in PP/coconut fiber[28], HDPE/sisal fiber[27], PP/maple wood fiber[25], PE/maple wood fiber[25], PP/aspen fiber[23], PP/oil palm fiber[31], PP/jute fiber[32] and Polycaprolactone/oil palm fiber[30]. Neilsen and Landel discussed the tensile strength of composites to be greatly affected by such factors as the perfection of packing and alignment of fibers, and by imperfection such as voids in the material.[24] The decrease in tensile strength in presence of short fiber could be attributed to 1) appreciable distances between each end of different fibers are ineffective in transmitting load from the matrix to the fibers; 2) the fiber ends tend to act as a stress concentrators and thus as crack initiators; 3) fibers that do not overlap one another substantially cannot contribute the composite strengthening; and 4) it is impossible to achieve perfect fiber orientation in short fibers as with continuous fibers. With increasing the content of the short coconut fiber in PVC/ASA matrix, the strength tended to be level off and not show a steady decreasing trend thus due to the shorter distances between fiber ends, the higher degree of fiber overlapping as well as greater fiber orientation from two roll mill processing. Tensile strength of PE/wood fiber composites was found to decrease as fiber content increased i.e. from a value of 24 MPa for unfilled PE to 14.2 MPa for the composite with 50 wt% fiber content.[25] Furthermore, in PP/coconut fiber composites, tensile strength was also found to decrease as fiber content increased i.e. from 30 MPa for unfilled PP to 20 MPa for the composite with 50 wt% fiber content.[33] As compared to the polyolefin/woodfiber systems, PVC/ASA/coconut fiber composites, without any surface treatment, was observed to show an ability to maintain relatively higher tensile strength even with high coconut fiber contents (i.e. 38 MPa at 50% wt% of coconut fiber).

Figure 3 presents the effect of coconut fiber content on flexural properties of PVC/ASA/coconut fiber composites. With increasing the coconut fiber content, flexural modulus of the composites also increased systematically from 3.25 GPa at 10 wt% fiber to 5.06 GPa at 50 wt% fiber. This significant increase in the flexural modulus of the PVC/ASA/coconut fiber composites is primarily attributed to the reinforcing effect imparted by the presence of the coconut fiber in the polymeric matrix as described in the tensile properties of the composites. The similar improvement in flexural modulus was also reported in the systems of PP/wood fiber composites.[13, 23, 29-33] Besides, the flexural strength of PVC/ASA/coconut fiber composites is also depicted in Figure 3. From the results, the flexural strength of the unfilled PVC/ASA at 50/50 mass ratio was determined to be 66 MPa and the strength of the composite showed an increasing trend up to 40 wt% of the fiber i.e. 83 MPa. Above 40 wt%, the flexural strength of the composite decreased from 83 MPa to 73 MPa (at 50 wt%). When the content of the polymer matrix decreased, the area of fiber for reinforcing was reduced, making the fiber easily slip off after applying stress.[33]

Dynamic mechanical properties of PVC/ASA wood composites

From DMA analysis, the effects of coconut fiber content on storage modulus and glass transition temperature (obtained from the peak of loss modulus) of the composites are illustrated in Figures 4-6 and also summarized in Table 3. From Figure 4, the storage modulus in glassy state of the PVC/ASA/coconut fiber composites was found to increase with increasing coconut fiber contents from the reinforcing effect of the more rigid coconut fiber to the PVC/ASA matrix. The trend was in good agreement with the tensile and flexural modulus as previously discussed. Furthermore, two glass transition temperatures of the composites were clearly observed from the two loss modulus peaks in each thermogram of the composite in Figure 5. It can be seen that T_{g1} of the composites continuously increased from about 95°C (at 10 wt% fiber) to 100°C (at 50 wt% fiber) while T_{g2} of the composites also increased from 113°C to 115°C at the same fiber contents. A similar behavior was also observed in the system of PVC/ENR/oil palm empty fruit bunch composites reported by Ratnam *et al.*[20] and PP/natural fiber composites reported by Tajvidi *et al.*[14]. The observed enhancement in T_g was attributed to a restriction effect on the motion of molecular chains of the polymer matrix due to impediment of a more rigid coconut fiber. This also implied some interfacial interaction to exist between the fiber and the matrix.

Additionally, the temperature dependence of tan δ of PVC/ASA/wood composite is illustrated in Figure 6. For the unfilled PVC/ASA, the broad transition zone was visible in the temperature range from 90 to 130 °C, corresponding to α relaxations of the PVC and ASA. Addition of coconut fiber resulted in a lowering of the tan δ peaks. As same as in many composite systems, the damping of polymer matrix is always greater than that of reinforced composites.[14, 15, 19, 24] With increasing coconut fiber content, loss tangent peaks of PVC/ASA matrix was flatten and shifted to higher temperature. The decrease in tan δ peak suggested the addition of the fiber contribute to the more elastic nature of the wood composites.

Thermal properties of PVC/ASA wood composites

The effects of coconut fiber contents on vicat softening temperature and heat distortion temperature (HDT) of PVC/ASA/coconut fiber composites are shown in Figure 7. From this figure, the vicat softening temperature of the unfilled PVC/ASA was determined to be about 83°C. It is evident that the vicat softening temperature and HDT of the composites increase with increasing coconut fiber contents i.e. vicat softening temperature increased from 85°C (at 10 wt% fiber) to 96°C (at 50 wt% fiber). For HDT, the unfilled PVC/ASA showed HDT to be 70°C and this value was also found to systematically increase with the coconut fiber content i.e. the HDT increased from 73°C (at 10 wt% fiber) to 82°C (at 50 wt% fiber). As compared with polyolefins wood composites, the thermal stability of our PVC/ASA/wood composites exhibited a substantially higher value thus allowed an application of these wood composites at significantly higher temperature.[21]

Water absorption and thickness swelling of PVC/ASAwood composites

The percentage of the water uptake as a function of time of the unfilled PVC/ASA and PVC/ASA/coconut fiber composites at different coconut fiber contents is shown in Figure 8. After 24 hours immersion, water absorption of the unfilled PVC/ASA was very low i.e. 0.18 w%, due to its relatively hydrophobic nature compared to natural fiber. Water uptake of the composites expectedly increased with an increase of the coconut fiber content as seen in the figure. With an addition of 10 wt% of coconut fiber, the water absorption value was raised to about 0.65 wt% and at up to 50 wt% fiber, the water absorption of the composites increased to 4.03 w%. These values are considered to be much lower than that of natural wood with the reported water absorption value as high as 39-70%.[2]

In a previous study, Ayrilmis and Jarusombuti[36] reported that the wood plastic composites containing a compatibilizer such as maleated polypropylene (MAPP) had significantly lower thickness swelling and water absorption than those without the MAPP. According to their research, the interfacial bonding between the wood fiber and the polymer matrix was an important factor influencing the water absorption and the thickness swelling of the wood plastic composites. High water absorption of the composite at high fiber content may be due to the hydrogen bonding between water molecule and free hydroxyl groups present in the coconut fiber and the diffusion of water molecule into the interface between fiber and matrix. In addition, larger amount of voids might exist between the hydrophilic filler and the hydrophobic polymer matrix thus further contributed to the much greater water uptake of the composites with very high fiber loading.[37] The relatively low water absorption value of our wood composites thus suggested good matrix and fiber wetting with substantial interaction interaction between to two components. Moreover, the thickness swelling values (Figure 9) of the composite samples showed similar trend as water absorption experiment. For the 24 hours immersion, the thickness swelling of PVC/ASA/coconut fiber at 50 wt% fiber loading was observed to be 2.5%.

Contact angle of PVC/ASA wood composites

Polarity of PVC/ASA and its composites was also examined by contact angle measurement. The average contact angle values of PVC/ASA/coconut fiber composites at various coconut fiber contents are present in Figure 10. The contact angle value of unfilled PVC/ASA was determined to be about 96.5°. For PVC/ASA/coconut fiber composites, contact angle values at low fiber contents were observed to be unaffected by the increasing portion of wood fibers. This suggested high degree of polymer coverage on the surface of the composite, resulting in a lower wettability of the same level as the PVC/ASA matrix itself. At above 40 wt% fiber, the contact angle values significantly decreased with increasing coconut fiber. E.g. with an addition of 40 wt% of coconut fiber, the contact angle value was about 95.2°. As increasing the coconut fiber to 50 wt%, the contact angle of the composites significantly decreased to 92.5°, this reduction in contact angle was mainly due to more hydrophilic coconut fiber exposed on the surface of the specimen.

Color change and impact retention after weathering of the PVC/ASA composites

Natural weathering up to 3 months of unfilled PVC/ASA blend and PVC/ASA/coconut fiber at various coconut fiber contents ranging in 0 to 50 wt% fiber was investigated and the measured color change of the samples as a function of time is shown in Figure 11. From this figure, the unfilled PVC/ASA blends exhibited very little change in color whereas its composites showed higher degree of color change with increasing coconut fiber content. Moreover it was noticed that the lightness difference was a major influence to the total color change i.e. the composites showed a fading in color under weathering. The addition of ASA into PVC was reported in our recent work to significantly reduce color change of the neat PVC. Figure 12 shows SEM micrographs of the unweathered and the 3-month naturally weathered composites. Interface cracking was observed at the surface of the weathered composites. With increasing coconut fiber content, greater and larger cracks between fiber and polymer matrix were observed. The phenomenon helps explain the fading behavior of the composites due to outdoor exposure. The gaps or cracks between the matrix and the fiber induce light scattering on the composite surface thus the observed whitening of the surface. From the research by

Fabiyi *et al.*[38,39], PVC and pine wood erosion was observed at the surface of weathered PVC composites by SEM. Crazing on the composite surface may be caused by differentially contact (resulting from wetting and drying) between wood and plastic interface during natural weathering, resulting in color fading.[39]

Conclusions

High impact strength PVC/ASA/coconut fiber composite at a fixed PVC/ASA mass ratio of 50/50 was developed as a wood-substituted product. With increasing coconut fiber content in the composites, tensile modulus, flexural modulus, and flexural strength of the PVC/ASA/coconut fiber composites systematically increased while tensile strength and notched Izod impact strength of the composites tended to decrease. In comparison with PVC/coconut fiber composites, PVC/ASA/coconut fiber composites was found to provide significantly higher impact strength value even at up to 50 wt% coconut fiber content. T_gs from DMA of PVC/ASA/coconut fiber composites systematically increase with the addition of coconut fiber in the composites and the result was consistent with the HDT and vicat softening temperature determination. Water absorption and swelling thickness of PVC/ASA/coconut fiber composites slightly increased with increasing coconut fiber content due to the hydrophilic nature of coconut fiber. Finally after natural weathering for 3 months, color fading of the composites was observed and tended to increase with increasing coconut fiber content due to more interfacial cracks observed between the fiber and the PVC/ASA matrix.

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Figure 1: Impact strength of wood composites at various fiber contents: (◆) PVC/ASA/coconut fiber composites, (●) PP/coconut fiber composites, (■) PVC/ABS/wood composites, (□) PP/pulp fiber composites.

Figure 2: Tensile properties of PVC/ASA/wood composites at various coconut fiber contents: (■) tensile strength, (▲) tensile modulus.

Figure 3: Flexural properties of PVC/ASA/wood composites at various coconut fiber contents: (■) flexural strength, (▲) flexural modulus.

Figure 4: Storage modulus of PVC/ASA/wood composites at various coconut fiber contents: (◇) 0%, (△) 10%, (□) 20%, (▲) 30%, (◆) 40%, (■) 50%.

Figure 5: Loss modulus of PVC/ASA/wood composites at various coconut fiber contents: (◇) 0%, (△) 10%, (□) 20%, (▲) 30%, (◆) 40%, (■) 50%.

Figure 6: Loss tangent of PVC/ASA/wood composites at various coconut fiber contents: (◇) 0%, (△) 10%, (□) 20%, (▲) 30%, (◆) 40%, (■) 50%.

Figure 7: Heat distortion temperature and vicat softening temperature of PVC/ASA/wood composites at various coconut fiber contents: (●) heat distortion temperature (▲) vicat softening temperature.

Figure 8: Water absorption of PVC/ASA/wood composites at various coconut fiber contents: (◇) 0%, (△) 10%, (□) 20%, (▲) 30%, (◆) 40%, (■) 50%.

Figure 9: Thickness swelling of PVC/ASA/wood composites at various coconut fiber contents: (◇) 0%, (△) 10%, (□) 20%, (▲) 30%, (◆) 40%, (■) 50%.

Figure 10: Contact angle of PVC/ASA/wood composites at various coconut fiber contents.

Figure 11: Color difference after weathering of PVC/ASA composite at various coconut fiber contents: ▨ 1 month, ▩ 2 months, ■ 3 months

Figure 12: Scanning electron micrographs (x100) of PVC/ASA/coconut fiber composites; (a) un-weathered PVC/ASA matrix, (b) 3-months exterior-weathered PVC/ASA matrix, (c) un-weathered composite with 10% of coconut fiber, (d) 3-months exterior-weathered composite with 10% of coconut fiber, (e) un-weathered composite with 50% of coconut fiber, (f) 3-months exterior-weathered composite with 50% of coconut fiber,

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S. Rimdusit et al., Table 1

Characteristic	**Standard**	**Value**
Viscosity index (ml/g)	ISO 1628-2	82
K-value (cyclohexanone)	DIN 53726	58
Polymerization degree	JIS K6721	680
Bulk density-compaction (kg/l)	ISO 1068	0.56
Volatile matter (%)	ISO 1269	≤ 0.3
Particle size (sieve analysis), (μm)	ISO 1624	120-150

S. Rimdusit et al., Table 2

Property	**ASA (PW 997S) extrusion grade**
Melt Flow Index (g/10min) at 220°C/10 kg	4
Notched Izod Impact Strength (Kg-cm/cm) at 6 mm thickness at 23°C	25
HDT (6 mm thickness at 0.45 MPa)	85
Flexural Strength (MPa)	65
Tensile Strength (MPa)	44

S. Rimdusit et al., Table 3

Fiber content (wt%)	**Storage modulus (GPa)**	**T_{g1} (°C)**	**T_{g2} (°C)**
10	2.63	94.8	113.4
20	3.00	95.0	114.0
30	3.68	95.8	114.0
40	4.29	96.8	114.3
50	4.85	100.1	114.5

S. Rimdusit et al., Table 4

Fiber content (wt%)	**Average water absorption**		**Thickness swelling**	
	at 2 hour immersion (wt%)	**at 24 hour immersion (wt%)**	**at 2 hour immersion (wt%)**	**at 24 hour immersion (wt%)**
0	0.09 ± 0.00	0.18 ± 0.01	-	-
10	0.19 ± 0.07	0.65 ± 0.01	0.00 ± 0.00	0.20 ± 0.16
20	0.34 ± 0.01	1.12 ± 0.02	0.16± 0.23	0.48 ± 0.23
30	0.46 ± 0.01	1.79 ± 0.04	0.32± 0.01	1.48 ± 0.19
40	0.72 ± 0.00	2.90 ± 0.14	0.52± 0.16	1.73 ± 0.08
50	1.01 ± 0.13	4.03 ± 0.28	0.66± 0.05	2.50 ± 0.30

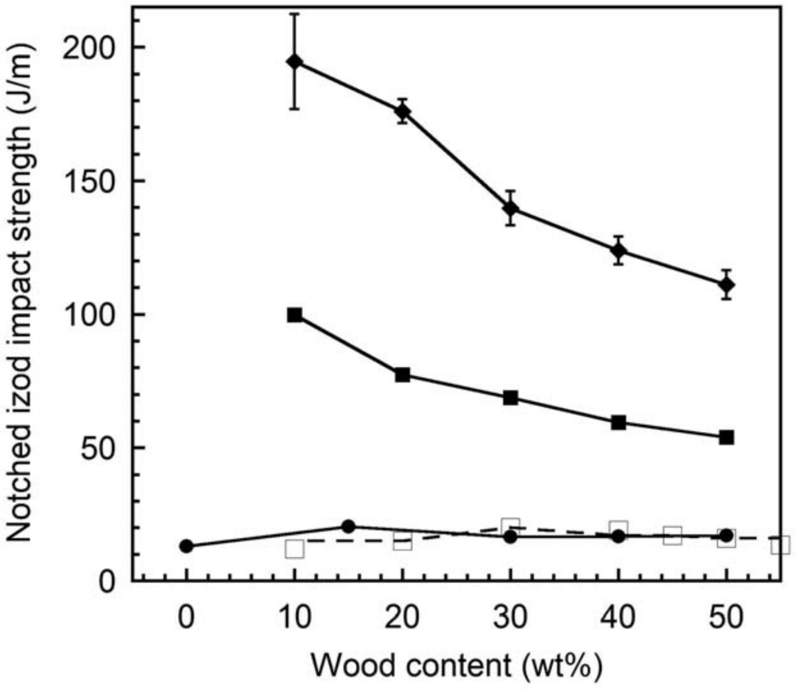

Figure 1: Impact strength of wood composites at various fiber contents: (↲) PVC/ASA/coconut fiber composites, ( ) PP/coconut fiber composites, (■) PVC/ABS/wood composites, (≤) PP/pulp fiber composites.
150x133mm (300 x 300 DPI)

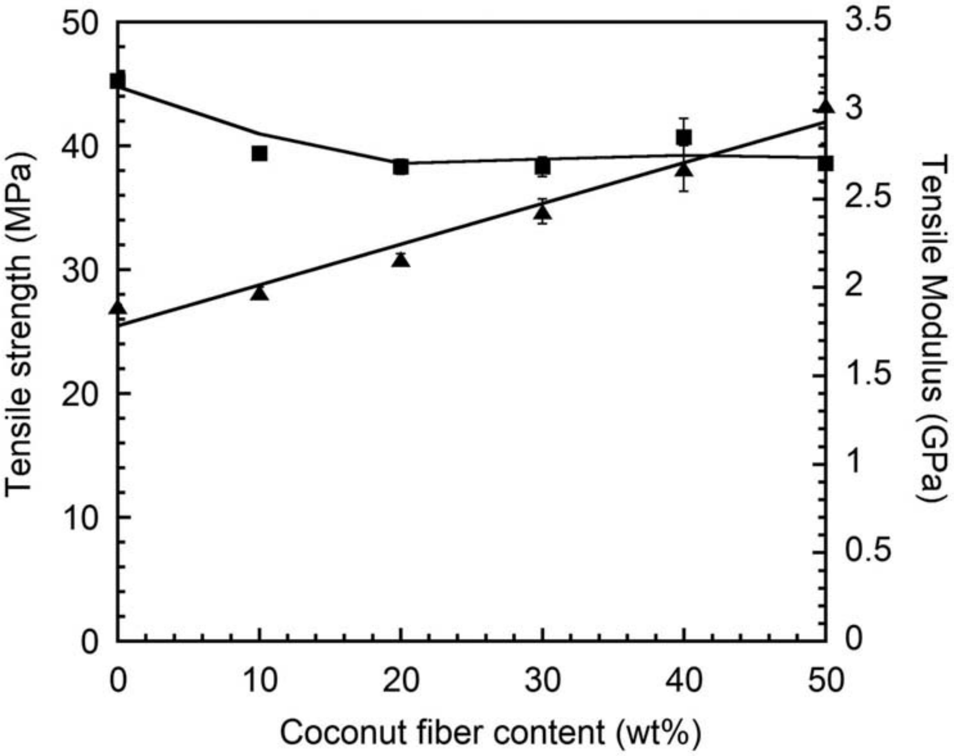

Figure 2: Tensile properties of PVC/ASA/wood composites at various coconut fiber contents: (■) tensile strength, (▲) tensile modulus.
150x118mm (300 x 300 DPI)

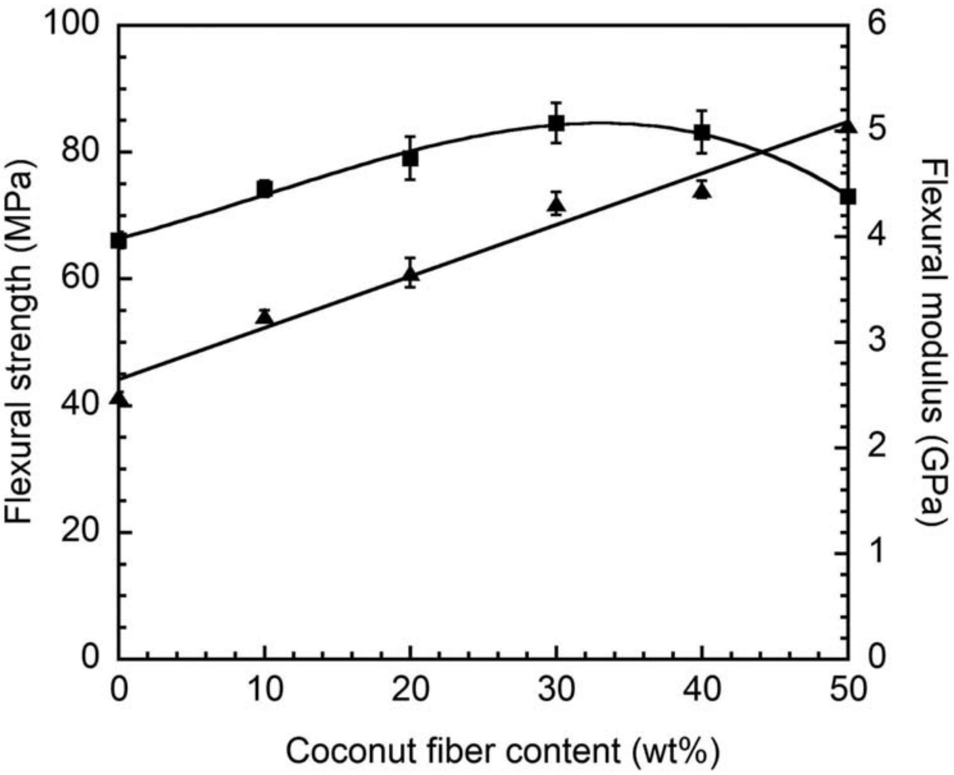

Figure 3: Flexural properties of PVC/ASA/wood composites at various coconut fiber contents: (■) flexural strength, (▲) flexural modulus.
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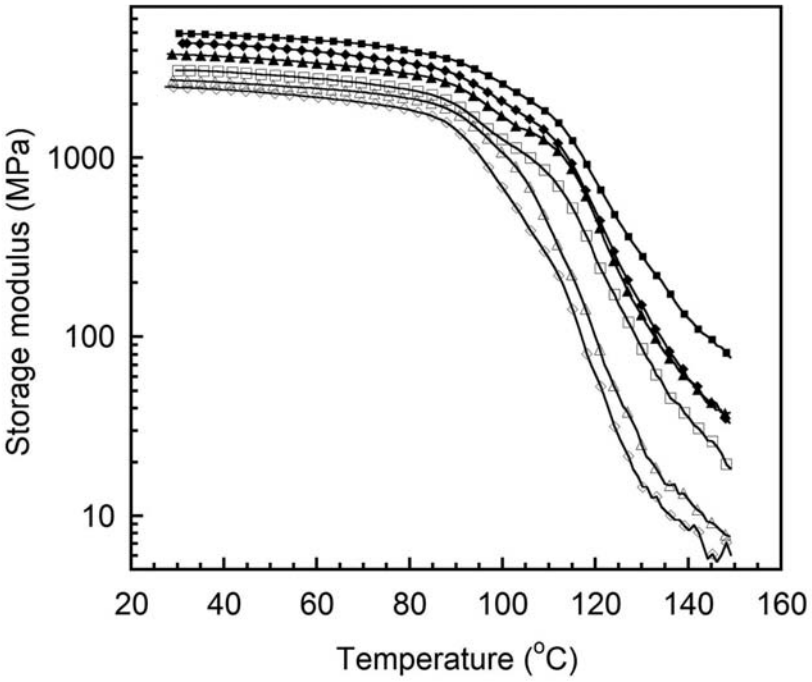

Figure 4: Storage modulus of PVC/ASA/wood composites at various coconut fiber contents: (↓) 0%, (ρ) 10%, (≤) 20%, (π) 30%, (↵) 40%, (′) 50%.

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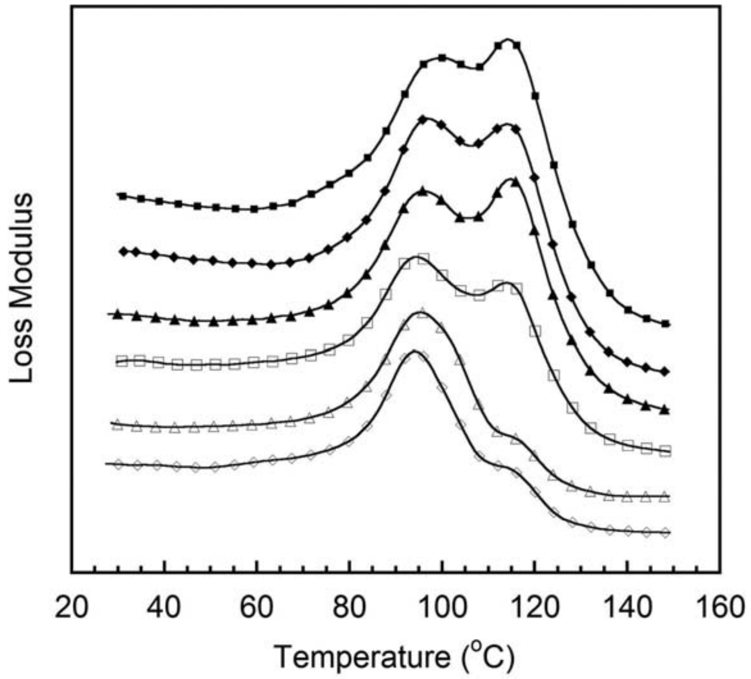

Figure 5: Loss modulus of PVC/ASA/wood composites at various coconut fiber contents: (↓) 0%, (ρ) 10%, (≤) 20%, (π) 30%, (↵) 40%, (′) 50%.

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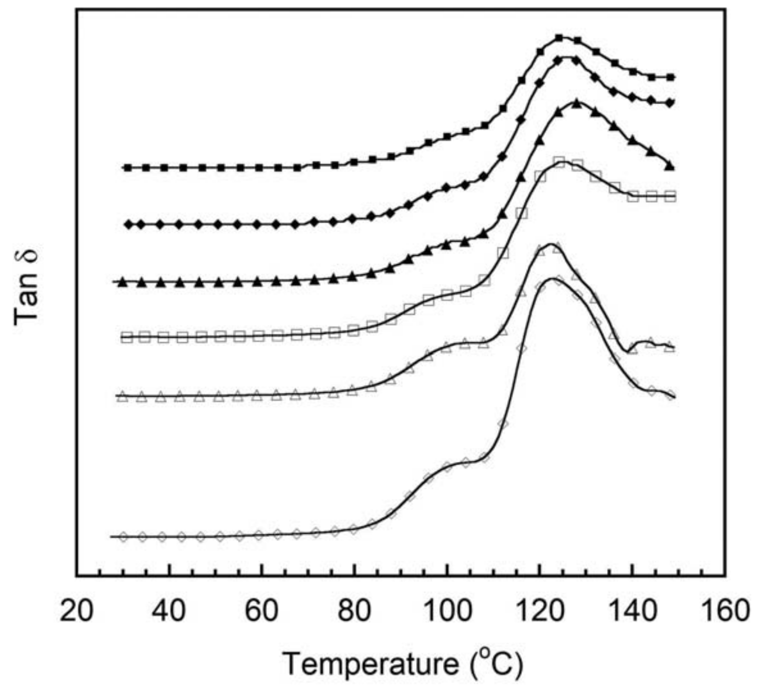

Figure 6: Loss tangent of PVC/ASA/wood composites at various coconut fiber contents: (↓) 0%, (ρ) 10%, (≤) 20%, (π) 30%, (↲) 40%, (′) 50%.

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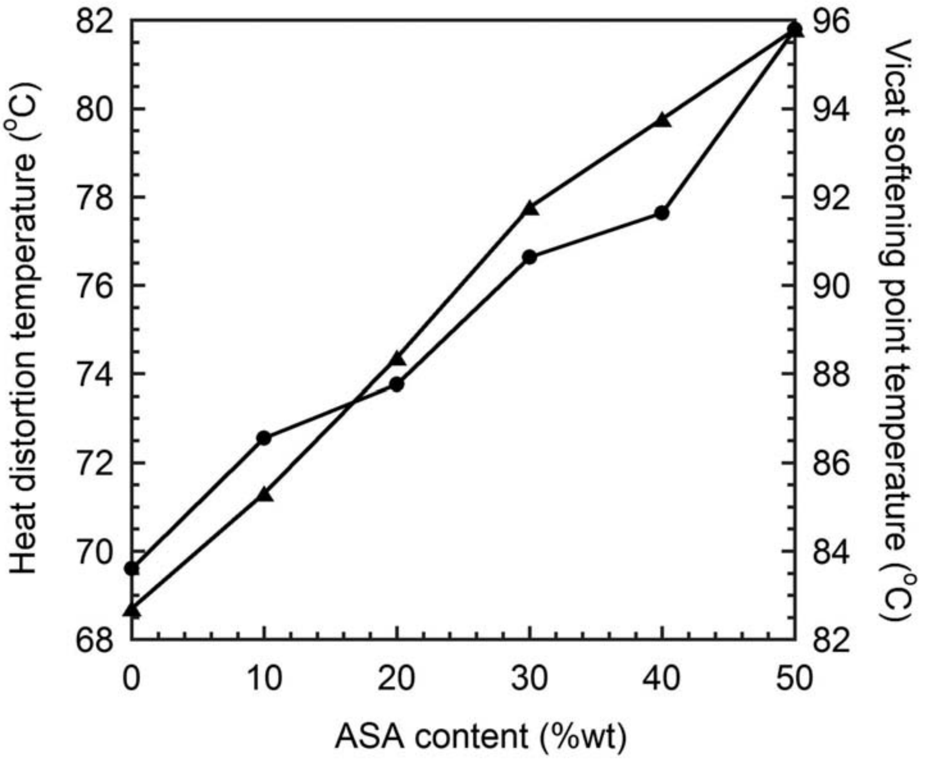

Figure 7: Heat distortion temperature and vicat softening temperature of PVC/ASA/wood composites at various coconut fiber contents: ( ) heat distortion temperature (π) vicat softening temperature.
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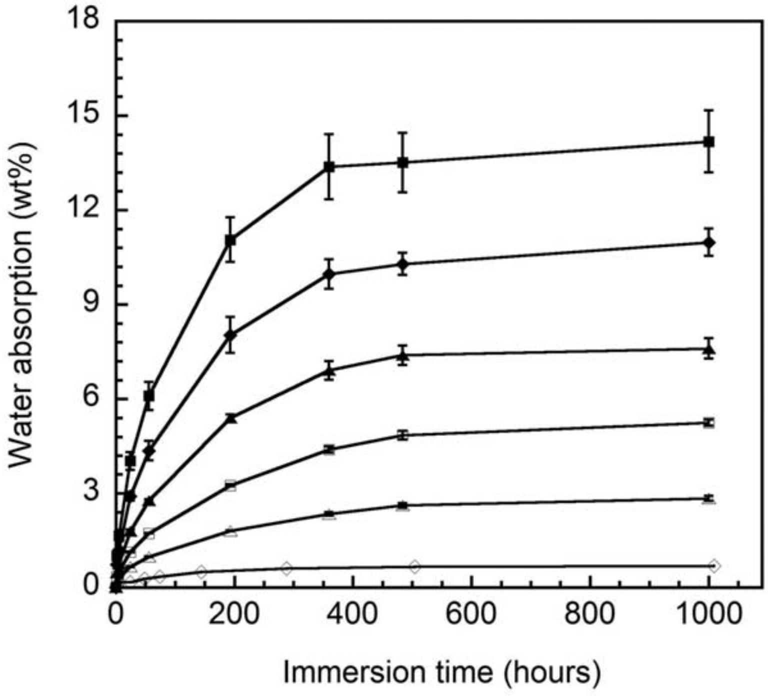

Figure 8: Water absorption of PVC/ASA/wood composites at various coconut fiber contents: (↓) 0%, (ρ) 10%, (≤) 20%, (π) 30%, (↲) 40%, (′) 50%.
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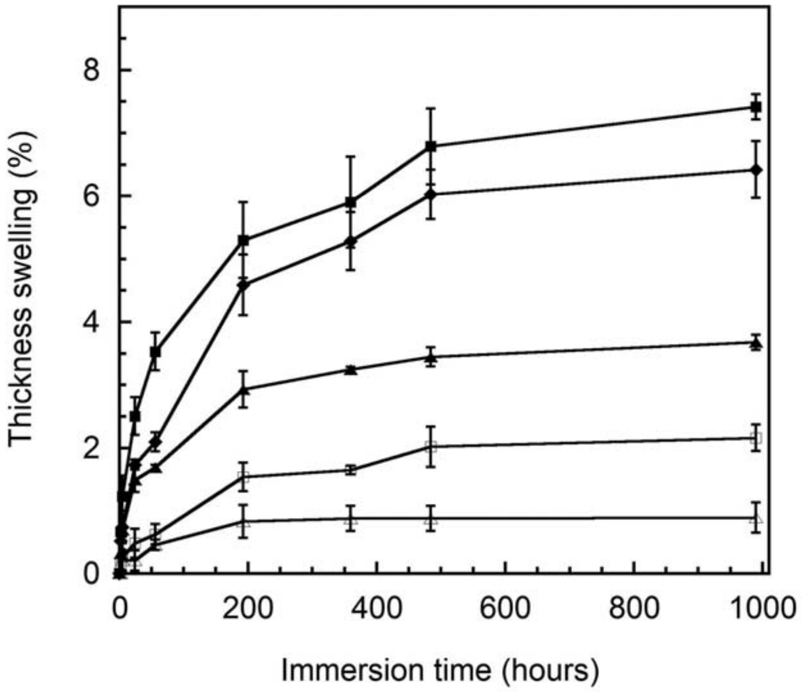

Figure 9: Thickness swelling of PVC/ASA/wood composites at various coconut fiber contents: ( ) 0%, ( ) 10%, ( ) 20%, ( ) 30%, ( ) 40%, ( ) 50%.
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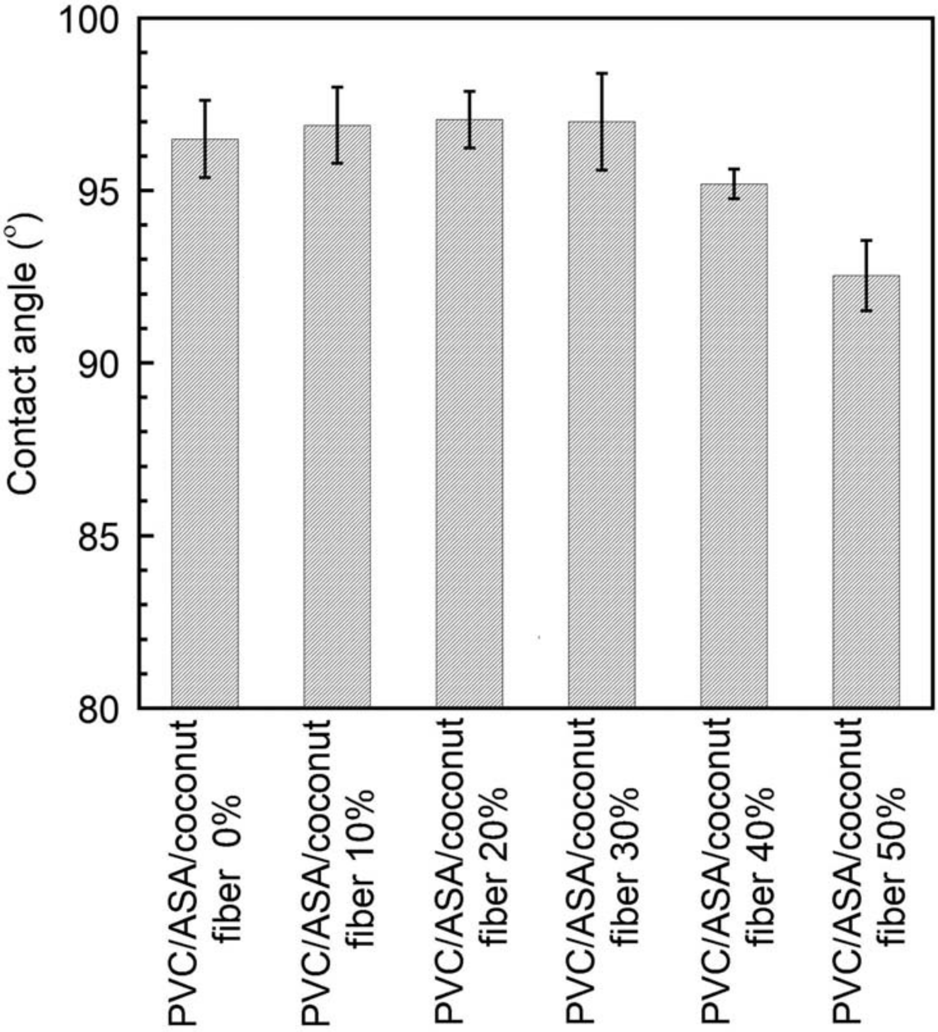

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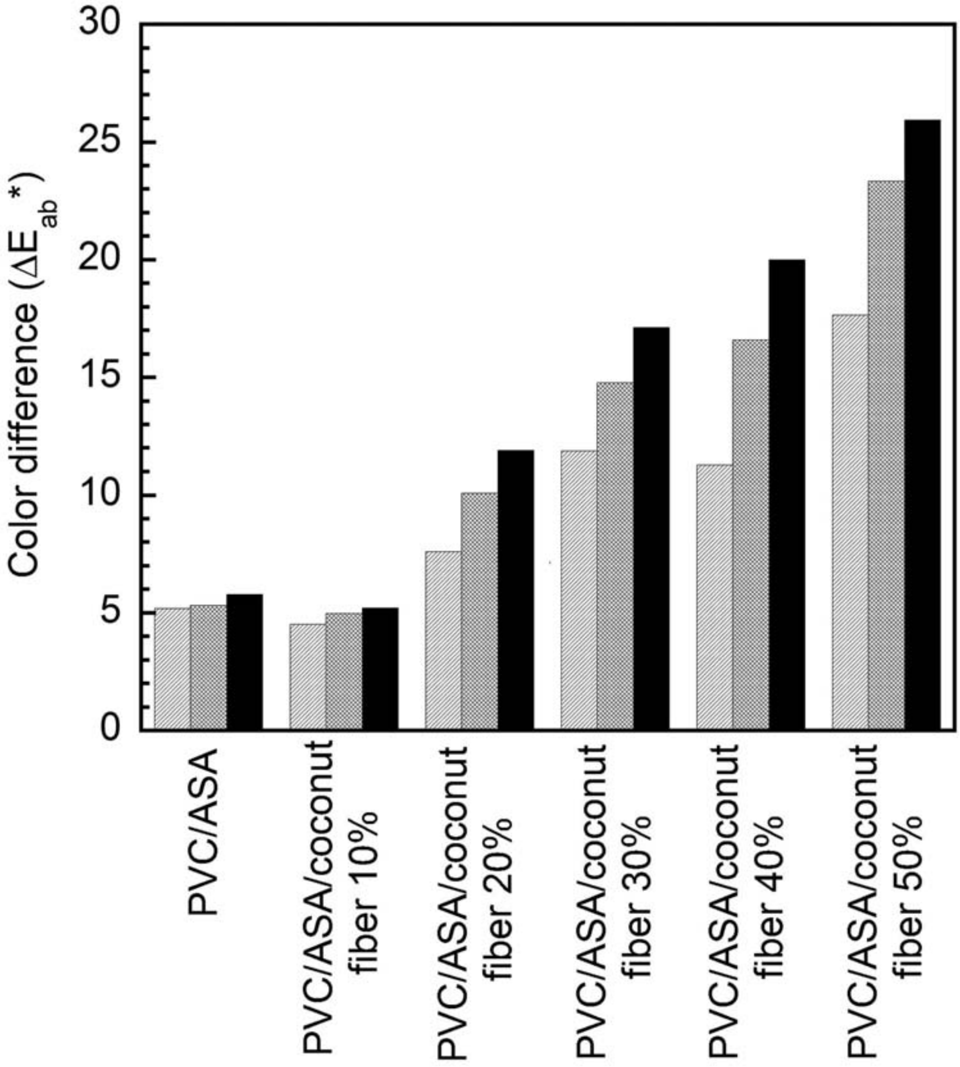

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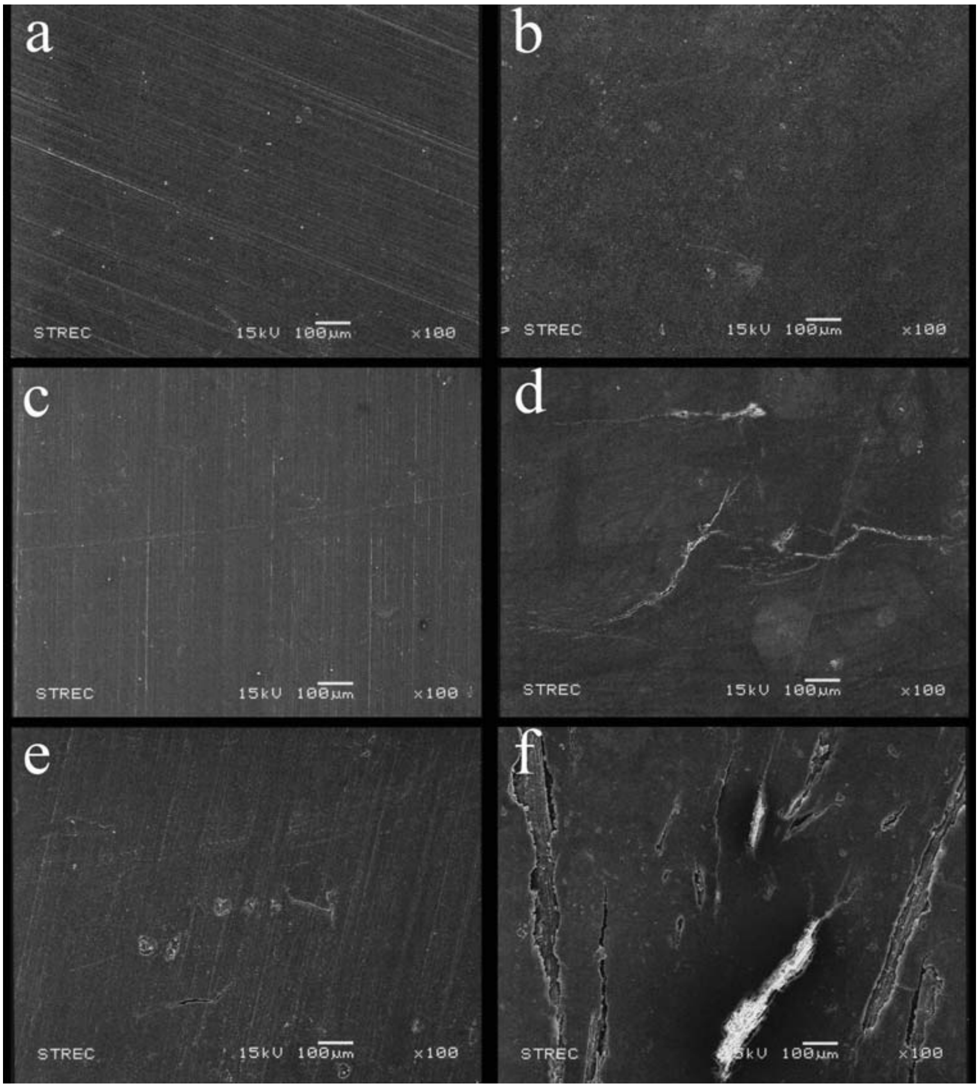

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Thermal and Mechanical Characteristics of PVC/ABS Blends

Dolhathai Atthakorn[1], **Siriporn Dumrongsakkul**[1], **Duangporn Saramas**[2],
Sarawut Rimdusit[1,*]
[1]Polymer Engineering Laboratory, Department of Chemical Engineering, Faculty of Engineering,
Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand.Tel.: 02-218-6443,
*Fax: 02-218-6877, *E-mail address: sarawut.r@chula.ac.th*
[2] Vinythai Public Company Limited, 14th Floor, Green Tower, 3656/41 Rama IV Road, Klongtoey,
Bangkok 10110, Thailand.

The purpose of this study is to focus on the effect of ABS content on thermal and mechanical properties of PVC/ABS blends. The ABS content in the blend was varied from 10-50%. The thermomechanical properties were studied by a dynamic mechanical analyzer (DMA). An incorporation of ABS improves thermal stability to PVC. It can help PVC to maintain its modulus at elevated temperature. The two values of T_g's of the PVC/ABS blends from DSC were observed. PVC showed T_g at approximately 80°C whereas the higher T_g of ABS appeared in a range of 100-105°C. The two values of T_g tended to shift toward each other. This behavior confirms the partially miscible nature of the blends.

1. Introduction

PVC is an interesting polymer which can be modified to obtain various kinds of products. Polymer blends can combine attractive properties of several polymers into one and can improve deficient characteristics of the other polymer. ABS is one of the copolymers which is composed of three building blocks containing polybutadiene phase and SAN phase. The latter gives compatibility with PVC [1]. The copolymer possesses excellent toughness, good thermal stability (high T_g), and ease of processing [2]. An incorporation of ABS in a composition range of 20-40% by weight with PC was reported to show compatibility with PC and significantly improve flow behavior and impact property of the PC [3]. The aim of this work was to investigate the effect of ABS on thermal and thermomechanical properties of its blends with PVC.

2. Methodology

The polymer used in this study was PVC, grade Siamvic 258RB (K-value = 58). The PVC additives used were Kane Ace 20 as processing aid, SAK-WP08-NP as heat stabiliser, and calcium stearate as external lubricant. PVC resin and those additives were kindly supported by Vinythai Public Co.,Ltd., Thailand, and Loixol P1141, an internal lubricant, was supported by Siam Chemicals Solutions Co., Ltd. ABS, grade SP200, was supplied by IRPC Public Co., Ltd. The compositions of ABS in the blends were 0, 10, 20, 30, 40, 50 and 100% by weight. PVC dryblend was mixed with the additives in a high speed mixer. The PVC/ABS blend was prepared by two-roll mills at 150ºC to yield a homogeneous mixture. The obtained compounded sheets were then compression-molded at 170°C and pressure of about 150 bar for 4 min. The compression-molded sheets were then cut into test pieces for further property evaluations.

Thermal characteristics of specimens were examined using a dynamic mechanical analyzer (NETZSH, model DMA242). The dimension of each specimen was 50 mm in length, 10 mm in width, and 2 mm in thickness. The test was performed under three point bending mode in a temperature range of 30 to 150°C using a heating rate of 2°C/min. The test amplitude and frequency used were 30 μm and 1 Hz, respectively. Nitrogen gas flow rate was maintained at 80 ml/min. Glass transition temperature of each sample was obtained from the peak of the loss modulus or tan δ curve.

Differential scanning calorimetry (DSC) was also used to examine T_g (glass transition temperature) and some thermal events of PVC and its blend with ABS. The sample weight was approximately 7-8 mg. The temperature was equilibrated at 30°C and the samples were heated from 30 to 150°C with the heating rate of 10°C/min. Nitrogen gas flow rate was maintained at 50 ml/min.

3. Results and Discussion

Dynamic Mechanical Analysis (DMA)

Fig. 1 illustrates the storage modulus values of PVC, ABS and their blends revealing obviously superior thermal stability of ABS to PVC. With increasing fraction of ABS in the blends, the lower room temperature storage modulus was obtained. In addition, the temperature, which exhibited the sharply decrease of the storage modulus, was observed to shift to higher values. Therefore, blending ABS into PVC can enhance thermal stability of the obtained mixtures. Storage modulus values at room temperature of PVC and ABS were about 3 and 2.3 GPa, respectively. For the blends, the storage modulus values were ranging from 2.5-2.8 GPa and increased by the PVC content.

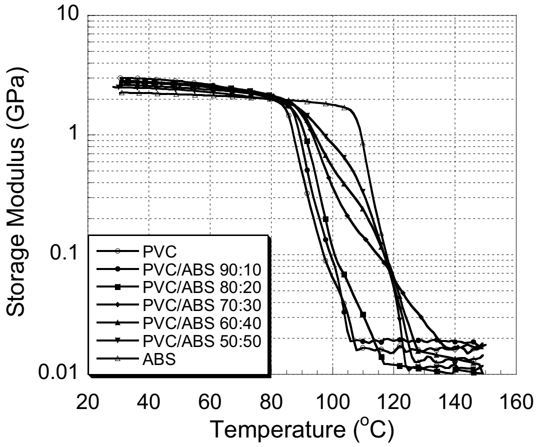

Figure 1 Storage modulus of PVC/ABS blends.

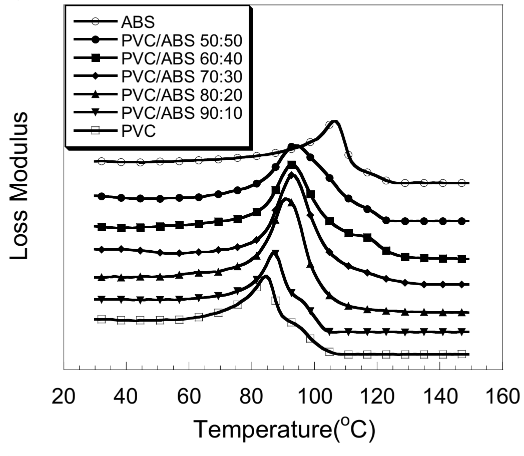

Figure 2 Loss modulus of PVC/ABS blends.

Fig. 2 exhibits T_g from loss modulus of the PVC, ABS, and their blends. T_g's of the blends were found to shift to higher temperature with the content of ABS in the blend as ABS possessed greater T_g than the PVC i.e., 104°C vs 85°C. The relatively broad single peak of T_g in the blends also suggested the highly compatible nature of the PVC and the ABS.

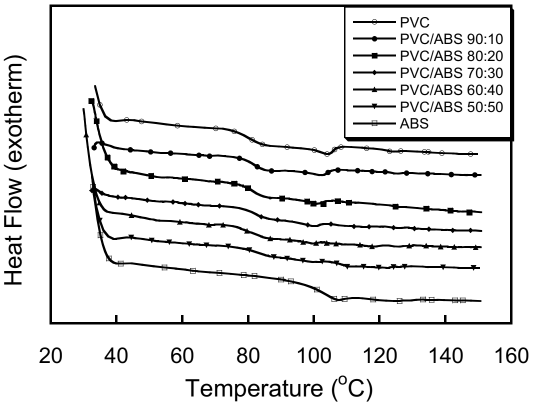

Figure 3 DSC curves at varied PVC/ABS blends.

Differential Scanning Calorimetry (DSC)

Thermal properties of PVC, ABS and PVC/ABS blends were also characterized by DSC. From Figure 3, PVC showed T_g at about 80°C whereas the higher T_g of ABS appeared in the range of 100-105°C and they were in good agreement with the DMA results. When increasing fraction of ABS, T_g of PVC phase is shifted to higher whereas ABS's is shifted to lower. This indicates that the PVC/ABS blends were partially miscible.

4. Conclusions and benefit for Thailand

Storage moduli of PVC/ABS blends were found to be lowered and the T_g of PVC were higher by the presence of the ABS. The shifting of the two T_g s of PVC and ABS in the blends suggested partially miscible nature of their blends. This PVC wood product is developed under the requirement of Vinythai PLC., a large PVC producer in Thailand.

5. Acknowledgements

The research grant of the Thailand Research Fund, Grant Number IUG52-Assoc. Prof. Sarawut Rimdusit and Vinythai PLC.

6. References

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IMPACT PROPERTY ENHANCEMENT OF PVC USING ABS

Dolhathai Atthakorn[1], Siriporn Dumrongsakkul[1], Duangporn Saramas[2], Sarawut Rimdusit[1,*]
[1]Polymer Engineering Laboratory, Department of Chemical Engineering, Faculty of Engineering,
Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand.
[2]Vinythai Public Co.,Ltd., 14th floor, Green tower, 3656/41 Rama IV Road,
Klongtoey, Bangkok 10110, Thailand.
*Corresponding Author E-mail: sarawut.r@chula.ac.th

Abstract: In this research, an incorporation of acrylonitrile-butadiene-styrene (ABS) into poly(vinylchloride) (PVC) for impact property enhancement is investigated. From the experimental results, when the composition of ABS is approximately 50% by weight, the obtained polymer blends showed a synergistic behavior in their impact properties i.e. the blends showed impact strength greater than both PVC and ABS. Furthermore, the glass transition temperature of PVC was found to shift toward higher temperatures possibly due to the partially miscible nature of the PVC and ABS.

1. Introduction: PVC is one of the most versatile polymers which can be easily modified and also has wide variety of products. PVC has excellent dimensional stability, outstanding resistance to weathering, fungi, water and alcohols, good resistance to acid, alkali, fats and petroleum hydrocarbons, good dielectric properties and inherently fire resistance [1]. However, the nature of the polymer is rigid and hard so it needs some modifications for high impact applications. Polymer blends can combine attractive properties of several polymers or can improve some deficient characteristics of the polymer [2]. PVC modification by polymer blending is one practical and effective measures to solve rigidity problem of PVC. One of the most interesting impact modifier for PVC and several engineering polymers is ABS, which is a copolymer of acrylonitrile, butadiene and styrene. ABS is one of copolymers containing elastomeric phase, used to enhance the impact strength of PVC. It has excellent toughness, good thermal stability (high T_g), and easy to process [3]. Moreover, an incorporation of ABS in composition range of 20-40% by weight with PC had been reported to significantly improve flow behavior and impact property of PC [4]. Some previous studies had also found that the copolymers of SAN containing between 11.5 and 26% acrylonitrile showed some degree of miscible with PVC [5].

2. Methodology: The polymer matrix used in this study was PVC, grade Siamvic 258RB (K-value = 58). The PVC additives used were Kane Ace 20 as processing aid, SAK-WP08-NP as heat stabiliser, and calcium stearate as internal lubricant. PVC resin and those additives were kindly supported by Vinythai Public Co.,Ltd., Thailand, and Loixol P1141 , external lubricant, were supported by Siam Chemicals Solutions Co.,Ltd. 3 Grades of ABS were supplied by IRPC Public Co.,Ltd. The mass ratios between PVC and ABS was varied at 100:0, 50:50 and 0:100. PVC dryblend was mixed with the additives in a high speed mixer. The PVC/ABS blends were prepared by two-roll mills at temperature of 175ºC to yield a homogeneous mixture. The obtained compounded sheets were then compression-molded at the temperature of 170°C and pressure of about 150 bar for 4 min. The dimension of the compression-molded sheet is 120 mm×120 mm×3.2 mm. The compression-molded sheets were then cut into test pieces for further property evaluations.

Notched izod impact strength of the specimens was determined by impact tester (Yasuda) according to ASTM D256. The dimension of the specimen was 12.7 mm×60 mm×3.2 mm.

Differential scanning calorimetry (DSC) was also used to examine T_g (glass transition temperature) and some thermal events of PVC and its blend with ABS. The sample weight was approximately 7-8 mg. The temperature was equilibrated at 30°C and the samples were heated from 30 to 160°C with the heating rate of 10°C/min. Nitrogen gas flow rate was maintained at 50 ml/min.

3. Results, Discussion and Conclusions:

Notched Izod Impact Strength

The effect of types of ABS on impact strength of PVC was evaluated by a Yasuda impact tester for three different compositions i.e. PVC/ABS1 100:0, 50:50 and 0:100. Fig. 1

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*Corresponding author; sarawut.r@chula.ac.th shows a sign of synergistic effect on notched izod impact strength from an in corporation of ABS into PVC, particularly for ABS of type ABS2 and ABS3 at 50% by weight. This may be due to the possibility of partial miscibility of those ABS and the PVC. Despite similarity of the impact strength of neat ABS1 and ABS2, when they both were blended with PVC, they gave different results. The blend of PVC/ABS1 gave some positive deviation in its impact property but with the least enhancement in impact strength as compared to PVC/ABS2 and PVC/ABS3. The blend of PVC/ABS2 exhibited greater enhancement of impact strength than PVC/ABS3. Both types of ABS have the same level of butadiene but different AN content in SAN which may attribute to different compatibility with PVC and impact strength value.

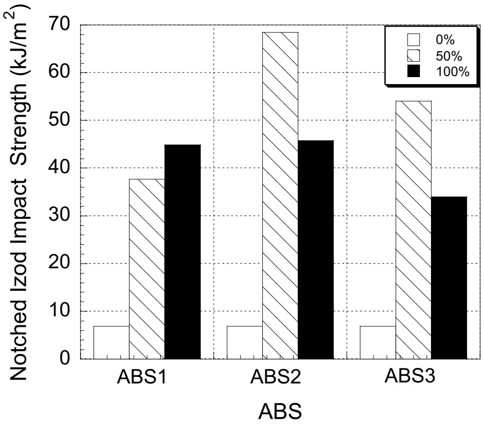

Figure 1 Notched Izod impact strength of various types of PVC/ABS blends.

Differential Scanning Calorimetry (DSC)

Thermal properties of PVC, ABS and PVC/ABS blends were also characterized by differential scanning calorimetry (DSC). From Figure 2, PVC showed T_g at about 80°C whereas the higher T_g of ABS appeared in the range of 100-105°C. The two values of T_g's the PVC/ABS blends were observed to confirm the partially miscible nature of the blends.

4. Conclusions:

Synergistic effect on impact strength of PVC/ABS blends with the maximum value using ABS2 was observed. Though, the neat ABS1 and ABS2 possessed the same level of impact strength, the different impact strength enhancement was obtained when blended with PVC. Thermal characteristics of PVC/ABS blends from DSC showed two values of T_g's suggesting partially miscible nature of the blends.

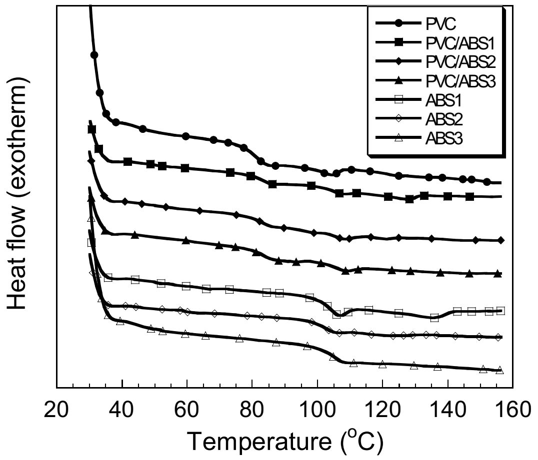

Figure 2 Differential scanning calorimetry of PVC, ABS and PVC/ABS blends:

(●) PVC (■) PVC/ABS1 (♦) PVC/ABS2 (▲) PVC/ABS3 (□) ABS1 (◇) ABS2 (△) ABS3.

5. References:

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Keywords: PVC/ABS, Polymer blends, Impact strength, Partially miscible blend, Glass transition temperature, Synergy.

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*Corresponding author; sarawut.r@chula.ac.th

Thermomechanical Characterization of PVC/ASA Blends

Patima Wongmanit[1], Siriporn Damrongsakkul[1], Duangporn Saramas[2], Sarawut Rimdusit[1,*]

[1]Polymer Engineering Laboratory, Department of Chemical Engineering, Faculty of Engineering,
Chulalongkorn University, Pathumwan, Bangkok 10330
Phone 0-2218-6443, Fax. 0-2218-6877, *E-mail: sarawut.r@chula.ac.th
[2]Vinythai Public Company Limited, 14th Floor, Green Tower, 3656/41 Rama IV Road, Klongtoey, Bangkok 10110

Abstract

The purpose of this research is to investigate the effect of ASA content on thermal properties of PVC/ASA blends. ASA is a copolymer system with good thermal stability, high impact property and outstanding weathering resistance which lack in PVC. The ASA content in the blend was varied from 0-50%. The thermomechanical properties were studied by a dynamic mechanical analyzer (DMA) and deflection temperature under load (Vicat softening point). The values of T_g of these polymer blends were investigated by differential scanning calorimeter (DSC) as well as DMA. The T_gs of the PVC resin and the ASA from DMA experiment showed values at approximately 97°C and 120°C. The blends of the two polymers exhibited two glass transition temperatures corresponded to those of the PVC and the ASA above. The two values of T_g also tended to shift toward each other. This behavior suggested the partially miscible nature of the blend. Finally, an incorporation of ASA to the PVC rendered the blend systems with enhancement in their thermal stability due to the greater thermal stability of the ASA compared to the PVC.

Keywords : PVC/ASA, Polymer blends, Thermomechanical properties, Glass transition temperature.

1. Introduction

Among the most important commercial thermoplastics, PVC occupies almost the head position of construction industry in the world in terms of commercial as well as application point of view. It has a long history of use in a variety of applications due to its versatility, durability, relative low-cost maintenance, and inherent fire resistance. Though PVC is a widely used material that can appropriately meet the required performance for construction materials, PVC also has some shortcomings. The main disadvantage of PVC is its low heat resistance. During processing or under outdoor conditions, PVC degrades as it is exposed to high temperatures, high mechanical stresses, or ultraviolet light, and in the presence of oxygen. Degradation of PVC may occur and cause discoloration, loss of mechanical properties, and a reduction in chemical resistance [1].

In order to improve thermal resistance of PVC, rubber-containing materials (i.e., ABS or ASA for high-temperature applications) are introduced to neat PVC. The obtained PVC/ABS blend not only exhibits good thermal stability, but also exhibits significantly improved notched Izod impact strength over PVC. ASA is one of the copolymers which are composed of three building blocks containing SAN phase and saturated polyacrylate phase which is relatively stable to sun light. ASA has a similar ability in improving impact properties like ABS with better weather ability, chemical resistance and color retention than ABS [2]. The aim of this research was to investigate the effect of ASA on thermomechanical properties of its blends with PVC.

2. Experimental Methods

2.1 Materials

Suspension grade PVC, Siamvic 258RB, with *K*-value 58 and degree of polymerization about 680. The additives used in PVC compound were Kane Ace 20 as processing aid, SAK-WP08-NP as heat stabilizer, and calcium stearate as internal lubricant. PVC resin and those additives were kindly supported by Vinythai Public Co., Ltd., Thailand, Loixol P1141, internal lubricant, was supplied by Siam Chemicals Solutions Co., Ltd. Extrusion grade ASA resin, KIBILAC PW-997S, with melt flow rate 4g/10min was purchased from Global Connections Co., Ltd., Thailand.

2.2 Blend Preparation

The compositions of ASA in the blends were 0, 10, 20, 30, 40, 50 and 100% by weight. Pure PVC and ASA were used as control samples. PVC dry blend was mixed with the additives in a high speed mixer. Then mixtures of PVC and ASA were first prepared by two-roll mills at temperature of 170ºC to yield homogeneous mixtures. The blended materials were prepared by compression-molding at temperature of 170°C and pressure of 150 bars for 4 min. The compression-molded sheets were then cut into test pieces for further property evaluations.

2.3 Dynamic Mechanical Analysis (DMA)

The thermomechanical characteristic of the materials were examined using dynamic mechanical analyzer (NETZSH, model DMA242) over a temperature range from 30°C to 150°C with a 2°C/min heating rate. The test amplitude and frequency used were 30 µm and 1 Hz, respectively. Rectangular polymer samples with a 50 mm in length, 10 mm in width, and 2 mm in thickness were tested in the three point bending mode. Nitrogen gas flow rate was maintained at 80 ml/min. Storage modulus and loss modulus were measured as a function of temperature.

2.4. Differential Scanning Calorimetry (DSC)

DSC measurement was also used to examine glass transition temperature and some thermal behavior of PVC and its blend with ASA. The sample weight was approximately 7-8 mg. The temperature was equilibrated at 30°C, and then DSC curves of samples under nitrogen flow rate at 50 ml/min were recorded at a heating rate of 10◦C/min between 30°C and 150°C.

2.5 Heat Deflection Temperature and Vicat Softening Point

HDT and Vicat represented an upper limiting point at which a plastic is expected to maintain its shape under load. In the Vicat softening point test the specimen was placed at the testing apparatus in a silicon oil bath at 30°C. A load of 50N was applied to the specimen and then the sample was heated at rate of 50°C/h until the needle penetrated 1 mm following ASTM D1525. The temperature at which the needle has penetrated to a depth of 1 ± 0.01 mm was recorded as the Vicat softening temperature. In the heat distortion temperature test the specimen was placed under the deformation measuring device. The specimen was then immersed in silicone oil with a mean of raising the temperature at 120°C/h or 2 ± 0.2°C/min until the midpoint of the beam deflected 0.25 mm following ASTM D648. This temperature was recorded as the deflection temperature under flexural load.

3. Results and Discussion

3.1 Dynamic Mechanical Analysis (DMA)

In this investigation, the thermal transition and miscibility of PVC and ASA blends were investigated. The thermal transition in polymer is described as the expansion of free volume. The T_g or glass transition temperature appears when the free volume of the chain greatly increases and large segment of the chain start moving [3].

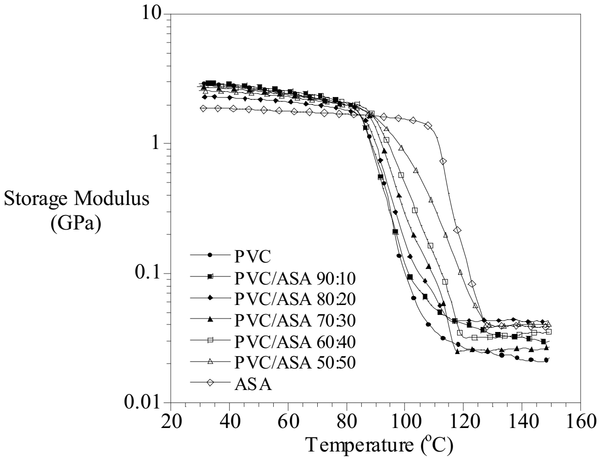

Fig. 1 Storage modulus of PVC/ASA blends.

Storage modulus (E'), tan δ, and loss modulus (E") of PVC, ASA and their blends are shown in Fig. 1-3.

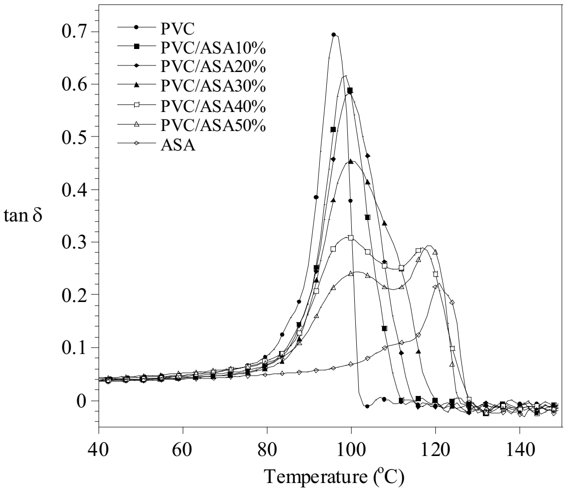

Fig. 2 tan δ of PVC/ASA blends.

Fig. 1 shows the storage modulus curves for PVC, ASA and the binary PVC/ASA blends. At room temperature, with increasing ASA content, the storage modulus of the blend decreased slightly. As heating continued, the sample with large amounts of ASA showed the higher storage modulus at the transition zone and the glass transition temperature was higher than that of the neat PVC due to the superior thermal stability of ASA. Therefore, blending ASA into PVC can enhance thermal stability of the obtained mixtures.

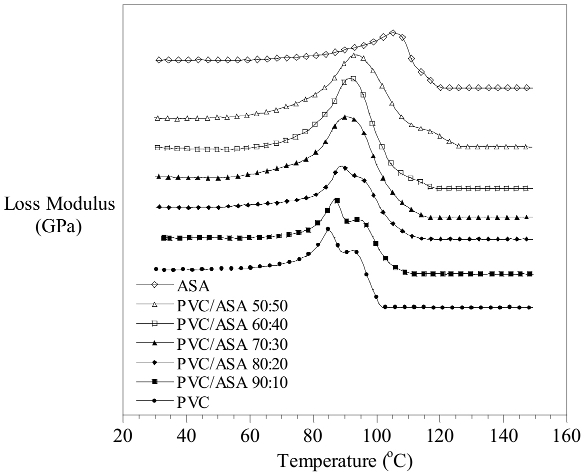

Fig. 3 Loss modulus of PVC/ASA blends.

DMA was also used to investigate the miscibility of the blends. Generally for an immiscible blend, the tan δ curves show the two peaks corresponding to the T_gs of individual components. For a highly miscible blend, the curves show only a single peak in between the T_gs of the component polymers. Whereas broadening of transition occurs in the case of partially miscible system [4]. Fig. 2 shows the tan δ curves for the PVC, ASA and their blends. As shown by a tan δ peak in the curve, the T_gs of the PVC and ASA are at 97°C and 120°C respectively. The tan δ curve for the blend showed a single peak between the two homopolymers, as ASA content was less than 30wt%. With increasing ASA content, the broader transition curve was observed. When the ASA content was over 40%, the tan δ curve showed two peaks of glass transition temperatures. These behaviors indicated partial miscibility of this blend [5].

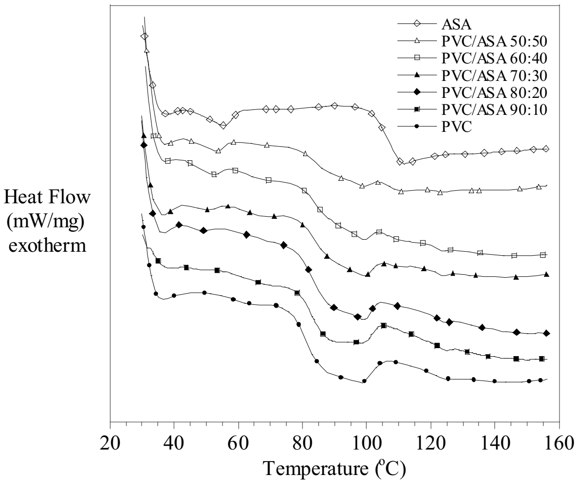

Fig. 4 DSC curves at varied PVC/ASA blends.

3.2 Differential Scanning Calorimetry (DSC)

Thermal properties of PVC, ASA and PVC/ASA blends were also characterized by DSC. From Fig. 4, PVC showed T_g at about 80°C whereas the higher T_g of ASA appeared at about 106°C. As increasing ASA content, T_g of PVC phase shifted to higher temperature whereas that of ASA shifted to lower value. This confirmed that the PVC/ASA blends were partially miscible.

3.3 Heat Deflection Temperature and Vicat Softening Point

In this study, thermal properties of PVC, ASA and their blends were measured and shown in Fig.5. The heat distortion temperature (HDT) of the neat PVC and ASA were determined to be 64°C and 77°C, respectively. In terms of Vicat softening temperature, the Vicat softening temperature (Vicat) of the neat PVC was approximately 77°C while ASA was up to 91°C. Blends had intermediate HDT and Vicat values and the relationship was linear to the amount of ASA added. The results suggested improved thermal stability of the blend with the presence of ASA in the PVC.

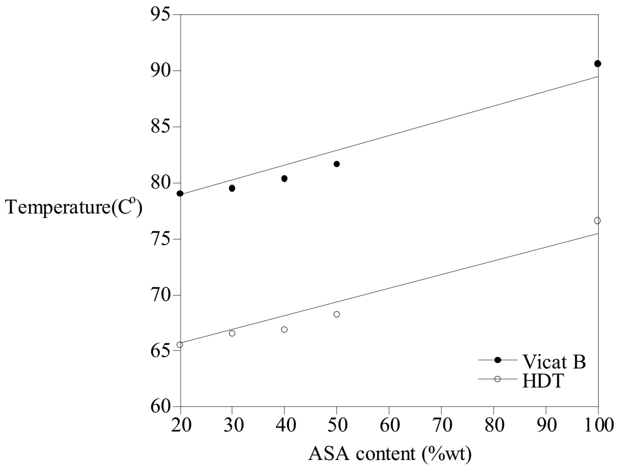

Fig. 5 HDT/Vicat of PVC/ASA blends.

4. Conclusion

Thermal properties of PVC/ASA blends were studied. The DMA and DSC results showed the shifting of the two glass transition temperatures of PVC and ASA in the blends towards each other suggesting partially miscible blends obtained. The HDT and Vicat results showed a systematic increase in their values with increasing ASA contents. This suggested the enhancement of thermal stability of PVC using ASA modifier.

5. Acknowledgments

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Influence of Blend Composition on the Mechanical Properties of Poly(vinyl chloride)/Acrylonitrile Styrene Acrylate Blends

Patima Wongmanit[1], Siriporn Dumrongsakkul[1], Duangporn Saramas[2], Sarawut Rimdusit[1]*

[1]*Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand.*

[2]*Vinythai Public Co.,Ltd., 14th floor, Green tower, 3656/41 Rama IV Road, Klongtoey, Bangkok 10110, Thailand.*

*Tel: +66-2-218-6862, *E-mail address: sarawut.r@chula.ac.th*

ABSTRACT

Poly(vinyl chloride)/Acrylonitrile styrene acrylate (PVC/ASA) blends for high impact applications were prepared by two-roll mills and compression molder at temperature of 170 ºC. The ASA content in the blends was varied from 10-50%. The effect of ASA content on mechanical properties, including flexural, tensile, and impact properties were investigated. From the experimental results, when adding ASA to the blends, the impact strength of the blend samples increased drastically at the ASA content of about 30-40% by weight. The blends also showed potential use as high impact plastic products for outdoor applications due to the outstanding weathering ability of the ASA.

Keywords: PVC/ASA, Partially miscible blend, Percolation effect, Brittle-ductile transition

1. Introduction

Poly(vinyl chloride) is one of the most useful and widely used thermoplastics. It possesses excellent dimensional stability, good resistance to acid, alkali and petroleum hydrocarbons and inherently fire resistance [1]. However, PVC is brittle at high deformation rate and sensitive to notch [2]. Therefore, PVC is usually blended with other polymers to improve impact strength such as acrylonitrile-butadiene-styrene (ABS) [3]. However, in the above-mentioned polymer blends, the ageing resistance is poor if the modifiers are polybutadiene (PB)-containing copolymers as they contain double bonds in the main chain while PVC itself can become yellowing after long period of sunlight exposure. Acrylonitrile styrene acrylate (ASA) copolymer has similar structure to ABS, but PB rubber core within ABS particles is substituted by saturated polybutylacylate rubber [4]. Since there are no double bonds in polyacrylate, the ageing resistance of ASA/PVC blends is much enhanced.

2. Materials and Methods

Siamvic 258RB with *K*-value 58 was used as a suspension PVC resin in this study. The additives used in PVC compound were Kane Ace 20 as processing aid, SAK-WP08-NP as heat stabilizer, and calcium stearate as internal lubricant. PVC resin and additives were kindly supported by Vinythai Public Co., Ltd., Thailand. Loixol P1141, internal lubricant, was supplied by Siam Chemicals Solutions Co., Ltd. Extrusion grade ASA resin, KIBILAC PW-997S, with melt flow rate 4g/10min was purchased from Global Connections Co., Ltd., Thailand. The compositions of ASA in the blends were 0, 10, 20, 30, 40 and 50% by weight. The mixtures of PVC and ASA were first prepared by two-roll mills at temperature of 170 ºC. The blended sheets were prepared by compression-molding at temperature of 170 °C and pressure of 150 bars for 4 min. The compression-molded sheets were then cut into test pieces for further property evaluations.

3. Results and Discussion

Notched Izod Impact Strength

Figure 1 shows the relationship between notched Izod impact strength as a function of ASA content in PVC/ASA blends. It was found that the impact strength increased slightly when ASA content was less than 30 wt%. As ASA content increase beyond 30 wt%, the remarkable increase

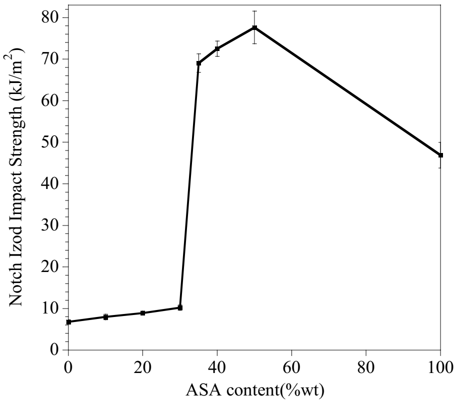

Figure 1: Notched Izod impact strength at various compositions of PVC/ASA blends.

in impact strength was observed. The content which drastic change happened was called the brittle ductile transition. That is brittle fracture mechanism of the blend turned into ductile fracture at this transition. When ASA content was added up to 40 wt%, the critical change in impact strength was negligible. This behavior suggested percolation effect in impact strength of PVC/ASA blend. The percolation effect of brittle-ductile transition in rubber-toughened PVC was also observed by Liu in PVC/nitrile rubber system [5].

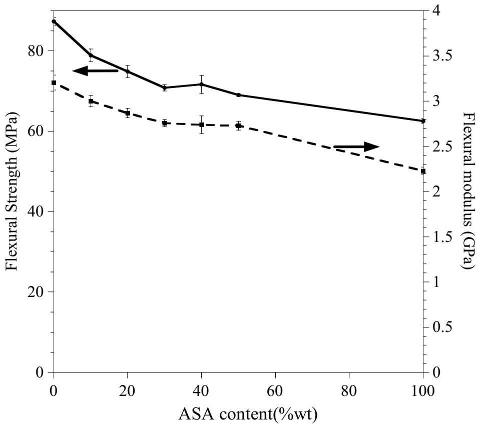

Figure 2: Flexural strength and flexural modulus of PVC/ASA blends.

Flexural Property Investigation

Figure 2 shows flexural strength and flexural modulus of PVC and ASA blends. Flexural strength and modulus were found to decrease systematically as ASA content was increased. However, both flexural strength and modulus further decreased only slightly as ASA content reached 30 wt%.

Tensile Property Evaluation

In Figure 3, tensile strength and tensile modulus were found to decrease as ASA content was increased. These followed the same trends in flexural properties as shown in Figure 2. At ASA content about 40-50 wt%, the blends showed tensile and flexural properties lower than the neat PVC but exhibited significant enhancement in impact property. These blends may therefore be suitable in broadening the range of applications of PVC systems. For a combination of flexural strength, impact resistance, and weather ability, the blends at ASA content of 35-50% may be used as weather roofing materials or a matrix in the manufacture of wood-plastic composites.

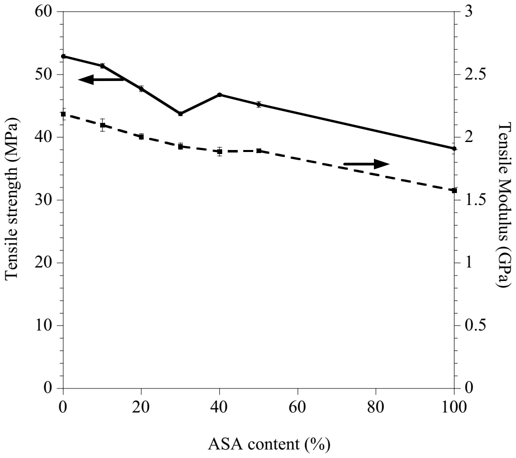

Figure 3: Tensile strength and tensile modulus of PVC/ASA blends.

4.Conclusion

ASA content has a significant effect upon notched Izod impact, flexural, and tensile properties of the obtained PVC/ASA blends. The blends revealed percolation behavior on impact strength with brittle ductile transition zone at about 35 wt% ASA content.

5. Acknowledgement

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