รายงานวิจัยฉบับสมบูรณ์

โครงการ การพัฒนาวัสดุประกอบแต่งสมรรถนะสูงจากระบบเส้นใยคาร์บอนและเบนซอกซาซีนเรซินที่ดัดแปรด้วยสารไดแอนไฮไดรด์

โดย อาจารย์ ดร. จันจิรา จับศิลป์ และคณะ

29 เมษายน 2555

สัญญาเลขที่ MRG5380077

รายงานวิจัยฉบับสมบูรณ์

โครงการ การพัฒนาวัสดุประกอบแต่งสมรรถนะสูงจากระบบเส้นใยคาร์บอนและเบนซอกซาซีนเรซินที่ดัดแปรด้วยสารไดแอนไฮไดรด์

โดย อาจารย์ ดร. จันจิรา จับศิลป์ และคณะ
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์
มหาวิทยาลัยศรีนครินทรวิโรฒ

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

(ความเห็นในรายงานนี้เป็นของผู้วิจัย สกว.ไม่จำเป็นต้องเห็นด้วยเสมอไป)

Acknowledgements

This research is supported by the Thailand Research Fund (TRF)-Commission on Higher Education (CHE), contact grant number MRG5380077 and Matching Fund of Srinakharinwirot University (2010-2012), contact grant number 083/2554, the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission (AM1076A), and 100th Anniversary of Chulalongkorn University Academic Funding through Ratchadapiseksomphot Endowment Fund, CU. Thai Polycarbonate Co., Ltd. (TPCC) for bisphenol A supply is also gratefully acknowledged.

บทคัดย่อ

รหัสโครงการ : MRG5380077

ชื่อโครงการ : การพัฒนาวัสดุประกอบแต่งสมรรถนะสูงจากระบบเส้นใยคาร์บอนและเบนซอกซาซีนเรซินที่ดัดแปรด้วยสารไดแอนไฮไดรด์

ชื่อนักวิจัย : อาจารย์ ดร. จันจิรา จับศิลป์
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ มหาวิทยาลัยศรีนครินทรวิโรฒ
โทรศัพท์ 02-649-5000 ต่อ 22119, 082-793-8809

E-mail Address: chanchira@swu.ac.th

ระยะเวลาโครงการ : 15 มิถุนายน 2553 ถึง 15 มิถุนายน 2555

งานวิจัยนี้ศึกษาผลของปริมาณเส้นใยคาร์บอนต่อสมบัติทางกลและทางความร้อนของวัสดุประกอบแต่งพอลิเบนซอกซาซีนชนิดบีสฟีนอลเอ-อะนีลีน (PBA-a) ดัดแปรด้วยสารไดแอนไฮไดรด์ชนิดไพโรเมลลิทิค (PMDA) รวมทั้งการศึกษาผลของสัดส่วนสารดัดแปร PMDA ต่อสมบัติการติดไฟ สมบัติทางกล และสมบัติทางความร้อนของวัสดุประกอบแต่ง PBA-a:PMDA ที่เสริมแรงด้วยเส้นใยคาร์บอน จากผลการทดสอบ พบว่า วัสดุประกอบแต่งมีความสามารถในการบรรจุเส้นใยคาร์บอนในเมทริกซ์ PBA-a:PMDA เท่ากับ 65% โดยน้ำหนัก สำหรับความสามารถในการทนไฟจะได้ว่า วัสดุประกอบแต่งพอลิเบนซอกซาซีนที่เสริมแรงด้วยเส้นใยคาร์บอนในปริมาณ 65% โดยน้ำหนัก (65wt% CF/PBA-a) มีค่าปริมาณออกซิเจนที่น้อยที่สุดที่ช่วยในการติดไฟ (LOI) เท่ากับ 26.0 ในขณะที่วัสดุประกอบแต่งพอลิเบนซอกซาซีนดัดแปรด้วยสารไอแอนไฮไดรด์ชนิด PMDA ที่เสริมแรงเส้นใยคาร์บอนในปริมาณ 65% โดยน้ำหนัก (65wt% CF/PBA-a:PMDA) มีค่า LOI เพิ่มสูงขึ้นเท่ากับ 49.5 นอกจากนี้วัสดุประกอบแต่ง 65wt% CF/PBA-a:PMDA ที่มีความหนาเพียง 1 มิลลิเมตร สามารถทนการติดไฟระดับสูงสุด คือ V-0 สำหรับค่าอุณหภูมิเปลี่ยนสถานะคล้ายแก้ว (T_g) และค่าสตอเรจมอดูลัส (E') ที่อุณหภูมิ 35^{o}C ของวัสดุประกอบแต่ง 65wt% CF/PBA-a:PMDA มีค่าสูงกว่าเมื่อเปรียบเทียบกับวัสดุประกอบแต่ง 65wt% CF/PBA-a โดยค่า T_g และค่า E' ที่อุณหภูมิ 35^{o}C ของวัสดุประกอบแต่ง 65wt% CF/PBA-a:PMDA มีค่าสูงถึง 237^{o}C และ 46 GPa ตามลำดับ ในขณะที่วัสดุประกอบแต่ง 65wt% CF/PBA-a มีค่า T_g และค่า E' ที่อุณหภูมิ 35^{o}C เท่ากับ 183^{o}C และ 41 GPa ตามลำดับ นอกจากนี้ จากผลการทดสอบความเสถียรภาพทางความร้อน จะได้ว่า ค่าอุณหภูมิการสลายตัวทางความร้อน (T_d) และปริมาณเถ้าที่อุณหภูมิ 800^{o}C ของวัสดุประกอบแต่ง 65wt% CF/PBA-a (405^{o}C และ 75.7% ตามลำดับ) มีค่าเพิ่มขึ้นเมื่อมีการเพิ่มสัดส่วนของสาร PMDA ในพอลิเบนซอกซาซีนเมทริกซ์ ซึ่งทำให้วัสดุประกอบแต่ง 65wt% CF/PBA-a:PMDA มีค่า สูงถึง 498^{o}C และปริมาณเถ้าที่อุณหภูมิ 800^{o}C เท่ากับ 82% ดังนั้นเนื่องด้วยสมบัติการทนการติดไฟ สมบัติทางกลและทางความร้อนที่ดีขึ้นของวัสดุประกอบแต่ง จึงมีศักยภาพในการใช้งานสำหรับวัสดุประกอบแต่งชั้นสูงที่ต้องการสมบัติทางกลที่ดีและเมื่อติดไฟแล้วสามารถดับไฟได้ด้วยตัวเอง

คำหลัก : พอลิเบนซอกซาซีน ไดแอนไฮไดรด์ โคพอลิเมอร์ เส้นใยคาร์บอน สมบัติทางความร้อน

Abstract

Project Code : MRG5380077

Project Title : Development of high performance composites based on carbon fiber and dianhydride-modified benzoxazine resin systems

Investigator : Dr. Chanchira Jubsilp
Department of Chemical Engineering, Faculty of Engineering
Srinakharinwirot University

E-mail Address : chanchira@swu.ac.th

Project Period : 15 June 2010 to 15 June 2012

In this research, the effects of carbon fiber (CF) contents on thermal and mechanical properties of carbon fiber-reinforced polybenzoxazine (PBA-a) modified with dianhydride (PMDA) are proposed. Moreover, the effects of the compositions between the polybenzoxazine and the dianhydride on flammability behavior of the obtained composites are also evaluated. From the results, the 65wt% CF-reinforced PBA-a:PMDA matrix provided a maximum packing, resulting in a remarkable increase in thermal and mechanical properties. In addition, the flammability of the composites made from 65wt% of CF and PBA-a modified with PMDA at different PMDA contents was examined by limiting oxygen index (LOI) and UL-94 vertical flame tests. The results showed that the LOI values increased from 26.0 for 65wt% CF/PBA-a to 49.5 for 65wt% CF/PBA-a:PMDA and an improvement in fire resistance of all 65wt% CF/PBA-a:PMDA composites as thin as 1.0 mm was also achieved the maximum V-0 fire resistant classification. Moreover, the incorporation of the PMDA into PBA-a matrix significantly enhanced the T_g and the storage modulus (E') values of 65wt% CF/PBA-a:PMDA composites rather than those of the 65wt% CF/PBA-a. The T_g values and storage modulus at 35^{o}C of the obtained 65wt% CF/PBA-a:PMDA composites were found to have relatively high value up to 237^{o}C and 46 GPa, respectively, while those values of the 65wt% CF/PBA-a is approximately 183^{o}C and 41 GPa, respectively. From TGA results, all 65wt% CF/PBA-a:PMDA composites exhibited relatively high degradation temperature up to 498^{o}C and substantial enhancement in char yield with a value of up to 82%, which are somewhat higher compared to those of the 65wt% CF/PBA-a composite, i.e. 405^{o}C and 75.7%, respectively. From the improvement of flame retardant, mechanical and thermal properties, it was found that the obtained CF/ PBA-a:PMDA composites exhibited high potential applications in advanced composite materials that required mechanical integrity and self-extinguishing property.

Keywords : Polybenzoxazine; Dianhydride; Copolymer; Carbon Fiber, Thermal Property

Executive Summary

Advanced polymer composites that combine light weight, high thermal properties, and excellent mechanical properties become increasingly important for aerospace industry and other industrial applications such as automotive, marine, and electronic packaging. One important group of polymeric composites is based on the carbon fiber-reinforced polymeric matrix composites which are often used in weight reduction and high specific strength.

A novel bisphenol-A-aniline type polybenzoxazine (PBA-a) modified with dianhydride was successfully prepared by reacting bisphenol-A-aniline based benzoxazine (BA-a) resin with dianhydrides, i.e. pyromellitic dianhydride (PMDA), 3,3′,4,4′biphenyltetracarboxylic dianhydride (s-BPDA), and 3,3′,4,4′–benzophenone tetracarboxylic dianhydride (BTDA). The miscible BA-a:BTDA mixtures at various BTDA contents were easily transformed into transparent PBA-a/dianhydride copolymers by thermal cure. Fourier transform infrared spectroscopy reveals the formation of ester linkage which is a covalent interaction between hydroxyl group of the PBA-a and the anhydride group in the dianhydride. The PBA-a/dianhydride copolymers show only one glass transition temperature (T_g) with the value as high as 263°C-300°C at BA-a:dianhydride = 1.5:1 mol ratio. The T_g of the copolymers was found to be in the order of PBA-a:PMDA > PBA-a:s- BPDA > PBA-a:BTDA. The difference in the T_g of the copolymers is related to the rigidity of the dianhydride components. The value is remarkably higher than that of the unmodified PBA-a, i.e. 160°C. In addition, the copolymers exhibit enhanced thermal stability with degradation temperature (T_d) at 10% weight loss ranging from 410°C to 426°C under nitrogen atmosphere and substantial enhancement in char yield with a value of up to 60% by weight. Moreover, flexibility of the PBA-a/dianhydride copolymer samples is also significantly enhanced compared to the unmodified PBA-a. Therefore, to systematically investigate the effect of carbon fiber contents on thermal and mechanical properties, composites based on carbon fiber (CF) and polybenzoxazine (PBA-a) modified with PMDA were investigated. The 65wt% CF-reinforced PBA-a:PMDA matrix provided a maximum packing, resulting in a remarkable increase in thermal and mechanical properties. In addition, the flammability of the composites made from 65wt% of carbon fiber and PBA-a modified with PMDA at different PMDA contents was examined by limiting oxygen index (LOI) and UL-94 vertical tests. Interestingly, the results showed that the LOI values increased from 26.0 for 65wt% CF/PBA-a to 49.5 for 65wt% CF/PBA-a:PMDA and an improvement in fire resistance of all 65wt% CF/PBA-a:PMDA composites as thin as 1.0 mm was also achieved the maximum V-0 fire resistant

classification. Moreover, the incorporation of the PMDA into PBA-a matrix significantly enhanced the T_g and the storage modulus (E') values of 65wt% CF/PBA-a:PMDA composites rather than those of the 65wt% CF/PBA-a. Moreover, all 65wt% CF/PBA-a:PMDA composites exhibited relatively high T_d up to 498^{o}C and substantial enhancement in char yield with a value of up to 82%, which are somewhat higher compared to those of the 65wt% CF/PBA-a composite, i.e. 405^{o}C and 75.7%, respectively. From the improvement of flame retardant, mechanical and thermal properties, the obtained CF/PBA-a:PMDA composites exhibited high potential applications in advanced composite materials that required mechanical integrity and self-extinguishing property.

Contents

Introduction

1.1 General introduction

Advanced polymer composites such as fiber-reinforced polymer composites have been extensively used in many high performance applications that require light weight, high thermal properties, and excellent mechanical properties especially in structural utilizations because of their outstanding specific modulus and specific strength [1–6]. One important group of polymeric composites is based on carbon fiber reinforcing systems which is often used in weight reduction and high specific strength requirement, i.e., aerospace, automotive, ballistic armor, or extreme sport applications. Recently, an improvement of polymeric material properties particularly by modification of the existing polymers to achieve high thermal properties, i.e. high char yield, and high glass transition temperature (T_g), becomes increasingly important for an fiber-reinforced polymer composites [2,6]. The technique of making high performance polymer can be mainly classified into two methods, i.e. modification of polymeric component and modification utilizing multi-component including polymer alloys, blend, and composites. In recent year, developed polybenzoxazine are a novel class of thermosetting polymers that combined the thermal properties and flame retardance of phenolic resin with mechanical performance and molecular design flexibility of epoxy resin. The polybenzoxazine are widely investigated especially utilization for electronic packaging materials as issued on in several US patents. Some of the advantages the polymer includes to render high glass transition temperature, high modulus, good dielectric properties, and dimensional stability. Moreover, polybenzoxazines possess several outstanding properties such as near-zero shrinkage after curing, low water absorption [7-9]. To obtain high performance polybenzoxazines by utilizing its molecular design flexibility, thermal and thermo-oxidative stabilities of polybenzoxazines have been substantially improved by altering the functional group on the phenol and/or amine [10-17]. Ishida and Sanders [10-12] invented a novel class of arylamine-based bifunctional benzoxazine resin. In their benzoxazine resins, a bifunctional bisphenol-A-xylidine type benzoxazine resin (BA-35x) provided superior thermal stability to a bisphenol-Aaniline type (BA-a) and a bisphenol-A-toluidine type (BA-mt) resins. At its fully cured stage, BA-35x's T_g and degradation temperaturewere reported to exhibit the values much greater than those of BA-a polymer due to the regioselectivity of the benzoxazine polymerization in the aromatic amine-based polybenzoxazines. Selectively protecting or activating sites on the pendant aromatic ring toward electrophilic aromatic substitution with alkyl groups allow a series of polybenzoxazines to be developed which contain various amount of phenolic Mannich bridges, arylamine Mannich bridges, and methylene linkages. In the case of BA-a polymer, the network structure consists of largely phenolic Mannich base structures with a small amount of the arylamine rings being cross-linked by Mannich bridges. Whereas the network structures of BA-mt and BA-35x polymers also contain increasing amount of methylene-bridged species in the network structure which give rise to significantly enhanced T_g. In addition, the power of the molecular design-approach to enhance thermal properties of polybenzoxazine was further demonstrated by Cao et al. in a novel cyano functionalized polybenzoxazine (BZCN) [14]. The authors reported that the completely cured materials could achieve high char yield and high T_g. The thermally activated curing of BZCN follows multiple curing mechanisms via the ring-opening polymerization of oxazine rings and the triazine ring-formation of cyano groups, which contribute to the stability of this polymer. More recently, thermal stability of 9,10-dihydro-9-oxa-10-phosphaphenanthrene (DOPO)-containing polybenzoxazine was reported by Sponton [15]. Thermal stability of the phosphorus-containing polybenzoxazines was evaluated by examining their degradation temperature (T_d) and char yield. The T_d at 5% weight loss and char yield under nitrogen atmosphere at 750^{o}C of the modified polybenzoxazines were reported to be 332^{o}C and 25%, respectively.

However, disadvantages of the modification of the molecular structure of the benzoxazine resins to obtain high performance polymer include difficulty of the resin preparation, the purification process, and the high cost of raw materials used. An ability of benzoxazine resins to form alloys with various other resins or polymers often renders a novel class of resin systems with intriguing properties [17-23]. For example, alloying between benzoxazine resin and epoxy resin is considered to be a potentially effective measure to enhance thermal or mechanical properties as well as flammability of the polymers [18-25]. Sponton et al. [17] developed a mixture of bis(m-aminophenyl)methylphosphine oxide based benzoxazine (Bz-BAMPO) and glycidylether (DGEBA). The authors reported that the Bz-BAMPO:DGEBA at 2:1 mol ratio showed T_d at 5% weight loss of about 347^{o}C compared to 333^{o}C of Bz-BAMPO. Ishida and Ohba [20] reported that maleimidefunctionalized benzoxazine could be copolymerized with epoxy to improve toughness and processibility without compromising their thermal properties. The resulting polymer with 10% by mol of epoxy resin (DGEBA) provided T_g with 25^{o}C higher than that of the obtained homopolymer. Moreover, Rimdusit et al. [18] reported that toughness of the alloys of rigid bisphenol-A-aniline type polybenzoxazine (PBA-a) and isophorone diisocyanate-based urethane prepolymers (PU) systematically increased with the amount of the PU toughener due to the addition of more flexible molecular segments in the polymer hybrids. The T_g of the PBA-a/PU alloys was found to be 220^{o}C which was substantially higher than that of the parent polybenzoxazine, i.e. 165^{o}C. In this work, polybenzoxazine obtained by thermal ring-opening polymerization of their precursors contains phenolic hydroxyl groups. These phenolic hydroxyl groups have a strong potential for reacting with NCO groups in the PU. This interaction resulted in enhancement of the cross-linked density of the polybenzoxazine. Takeichi et al. [22] revealed a performance improvement of bisphenol-A-aniline type polybenzoxazine (PBA-a) by alloying with polyimide (PI). They reported that T_g values and thermal stabilities of the alloys increased as the PI component increased. T_gs of the PBA-a:PI alloys were in a range of 186^{o}C-205^{o}C and were higher than that of the polybenzoxazine, i.e. 152^{o}C.

In this work, dianhydride modified polybenzoxazine matrix will be investigated due to the dianhydride, such as s-BPDA, BTDA and PMDA, have been used as co-monomers for materials, i.e., high tensile strength polyimide films, jet aircraft structures and space rocket bodies. The co-monomers rely on improved chemical resistance, good mechanical and electrical properties as well as the excellent heat insulation and fire retardant properties of the materials. In addition, the dianhydride functions as curing agents for high performance-epoxy resins used in electric insulations, composites and powder coating. Therefore, an incorporation of the dianhydrides into the polybenzoxazine expecting the enhancement of both the thermal and mechanical properties as well as flammability of the polybenzoxazine, which makes them suitable for more extensive applications as a high performance polymer matrix for carbon fiber-reinforced polymer composites through the investigation of T_g, thermal degradation temperature, and dynamic moduli as well as the mechanical and thermal properties of their carbon fiber polymer composites will also be investigated.

1.2 Objectives of this research

1.2.1 To develop advanced polymer composites of carbon fiber-reinforced polybenzoxazine modified with dianhydride.

1.2.2 To study effects of dianhydride contents on curing reaction, thermal, and mechanical and fire resistant properties of polybenzoxazine.

1.2.3 To examine carbon fiber contents on density, flammability, glass transition temperature and mechanical properties of carbon fiber-reinforced polybenzoxazine modified with dianhydride composites.

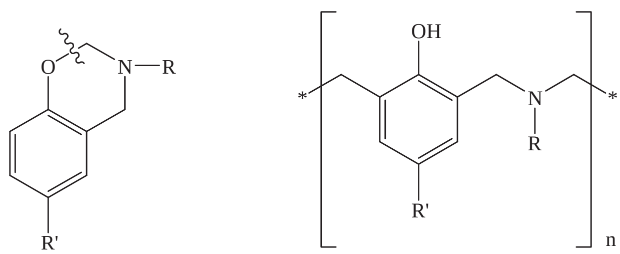
1.2.4 To evaluate the interfacial bonding between dianhydride-modified polybenzoxazine matrix and carbon fiber reinforcing.

Theory

2.1 Benzoxazine resin

Benzoxazine resin is a story class of phenolic resin which was developed to defeat almost all shortcomings of the phenolic resins and was expected to replace conventional phenolic, polyesters, vinyl esters, epoxies, BMI, cyanate esters and polyimides in numerous respects. They demonstrate several remarkable properties that have not been regularly observed by other well-known polymers, as follow excellent processability owing to low melt viscosity, solvent-less method for benzoxazine resin preparation, near-zero shrinkage upon polymerization, fast mechanical property build-up as a function of degree of polymerization [9,26,27] and benzoxazine resins can be synthesized from low-cost raw materials. The ring opening polymerization is readily achieved by basically heating the purified monomer typically at temperatures in the range between 160°C and 220°C [27] and gelation takes place in a metter of minutes to tens of minutes at these temperatures if no initiators are employed.

Additionally, the ring opening mechanism occurs by breaking of a C-O bond of the oxazine ring as shown in Fig. 2.1 and benzoxazines cure without the support of strong acid catalysis, do not release by-products during the polymerization [38]. The curing behavior of the as-synthesized benzoxazine precursor studied is autocatalytic [39]. The fantastic molecular design flexibility of the benzoxazine resins allows the properties of cured materials to be tailord for the particular requirements of personality applications [27].



(a) (b)

Fig. 2.1 Benzoxazine resin (a), and ring-opening polymerization of the resin (b)
(R = amine group, R' = phenol group)

Furthermore, good mechanical properties, such as tensile strength, i.e. 64 MPa, tensile modulus, i.e. 5.2 GPa, elongation at break, i.e. 1.3%, high thermal stability, i.e. T_d =

334^{o}C at 5 % wt loss which is possibly owing to the stabilization of the Mannich bridges by the very strong intramolecular hydrogen bonding between the phenolic OH groups and the nitrogen atom of Mannich bridge. The glass transition tmperature (T_g) exhibit in the range 160^{o}C-340^{o}C depending on the sturcture, high char-yield due to char formation usually increases with increased content of benzene content, no dark smoke, self extinguishing, low heat release rate, and low total heat release make them an desirability applicant as non-flmmable materials for the transportation industry.

Benzoxazine resin can be classified into a monofuctional and a bifunctional type depending on a type of phenol used as shown in Fig. 2.2 and Fig. 2.3 and Table 2.1 compares the properties of polybenzoxazine with those of the state- of-the-art matrices [9].

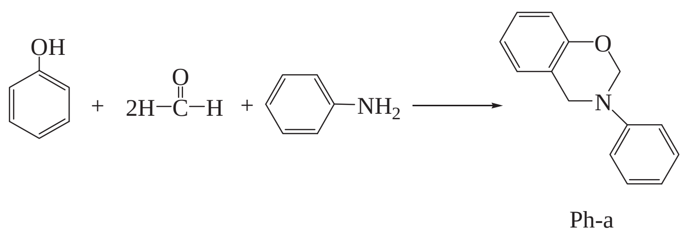


Fig. 2.2 Synthesis of phenol-aniline type benzoxazine monomer.

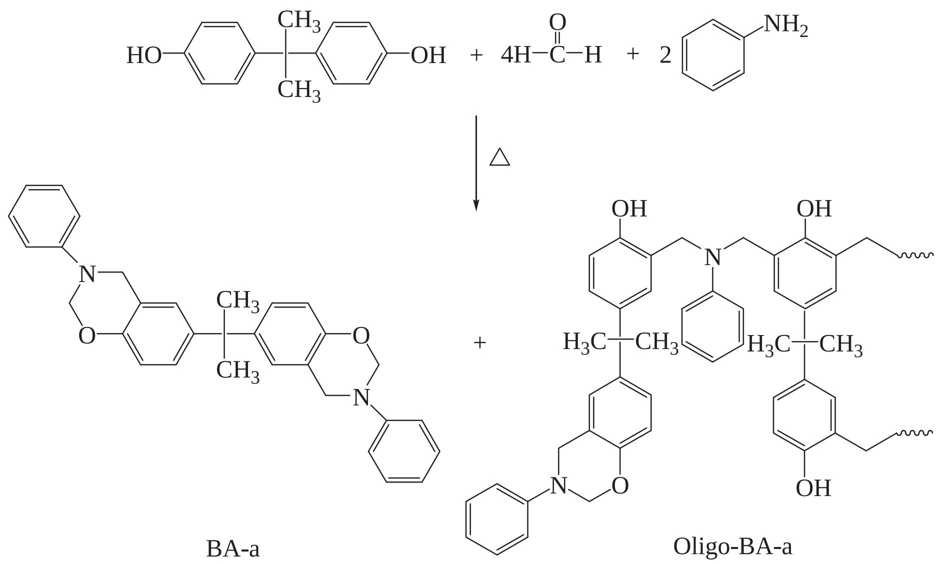


Fig. 2.3 Synthesis of bisphenol A and aniline based benzoxazine (BA-a) monomer [28].

Table 2.1 Comparison of the physical and mechanical properties of cross-linked polybenzoxazine with an epoxy and phenolic resin [27]

Property	BA-m Benzoxazine	BA-a Benzoxazine	Epoxy	Phenolic
Tensile Properties				
Modulus (GPa)	4.3	5.2	2.7	3.8
Strength (MPa)	44	64	59	48
Elongation at break (%)	1.0	1.3	4.5	1.8
Flexural Properties				
Modulus (GPa)	3.8	4.5	2.9	
Strength (MPa)	103	126	119	
Strain at break (%)	2.6	2.9	4.5	
Impact Strength (J/m, 3.2 mm thick)	31	18	32	17
Dynamic Mech. Properties				
G′ at R.T. (GPa)	1.8	2.2		
G′ at 50 oC above T_g (MPa)	<4.5	2.2		
Density				
Monomer (g/cm^3)	1.159	1.200	1.16	
Polymer (g/cm^3)	1.122	1.195	1.26	1.28
Coefficient of Thermal Expansion				
α (x 10^4 cm^3/cm^3.°C)	2.1	1.7	2.3	
β (x 10^6 cm/cm.°C)	69	58	65	68
Glass transition temperature (°C)	180	170	165	170
Cure shrinkage (%)		2.9/0	4.5	
Water Absorption (% at R.T.)				
24 h	0.17	0.11	0.12	0.23
7 day	0.40	0.28	0.62	
120 day	1.15	0.98	1.8	
Saturation	1.3	1.9		
Diffusion coefficient (×10^9 cm^2/s)	3.6	0.5	7.2	

2.2 Dianhydrides

Dianhydrides have been used as a precusor to produce polymers such as polyimides [22]. For example, Pyromellitic dianhydride (PMDA) is prepared by the vapor phase oxidation of durene, which is 1,2,4,5 tetramethylbenzene, using a supported vanadium oxide catalyst. The synthesis is completely analogous to the synthesis of phthalic anhydride [29,30].

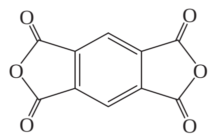


Fig. 2.4 Pyromellitic dianhydride (PMDA)

Table 2.2 Physical and chemical properties of PMDA.

Physical State	Powder
Color	white to light beige
Vapor Pressure	< 0.01hPa @ 20^{o}C
Boiling Point	397 - 400 ^{o}C @ 760mmHg
Freezing / Melting Point	283 - 287 deg C
Flash Point	380 deg C (716.00^{o}F)
Solubility in water	Decomposes.
Solubility in other solvents	Soluble in acetone.
Molecular Formula	$C_{10}H_2O_6$
Molecular Weight	218.12
Chemical Stability	Stable under normal temperatures and pressures. Moisture sensitive

3,3′,4,4′–benzophenonetetracarboxylic dianhydride (BTDA)

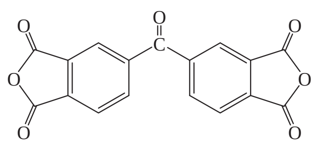


Fig. 2.5 3,3′,4,4′–benzophenonetetracarboxylic dianhydride (BTDA)

Table 2.3 Physical and chemical properties of BTDA.

Synonyms	4,4′-Carbonyldiphthalic anhydride
Empirical Formula (Hill Notation)	$C_{17}H_6O_7$
Appearance	White or light yellow powder
Molecular Weight	322.23
Vapor Density	1.4 (vs air)
Density	1.57 g/cm^3
Vapor Pressure	<0.1 mmHg (0°C)
Autoignition Temp.	975°F
Melting Point	218-222°C
Chemical Stability	Sensitive to humidity
Assay	96%

3,3′,4,4′–biphenyltetracarboxylic dianhydride (s-BPDA)

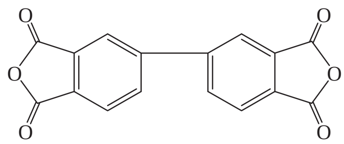


Fig. 2.6 3,3′,4,4′–biphenyltetracarboxylic dianhydride (s-BPDA)

Table 2.4 Physical and chemical properties of s-BPDA.

IUPAC Name	5-(1,3-dioxo-2-benzofuran-5-yl)-2-benzofuran-1,3-dione
Nomenclature	3,3',4,4'-Biphenyl tetracarboxylic dianhydride (s-BPDA)
Synonyms	4,4'-Biphthalic anhydride, 4,4'-Biphthalic dianhydride
Physical State	Light grey, odorless powder
Molecular Formula	$C_{16}H_6O_6$
Molecular Weight	294.215240 (g/mol)
H-Bond Donor	0
H-Bond Acceptor	6
Purity	99.5% min
Sp. Gr.	1.56
Melting Point	300

2.3 Carbon fiber [31]

Carbon and its graphite derivatives have emerged prominently in twentieth century technology. Carbon fibers are fine filament composed largely or of carbon with structures and properties varying from those of amorphous carbon to those of well-developed crystalline graphite. The fibers have the widest variety of strengths and moduli. Carbon fibers are divided into high-strength and high modulus according to their mechanical properties.

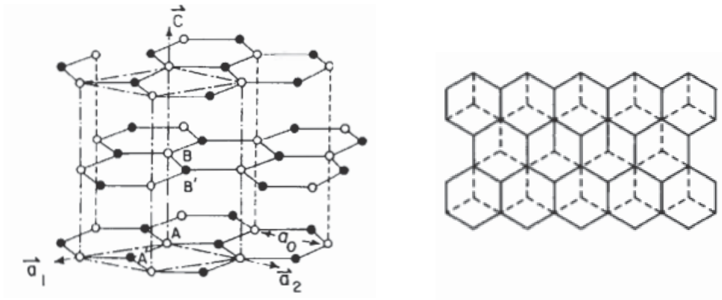
(a) (b)

Fig. 2.7 Carbon fiber roving (a), Carbon fiber fabric plain weave (b) [32,33]

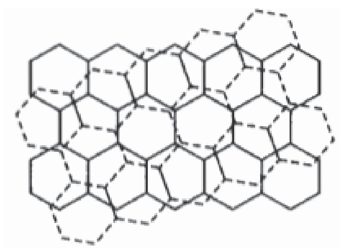
Possible strength of carbon fiber is estimated to be about 100 GPa. Though the theoretical tensile strength of single crystal of graphite is 150 GPa, highest of all the materials known. The commercial high-strength carbon fibers have a maximum strength of 7 GPa. The ratio of stiffness to density is very high for most carbon fiber because the density of carbon is low. For this reason, they are the most widely used and are notably effective as reinforcing elements in advanced composite materials.

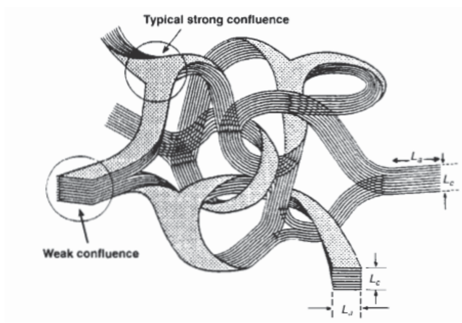
The structure and properties of carbon fiber depend on the raw material used, generally a polymer fiber. Numerous precursors have been tried to produce carbon fiber. The most important type commercially is the fiber made from polyacrylonitrile (PAN), which was initially developed for aircraft applications. It was attractive because of its high strength and modulus, and because it is not subject to creep or fatigue failure. Composites made from PAN-based carbon fiber allowed for reduction in aircraft weight, and improvement in range, payload and performance. The composites were first adopted in military aircraft, but rapidly spread to commercial aircraft and then to other applications such as sporting goods. Pitch-based general purpose (isotropic) fibers have been used in Japan for large-volume reinforcement of cementitious matrices, especially exterior building panels. Pitch-based high performance (mesophase) fibers were developed for space applications. They are capable of very high Young's modulus (up to that of in-plane graphite) and have a high negative coefficient of thermal expansion along the fiber axis. This makes possible composites with a zero coefficient of thermal expansion, which is important for space applications. When a panel is facing the sun, it may reach 200°C, and when it is facing away from the sun, it may drop to 200°C below zero.

The word 'graphite' is much misused in carbon fiber literature. The word refers to a very specific structure, in which adjacent aromatic sheets overlap with one carbon atom at the center of each hexagon as shown in Fig. 2.8a. This structure appears very rarely in carbon fibers, especially in PAN-based fibers, even though they are conventionally called graphite fibers. While high-performance fibers are made up of large aromaticsheets, these are randomly oriented relative to each other, are described as 'turbostratic' (turbulent and stratified) and are shown in Fig. 2.8b. Many physical properties depend merely on the large aromatic sheets. The aromatic character of the isotropic carbon is shown in Fig. 2.8c.



(a) Graphite





(b) Turbostratic carbon (d)Isotropic carbon

Fig. 2.8 Form of carbon [31]

2.3.1 Properties of carbon fiber

Because of the rich variety of carbon fibers available today, physical properties vary over a broad domain. ‘General purpose’ fibers made from isotropic pitch have modest levels of strength and modulus. However, they are the least expensive pitch-based fiber, and are useful in enhancing modulus or conductivity in many applications. PAN-based fibers are the strongest available; however, when they are heat treated to increase modulus the strength decreases. Mesophase pitch fibers may be heat treated to very high modulus values, approaching the in-plane modulus of graphite at 1 TPa. The Achilles heel of mesophase pitch-based fibers in composite applications is low compressive strength. Mesophase pitch fibers have the highest conductivity and lowest resistivity.

Finally, there is a property of high-performance carbon fibers, both PAN and mesophase pitch-based, which sets them apart from other materials. They are not subject to creep or fatigue failure. These are important characteristics for critical applications. In a comparison of materials for tension members of tension leg platforms for deep-sea oil production described by Salama (1997), carbon fiber strand survived 2,000,000 stress cycles between 296 and 861 MPa. In comparison, steel pipe stressed between 21 and 220 MPa failed after 300,000 cycles. Creep studies on PAN and pitch-based carbon fibers were conducted by Sines et al. (1989) and Kogure et al. (1996) at 2300°C and stresses of the order of 800 MPa. Projections of the data obtained to ambient temperatures indicate that creep deformations will be infinitesimally small.

2.3.2 Applications of Carbon Fiber

Large weight savings are possible when carbon fiber composites are used to replace more conventional materials; they are frequently applied in areas where weight reductions are valuable. Especially, they are used in variety of aerospace components. Typical aerospace-grade tow size range from 1K to 12K PAN- and pitch-based 12K carbon fibers are available with a moderate (33 to 35 million pounds per square inch, Msi), intermediate (40 to 50 Msi), high (50 to 70 Msi), and ultrahigh (70 to 140 Msi) modulus. Heavy tow carbon fibers with filament counts from 48K up to 320K are available at a lower cost than aerospace-grade fibers. They typically have a 33 to 35 Msi modulus and 550 Ksi tensile strength and are used when fast part build-up is required, most commonly in recreational industrial, construction and automotive markets. Carbon fibers and their composites exhibit many characteristics apart from their basic mechanical properties and weight saving. Electrical conductivity is coupled with excellent mechanical properties in thermoplastics molding compounds for structures in electronic equipment. Corrosion resistance is useful for making pipes, reactions or containers for chemical plants or in marine environment. Examples of sports equipment that contain carbon fiber reinforcement include skis and ski poles, golf clubs tennis racquets, fishing rods, and racing cycles.

Fig. 2.9 Applications of carbon fiber [34-37]

Literature Reviews

Ning and Ishida (1994) [7,38] investigated the synthesis of bifunctional benzosazine precursors. These polyfunctional benzoxazine were found to exhibit excellent mechanical and thermal properties with good handling capability for resin processing and composites manufacturing, e.g., the glass transition temperature of 190^{o}C, tensile modulus of 3.2 GPa, and tensile strength of 58 MPa. In addition, they offered greater flexibility than conventional phenolic resins in term of molecular design. They do not release by-products during curing reaction and there is no solvent needed in the resin production.

Rimdusit and Ishida (2000) [39,40] developed highly thermally conductive molding compounds for electronic packing application based on polybenzosazine system. They investigated thermal conductivity of boron nitride-filled benzoxazine resin as a function of filler content and particle size. The investigators used large aggregates of flake-like boron nitride crystals and were able to make a composite with a maximum boron nitride content of 78.5% by volume with a corresponding thermal conductivity value of 32.5 W/mK. Low melt viscosity with suitable period of time was achieved e.g. 0.3 Pa.s constant up to 1000 seconds at 100^{o}C. The gel time at 140^{o}C ranges from 5 min to 30 min and less than 5 min at 180^{o}C which is suitable to the “B-stage” time or gel time for prepregs (1 min to 15 min at a temperature range 90^{o}C to 210^{o}C), and a glass transition temperature as high as 170^{o}C. The fully cured polymer mixtures show relatively high degradation temperature, reported at 5% weight loss, i.e. up to 370^{o}C. The char yield of the ternary systems increase significantly compared with the pure epoxy resin. That is due to the fact that both polybenzoxazine and phenolic novolac are known to give higher char yield compared with epoxy resin. The remarkably high thermal conductivity value was obtained using the well-recognized concept of thermal management in composite materials by maximizing the formation of conductive networks while minimizing the thermal barrier resistance along the heat-flow path. The concept was accomplished by using highly thermally conductive filler with a matrix resin which had low melt viscosity and good adhesion to the filler. In addition, a large particle size with multimodal particle size distribution was use. Boron nitride and polybenzosazine have properties that meet all those requirements and thus exhibit a very high thermal conductivity value.

Zhao et al. (2007) [41] studied polyimides that were prepared by polycondensation of 2-amino-5-[4-(40-aminophenoxy)phenyl]-thiazole (APPT) with various aromatic dianhydride, such as pyromellitic dianhydride (PMDA) and 3,3′,4,4′–benzophenonetetracarboxylic dianhydride (BTDA). The thermal properties of the polyimides, which were evaluated by differential scaning calorimetry (DSC) and thermogravimetric analysis (TGA) methods, are listed in Table 3.1.

Table 3.1 Data of thermal analysis of the polyimides.

Polymer	T_g [a] (°C)	In N_2 [b] (°C)		In air [b] (°C)		Char yield [c] (%)
		T_5	T_{10}	T_5	T_{10}	
APPT-BTDA	320.2	489	523	439	482	59.31
APPT-PMDA	328.8	507	548	458	499	63.33

[a] T_g measured by DSC at a scanning rate of 10°C/min in flowing nitrogen.

[b] Temperature at a 5 or 10% weight loss at a 20°C/min heating rate.

[c] Residual weight (%) at 800°C in nitrogen.

DSC curves of the polyimides are shown in Fig. 3.1. The experimental results indicate that APPT-PMDA have higher glass transition temperature than APPT-BTDA due to the structure of the dianhydride component.

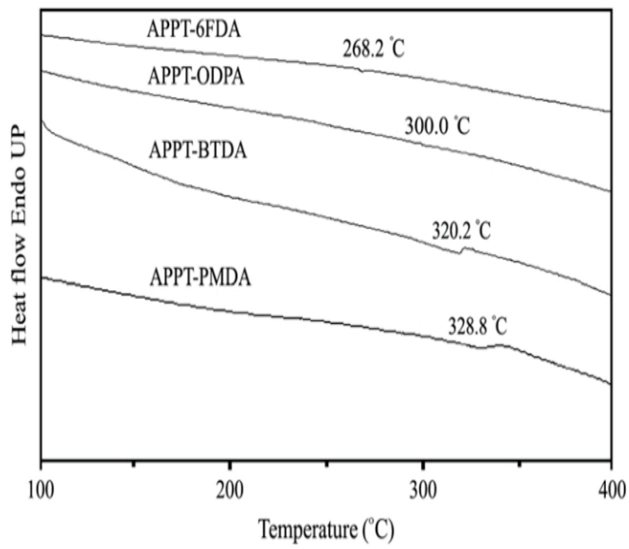


Fig. 3.1 DSC thermograms of PIs at heating rate of 20°C/min in nitrogen.

Takeichi et al. (2005) [22] studied the polymer alloys of polybenzoxazine (BA-a) and polyimide (PI). The cast films were yellow and transparent, similar with that of the blend solution, and became deep wine-color and transparent after the cure at 240^{o}C. From Fig. 3.2, it is clear that all the samples of polymer alloys from PI/BA-a have only one glass transition temperature (T_g) from both loss modulus (E'') and tan δ maxima and the T_g shifted to higher temperature as PI content increased.

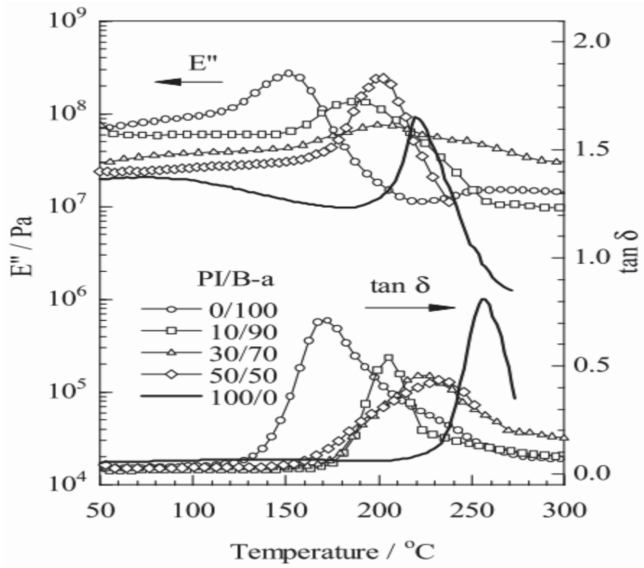


Fig. 3.2 Loss modulus (E”) and tan δ of PI/BA-a films with various ratios.

The stress–strain curves for PI/BA-a films are shown in Fig. 3.3. The tensile properties of the PI/BA-a films confirmed that the poly(BA-a) enhanced the modulus of PI, while PI improved the toughness of poly(BA-a).

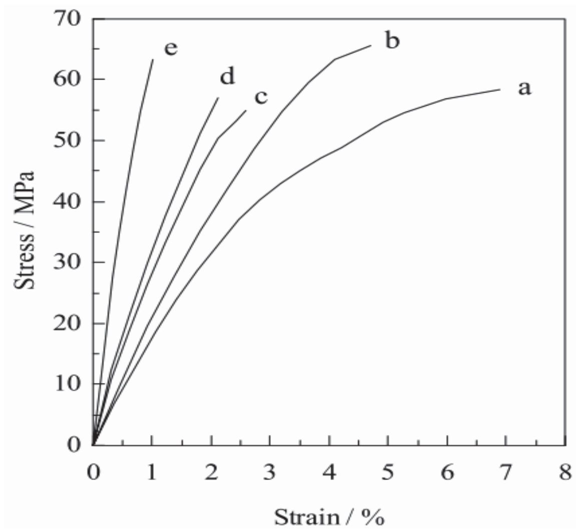


Fig. 3.3 Tensile properties of PI/BA-a films after cured at 240^{o}C/2 h with PI/BA-a ratio of 100/0 (a), 50/50 (b), 30/70 (c), 10/90 (d), and 0/100 (e).

The thermal stabilities of polymer alloy films from PI/BA-a were investigated by thermogravimetric analysis (TGA), and shown in Fig. 3.4. The initial decomposition temperatures (defined at 5% and 10% weight loss) of the polymer alloys from PI/BA-a increased obviously with the increase of PI content due to higher thermal stability of PI than that of poly(BA-a). They also notice that char yield increased by the addition of only small amount of PI.

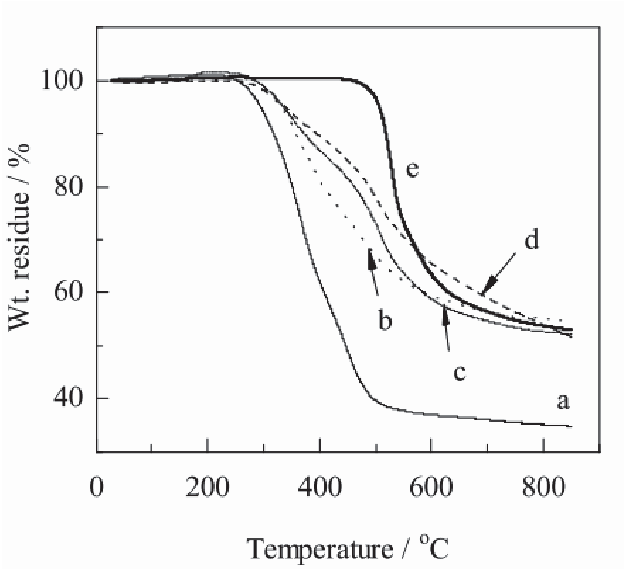


Fig. 3.4 TGA of PI/BA-a films with PI/BA-a ratio of 0/100 (a), 10/90 (b), 30/70 (c), 50/50 (d), and 100/0 (e).

Shen and Ishida (1996) [7] developed high-performance composites from carbon fiber and two kinds of polybenzoxazines that could provide good mechanical and thermal properties. The two benzoxazine monomers used were 8,8'-bis(3,4-dihydro-3-phenyl-2H-1,3-benzoxazine) (22Pa) and 6,6'-bis(2,3-dihydro-3-phenyl-4H-1,3-benzoxazinyl)ketone (44Oa). They found that both of the composites showed good mechanical properties in terms of flexural strength, modulus, toughness, and also interlaminar shear strength. The char yields are 87% and 92% for CF/ 22Pa and CF/440a composites, respectively, which are quite high in comparison with the other polymer composites. These composites are good candidates for fire resistant materials.

Table 3.2 The thermal characteristics of polybenzoxazine composites and other high-performance composites.

Composites	T_g (°C)	T_d^* (°C)	2% Weight Loss Temp.** (°C)	Char Yield (%)
CF/22Pa (290°C/1h)	268	330	260	87
CF/44Oa (290°C/1h)	350	370	260	92
CF/Bismaleimid	250-300	450-500	-	50-70
CF/Polyimide	230-380	560-600	-	-

* 1.5% weight loss temperature for composites with 30wt% resin contents when subjected to TGA in nitrogen at a heating rate of 20°C/min.

** 2% weight loss temperature when subjected to isothermal aging for 200h in static air

Jang and Yang (2000) [3,42] modified polybenzoxazine with liquid rubber (ATBN and CTBN) to improve the delamination toughness of carbon-fiber/polybenzoxazine composites. They conclude that ATBN improved the delamination toughness and interfacial bonding in the composites more effectively. Despite such improvement, there are some disadvantages from this rubber modified resin approach including the considerable reduction of strength, modulus, and glass transition temperature such as decrease in flexural strength with increase in CTBN (~380 MPa of 0% CTBN to ~200 MPa of 20% CTBN). In addition, they have improved the mechanical properties of CF/polybenzoxazine composites using carbon fiber surface treatments. The influences of oxygen plasma treatment and nitric acid treatment on the mechanical properties were studied. The flexural strength of 60 min oxidized CF/polybenzoxazine composites is 2.4 times as high as that of untreated ones and is even more than that of plasma-treated ones (~850 MPa of nitric acid treatment, ~600 MPa of oxygen plasma treated, and ~380 MPa of untreated). They observed the cohesive failure occurred in the matrix region due to the improvement of the interfacial adhesion strength between CF and matrix by the nitric acid treatment.

Ishida and Chaisuwan (2003) [8] improved the mechanical properties of carbon fiber-reinforced polybenzoxazine composites by rubber interlayering. The resin used is BA-35x because it shows the highest thermal stability achieved from neat benzoxazine based on bisphenol-A and unfunctionallized aniline derivatives (T_g = 236°C of BA-35x and T_g = 170°C of BA-a). Carbon fiber woven fabric (T300) was used either as-received or desired condition. The fiber content of the composite is about 60% by volume. They reported the optimizing concentration of ATBN rubber provided the mechanical properties comparable or superior to those of modified epoxy and phenolic matrices i.e. flexural strength: ~800 MPa of rubber interlayered BA-35x, 780 MPa of modified epoxy, and 650 MPa of modified phenolic; flexural modulus: 58 GPa of rubber interlayered BA-35x, 58 GPa of modified epoxy, and 56 GPa of modified phenolic.

Rimdusit et al. (2009) [43] evaluated characteristics of the ternary systems of benzoxazine, epoxy, and phenolic resin systems for utilizing as a matrix of carbon fiber prepregs such as viscosity, gelation time, shelf-life, and curing properties as well as the mechanical and thermal properties of their fully cured polymers and their carbon fiber composites. The ternary mixtures can provide a relatively wide processing window ranging from 50 to 200°C by maintaining their low A-stage viscosity for a relatively long time which is crucial in the fiber pre-impregnating process. Furthermore, relatively long shelf-life of the ternary mixtures stored at room temperature (∼30°C) up to 270 days is obtained with minimal effect on their processability. Furthermore, the carbon fiber composite based on BEP362 was found to exhibit a relatively high modulus value of 57.7 GPa comparing with about 4.0 GPa of the neat BEP362 alloy

Literature Reviews

Ning and Ishida (1994) [7,38] investigated the synthesis of bifunctional benzosazine precursors. These polyfunctional benzoxazine were found to exhibit excellent mechanical and thermal properties with good handling capability for resin processing and composites manufacturing, e.g., the glass transition temperature of 190^{o}C, tensile modulus of 3.2 GPa, and tensile strength of 58 MPa. In addition, they offered greater flexibility than conventional phenolic resins in term of molecular design. They do not release by-products during curing reaction and there is no solvent needed in the resin production.

Rimdusit and Ishida (2000) [39,40] developed highly thermally conductive molding compounds for electronic packing application based on polybenzosazine system. They investigated thermal conductivity of boron nitride-filled benzoxazine resin as a function of filler content and particle size. The investigators used large aggregates of flake-like boron nitride crystals and were able to make a composite with a maximum boron nitride content of 78.5% by volume with a corresponding thermal conductivity value of 32.5 W/mK. Low melt viscosity with suitable period of time was achieved e.g. 0.3 Pa.s constant up to 1000 seconds at 100^{o}C. The gel time at 140^{o}C ranges from 5 min to 30 min and less than 5 min at 180^{o}C which is suitable to the “B-stage” time or gel time for prepregs (1 min to 15 min at a temperature range 90^{o}C to 210^{o}C), and a glass transition temperature as high as 170^{o}C. The fully cured polymer mixtures show relatively high degradation temperature, reported at 5% weight loss, i.e. up to 370^{o}C. The char yield of the ternary systems increase significantly compared with the pure epoxy resin. That is due to the fact that both polybenzoxazine and phenolic novolac are known to give higher char yield compared with epoxy resin. The remarkably high thermal conductivity value was obtained using the well-recognized concept of thermal management in composite materials by maximizing the formation of conductive networks while minimizing the thermal barrier resistance along the heat-flow path. The concept was accomplished by using highly thermally conductive filler with a matrix resin which had low melt viscosity and good adhesion to the filler. In addition, a large particle size with multimodal particle size distribution was use. Boron nitride and polybenzosazine have properties that meet all those requirements and thus exhibit a very high thermal conductivity value.

Zhao et al. (2007) [41] studied polyimides that were prepared by polycondensation of 2-amino-5-[4-(40-aminophenoxy)phenyl]-thiazole (APPT) with various aromatic dianhydride, such as pyromellitic dianhydride (PMDA) and 3,3′,4,4′–benzophenonetetracarboxylic dianhydride (BTDA). The thermal properties of the polyimides, which were evaluated by differential scaning calorimetry (DSC) and thermogravimetric analysis (TGA) methods, are listed in Table 3.1.

Table 3.1 Data of thermal analysis of the polyimides.

Polymer	T_g [a] (^oC)	In N_2 [b] (^oC)		In air [b] (^oC)		Char yield [c] (%)
		T_5	T_{10}	T_5	T_{10}	
APPT-BTDA	320.2	489	523	439	482	59.31
APPT-PMDA	328.8	507	548	458	499	63.33

[a] T_g measured by DSC at a scanning rate of 10^oC/min in flowing nitrogen.

[b] Temperature at a 5 or 10% weight loss at a 20^oC/min heating rate.

[c] Residual weight (%) at 800^oC in nitrogen.

DSC curves of the polyimides are shown in Fig. 3.1. The experimental results indicate that APPT-PMDA have higher glass transition temperature than APPT-BTDA due to the structure of the dianhydride component.

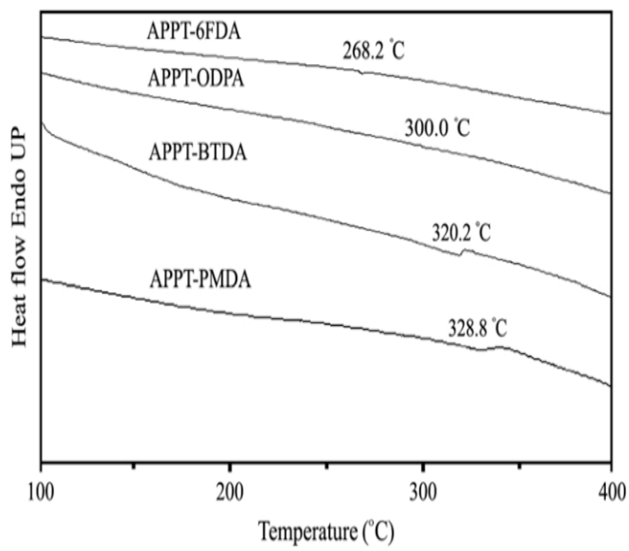


Fig. 3.1 DSC thermograms of PIs at heating rate of 20^oC/min in nitrogen.

Takeichi et al. (2005) [22] studied the polymer alloys of polybenzoxazine (BA-a) and polyimide (PI). The cast films were yellow and transparent, similar with that of the blend solution, and became deep wine-color and transparent after the cure at 240°C. From Fig. 3.2, it is clear that all the samples of polymer alloys from PI/BA-a have only one glass transition temperature (T_g) from both loss modulus (E'') and tan δ maxima and the T_g shifted to higher temperature as PI content increased.

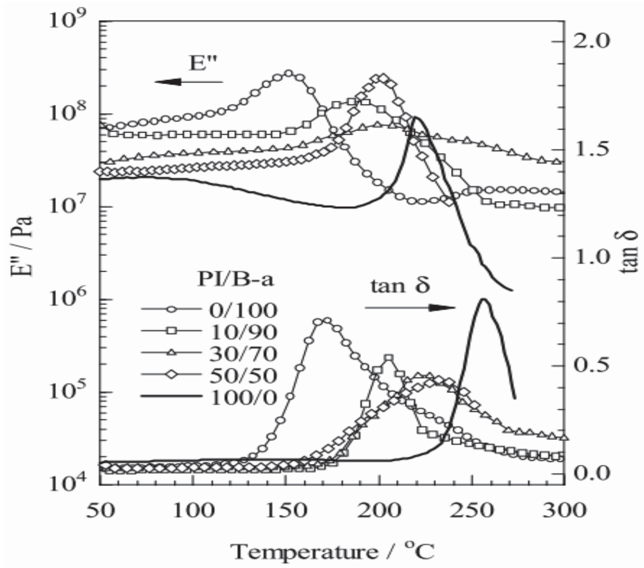


Fig. 3.2 Loss modulus (E”) and tan δ of PI/BA-a films with various ratios.

The stress–strain curves for PI/BA-a films are shown in Fig. 3.3. The tensile properties of the PI/BA-a films confirmed that the poly(BA-a) enhanced the modulus of PI, while PI improved the toughness of poly(BA-a).

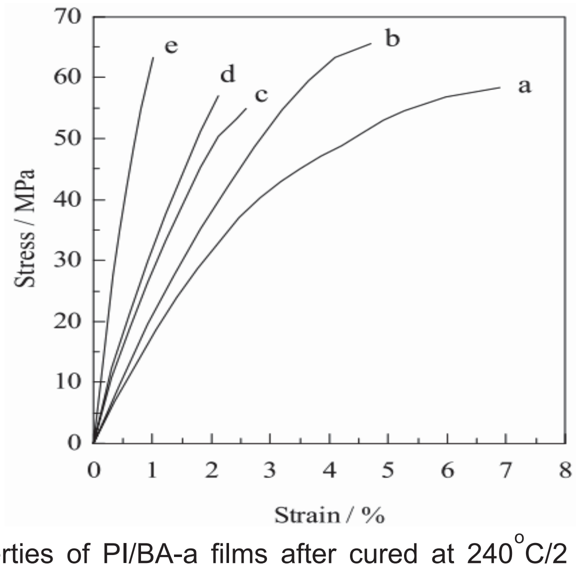


Fig. 3.3 Tensile properties of PI/BA-a films after cured at 240°C/2 h with PI/BA-a ratio of 100/0 (a), 50/50 (b), 30/70 (c), 10/90 (d), and 0/100 (e).

The thermal stabilities of polymer alloy films from PI/BA-a were investigated by thermogravimetric analysis (TGA), and shown in Fig. 3.4. The initial decomposition temperatures (defined at 5% and 10% weight loss) of the polymer alloys from PI/BA-a increased obviously with the increase of PI content due to higher thermal stability of PI than that of poly(BA-a). They also notice that char yield increased by the addition of only small amount of PI.

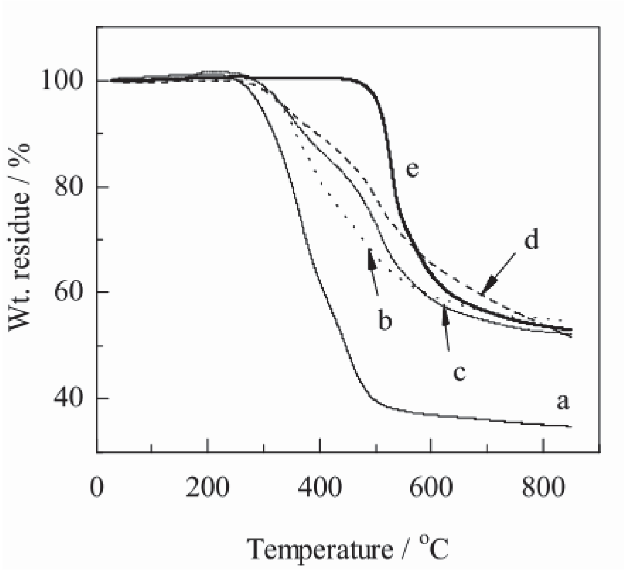


Fig. 3.4 TGA of PI/BA-a films with PI/BA-a ratio of 0/100 (a), 10/90 (b), 30/70 (c), 50/50 (d), and 100/0 (e).

Shen and Ishida (1996) [7] developed high-performance composites from carbon fiber and two kinds of polybenzoxazines that could provide good mechanical and thermal properties. The two benzoxazine monomers used were 8,8’-bis(3,4-dihydro-3-phenyl-2H-1,3-benzoxazine) (22Pa) and 6,6’-bis(2,3-dihydro-3-phenyl-4H-1,3-benzoxazinyl)ketone (44Oa). They found that both of the composites showed good mechanical properties in terms of flexural strength, modulus, toughness, and also interlaminar shear strength. The char yields are 87% and 92% for CF/ 22Pa and CF/440a composites, respectively, which are quite high in comparison with the other polymer composites. These composites are good candidates for fire resistant materials.

Table 3.2 The thermal characteristics of polybenzoxazine composites and other high-performance composites.

Composites	T_g (°C)	T_d* (°C)	2% Weight Loss Temp.** (°C)	Char Yield (%)
CF/22Pa (290°C/1h)	268	330	260	87
CF/44Oa (290°C/1h)	350	370	260	92
CF/Bismaleimid	250-300	450-500	-	50-70
CF/Polyimide	230-380	560-600	-	-

* 1.5% weight loss temperature for composites with 30wt% resin contents when subjected to TGA in nitrogen at a heating rate of 20°C/min.

** 2% weight loss temperature when subjected to isothermal aging for 200h in static air

Jang and Yang (2000) [3,42] modified polybenzoxazine with liquid rubber (ATBN and CTBN) to improve the delamination toughness of carbon-fiber/polybenzoxazine composites. They conclude that ATBN improved the delamination toughness and interfacial bonding in the composites more effectively. Despite such improvement, there are some disadvantages from this rubber modified resin approach including the considerable reduction of strength, modulus, and glass transition temperature such as decrease in flexural strength with increase in CTBN (~380 MPa of 0% CTBN to ~200 MPa of 20% CTBN). In addition, they have improved the mechanical properties of CF/polybenzoxazine composites using carbon fiber surface treatments. The influences of oxygen plasma treatment and nitric acid treatment on the mechanical properties were studied. The flexural strength of 60 min oxidized CF/polybenzoxazine composites is 2.4 times as high as that of untreated ones and is even more than that of plasma-treated ones (~850 MPa of nitric acid treatment, ~600 MPa of oxygen plasma treated, and ~380 MPa of untreated). They observed the cohesive failure occurred in the matrix region due to the improvement of the interfacial adhesion strength between CF and matrix by the nitric acid treatment.

Ishida and Chaisuwan (2003) [8] improved the mechanical properties of carbon fiber-reinforced polybenzoxazine composites by rubber interlayering. The resin used is BA-35x because it shows the highest thermal stability achieved from neat benzoxazine based on bisphenol-A and unfunctionallized aniline derivatives (T_g = 236°C of BA-35x and T_g = 170°C of BA-a). Carbon fiber woven fabric (T300) was used either as-received or desired condition. The fiber content of the composite is about 60% by volume. They reported the optimizing concentration of ATBN rubber provided the mechanical properties comparable or superior to those of modified epoxy and phenolic matrices i.e. flexural strength: ~800 MPa of rubber interlayered BA-35x, 780 MPa of modified epoxy, and 650 MPa of modified phenolic; flexural modulus: 58 GPa of rubber interlayered BA-35x, 58 GPa of modified epoxy, and 56 GPa of modified phenolic.

Rimdusit et al. (2009) [43] evaluated characteristics of the ternary systems of benzoxazine, epoxy, and phenolic resin systems for utilizing as a matrix of carbon fiber prepregs such as viscosity, gelation time, shelf-life, and curing properties as well as the mechanical and thermal properties of their fully cured polymers and their carbon fiber composites. The ternary mixtures can provide a relatively wide processing window ranging from 50 to 200^{o}C by maintaining their low A-stage viscosity for a relatively long time which is crucial in the fiber pre-impregnating process. Furthermore, relatively long shelf-life of the ternary mixtures stored at room temperature (∼30^{o}C) up to 270 days is obtained with minimal effect on their processability. Furthermore, the carbon fiber composite based on BEP362 was found to exhibit a relatively high modulus value of 57.7 GPa comparing with about 4.0 GPa of the neat BEP362 alloy

Experimental

4.1 Raw materials

Materials used in this study are bisphenol-A-aniline based bifunctional benzoxazine resin (BA-a), dianhydrides, 1-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF) as solvent. The BA-a based on bisphenol-A, paraformaldehyde, and aniline was synthesized according to the patented solventless technology [26]. Bisphenol-A (polycarbonate grade) was provided by Thai Polycarbonate Co., Ltd. (TPCC). Paraformaldehyde (AR grade) and aniline (AR grade) were purchased from Merck Co. and Panreac Quimica SA, respectively. Aromatic carboxylic dianhydrides used in this work were pyromellitic dianhydride (PMDA) purchased from Acros organics, 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) obtained from Japan Aerospace Exploration Agency, JAXA, (Prof. R. Yokota), and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) supplied by Sigma Aldrich Co. NMP and DMF solvents were purchased from Fluka Chemical Co. and Fisher Scientific UK Limited, respectively. Carbon fiber plain fabric (BN CC200P) in 3k-tows with a fiber areal weight of 200 g/m^2 was purchased from Rattanakosin Composites Ltd., Partnership. All chemicals and the carbon fiber were used as-received.

4.2 Preparation of benzoxazine-dianhydride copolymers

BA-a resin was blended with various types of dianhydrides (DA), i.e. BTDA, s-BPDA, and PMDA, at BA-a:DA = 4:1, 3:1, 2:1, 1.5:1, and 1:1 mole ratio. The BA-a:DA mixtures were dissolved in solvent and stirred at 80^{o}C until a clear homogeneous mixture was obtained. The solution was cast on Teflon sheet and dried at room temperature for 24h. Additional drying was carried out at 80^{o}C for 24h in a vacuum oven followed by thermal curing at 150^{o}C for 1h, 170^{o}C for 1h, at 190^{o}C, 210^{o}C, 230^{o}C for 2h each, and 240^{o}C for 1h to guarantee complete curing of the mixtures.

4.3 Prepreg and Composite Manufacture

Carbon fiber plain fabrics were pre-impregnated with benzoxazine-PMDA mixture solution. After brushing, the prepreg was removed and cut to appropriate sizes. The DMF solvent was then removed by drying the prepreg at room temperature for 12h followed by conditioning at 60°C for 2h in a vacuum oven. The composite laminates were preheated at 130°C for 40 min and cured at 210°C for 2h in the compression molder using a pressure of 4 MPa. After the cured cycle all sample was post-cured in an air-circulating oven at 230°C to 240°C for 3h to guarantee complete curing of the samples. The samples were finally left to cool down to room temperature and were ready for characterizations. The curing cycle of this carbon fiber composite is shown in Fig. 4.1

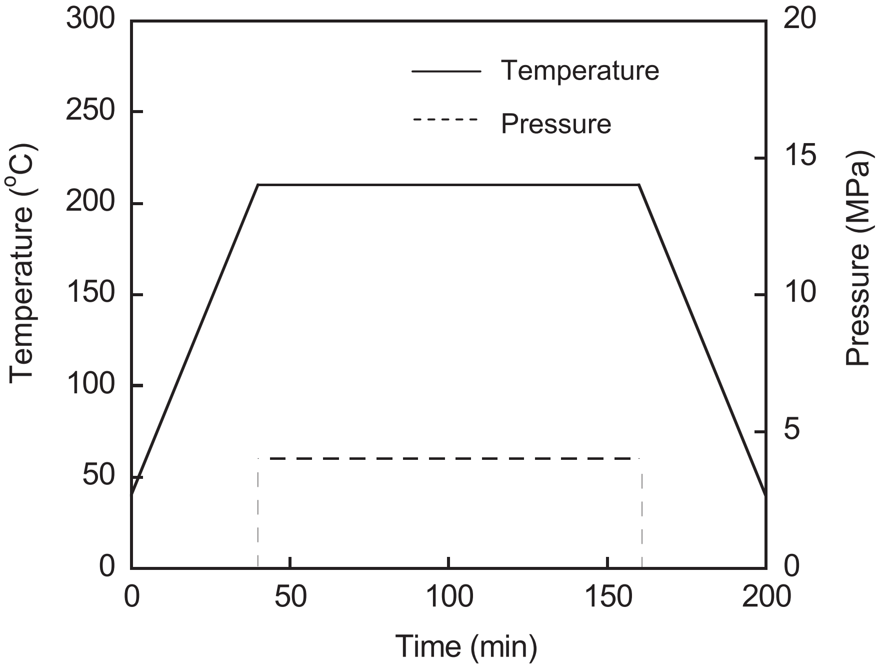


Fig. 4.1 Curing cycle of carbon fiber-reinforced PMDA-modified bisphenol-A/aniline polybenzoxazine composites.

4.4 Sample characterizations

4.4.1 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectra of fully cured samples were acquired at room temperature using a Spectrum GX FTIR spectometer from Perkin Elmer with an ATR accessory. In the case of a BA-a resin and a pure aromatic carboxylic dianhydride, a small amount of aromatic carboxylic dianhydride powder was cast as thin film on a potassium bromide (KBr) window. All spectra were taken with 64 scans at a resolution of 4 cm^{-1} and in a spectral range of 4000-400 cm^{-1}.

4.4.2 Density measurement

A density of each specimen was determined by a water displacement method according to ASTM D 792 (Method A). All specimens were prepared in a rectangular shape (25 mm $\times$ 50 mm $\times$ 1 mm). The density was calculated by the following equation:
The average value from at least three specimens was calculated.

$$\rho = \left(\frac{A}{A - B} \right) \times \rho_0 \tag{4.1}$$

Where ρ is density of the sample (g/cm^3), A is weight of the sample in air (g), B is weight of the sample in liquid (g), ρ_0 = density of the liquid at the given temperature (g/cm^3)

4.4.3 Dynamic mechanical analyzer

Dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH was used to investigate the viscoelastic properties of all samples. The dimension of the copolymer samples was 7.0 mm $\times$ 10 mm $\times$ 0.1 mm for a tension mode and 50 mm $\times$ 10 mm $\times$ 1 mm for bending mode at a frequency of 1 Hz with strain amplitude of 0.1% and at a heating rate of 2^{o}C/min from 30^{o}C to 400^{o}C under constant nitrogen flow of 80 ml/min. The storage modulus (E'), loss modulus (E''), and loss tangent or damping curve (tan δ) were then obtained. The $T_{g,DMA}$ was taken as the maximum point on the loss modulus curve in a DMA thermogram.

4.4.4 Flexural property measurement

Flexural modulus and flexural strength of composite samples were determined utilizing a universal testing machine (model 5567) from Instron Instrument. The test method used was a three-point bending mode with a support span of 48 mm at the crosshead speed of 0.85 mm/min according to ASTM D 790. The dimension of the samples was 50 mm $\times$ 25 mm $\times$ 1 mm.

4.4.5 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to evaluate the degradation temperature (T_d) and char yield of the all samples. The testing temperature program was ramped at a heating rate of 20^{o}C/min from room temperature to 1000^{o}C under nitrogen atmosphere. The sample mass used was measured to be approximately 8-15 mg. Weight loss of the sample was measured as a function of temperature. The degradation temperature (T_d) of cured samples was reported at their 5% and 10% weight loss and char yields were also reported at 800^{o}C.

4.4.6 Differential scanning calorimetry (DSC)

Glass transition temperature (T_g) of all samples were examined using a differential scanning calorimeter (DSC) model 2910 from TA Instruments. The thermogram was obtained using a heating rate of 10^{o}C/min from 30^{o}C to 300^{o}C under nitrogen purging with a constant flowrate of 50 ml/min. A sample with a mass in a range of 8-10 mg was sealed in an aluminum pan with lid. The $T_{g,\ DSC}$ was obtained from the temperature at half extrapolated tangents of the step transition midpoint.

4.4.7 Limited oxygen index (LOI) test

LOI values were measured using an LOI instrument on rectangular shape 70 mm $\times$ 7 mm $\times$ 1 mm according to the standard oxygen index test (ASTM D2863). The test was based on the determination of the lowest volume concentration of oxygen in a gas mixture of nitrogen and oxygen (O_2 and N_2) required for ignition and the onset of burning. LOI values were calculated according to the following equation.

$$\mathrm{LOI} = \frac{\mathrm{O_2}}{\mathrm{O_2} + \mathrm{N_2}} \tag{4.2}$$

Where LOI is the limiting oxygen index, O_2 is the volumetric flow of oxygen (mm^3/s), and N_2 is the volumetric flow of nitrogen (mm^3/s).

4.4.8 UL-94 flame test

UL-94 vertical flame tests were performed on vertical testing apparatus as shown in Fig. 4.2. Five specimens 12 mm $\times$ 120 mm $\times$ 1 mm were used for testing. The specimen was placed in a holder in a vertical position the lower end of specimen is contacted by a flame for 10 second thus initiating burning. A second ignition was made after self-extinguishing of the flame at the sample for 10 second. The burning process is characterized by the times t_1 and t_2 pertaining to the two burning steps. The parameters t_1 and t_2 denote the time between removing the methane flame and self-extinguishing of the sample. Moreover, it is always noted whether drips from the sample are released or drips make absorbent cotton flame during the burning times t_1 and t_2. If $t_1 + t_2$ were less than 10 second with no dripping, it would be considered a V-0 material.

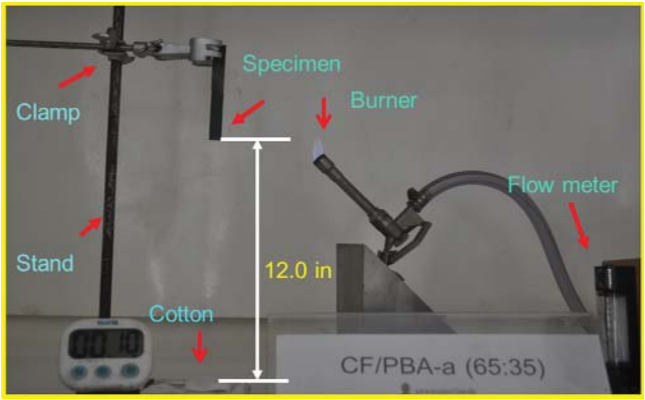


Fig. 4.2 UL-94 vertical flame test.

4.4.9 Hardness measurement

Nanoindentation experiment was carried out on UMIS-2000 nanoindenter with a diamond Berkovich tip (a three-sided pyramidal diamond tip) from CRIRO, Australia. A maximum load of 50 mN with loading/unloading cycles and holding time of 60s was used to evaluate the hardness from the penetration depth. The 3 $\times$ 3 arrays of indents were performed in the central region of a sample to eliminate edge effect.

4.4.10 Interfacial bonding examination

Interfacial bonding of a filled sample was investigated using a ISM-5400 scanning electron microscope (SEM) at an acceleration voltage of 15 kV. All samples were coated with thin film of gold using a JEOL ion sputtering device (model JFC-1100E) for 4 min to obtain a thickness of approximately 30Å and the micrographs of the specimen fracture surface were taken. The obtained micrographs were used to qualitatively evaluate the interfacial interaction between the matrix resin and the carbon fiber.

Results and Discussion

5.1 Effect of dianhydride contents on thermomechaical properties of polybenzoxazine modified with dianhydrides

5.1.1 FTIR study of the BA-a/BTDA systems

The IR spectra of bisphenol-A-aniline based benzoxazine (BA-a) resin, BTDA, bisphenol-A-aniline type polybenzoxazine (PBA-a), and PBA-a/BTDA copolymers are shown in Fig. 5.1. From the figure, the BA-a resin (Fig. 5.1a) was characterized by the band at 1232 cm^{-1} from the aromatic ether C–O–C stretching mode of an oxazine ring whereas the band around 947 cm^{-1}, and 1497 cm^{-1} were attributed to the tri-substituted benzene ring. After thermal cure, these bands completely disappeared indicating a complete loss of the oxazine ring in the BA-a resin. In addition, new absorption peaks at 878 cm^{-1} and 1488 cm^{-1} of the tetra-substituted aromatic ring were observed suggesting the ring-opening reaction to take place *ortho* to the phenolic moiety as displayed in Fig. 5.1(c) [12,44]. Furthermore, an indication of ring opening reaction of the BA-a resin upon thermal treatment could also be observed from the appearance of a broad peak about 3300 cm^{-1} which was assigned to the phenolic hydroxyl group formation. For the BTDA material, the IR spectrum, in Fig. 5.1(b), revealed carbonyl characteristic absorption peaks in anhydride at 1780 and 1860 cm^{-1}, and the benzophenone carbonyl band near 1665 cm^{-1}. Furthermore, the band centered at 1232 cm^{-1} associated with the C–O–C stretching mode in the BTDA was also detected [45,46].

Polybenzoxazine obtained by thermal ring-opening polymerization of benzoxazine resin has phenolic hydroxyl groups in their structure [12]. We expect that these phenolic hydroxyl groups have a strong potential for interaction with carbonyl groups in BTDA to form ester linkage as similarly demonstrated by the covalent reaction between free hydroxyl groups of epoxy resin and carbonyl groups in dianhydride [47]. This characteristic provides a potential copolymer formation from the two monomers. As exemplification in Fig. 5.1(d) of the BA-a:BTDA = 1.5:1 mol ratio, we can see that the carbonyl stretching bands of BTDA at 1860 and 1780 cm^{-1} completely disappeared, indicating the reaction was completed. It was postulated therefore that the reaction between the phenolic OH of the PBA-a and the carbonyl group of the BTDA could occur to form ester linkage as evidenced by the observed peak in the spectrum at 1730 cm^{-1}. Generally, IR spectra for esters feature an intense band in the range 1730-1750 cm^{-1} of its C=O stretching band. This peak varies slightly depending on the functional groups attached to the carbonyl. For example, a benzene ring or double bond in conjugation with the carbonyl will bring the wavenumber down about 30 cm^{-1}. In addition, the characteristic absorption band of ester linkage C–O band at 1250-1310 cm^{-1} was observed. However, there was no frequency shift in the benzophenone carbonyl band near 1665 cm^{-1} indicating that the carbonyl group between the two phenyl rings in the BTDA did not participate in any chemical reaction [48]. Furthermore, the carboxylic acid occurred after thermal curing of the BA-a:BTDA mixture can be followed by monitoring the appearance band at 1613 cm^{-1} due to C=O stretching of the free acid [49]. In addition, carboxylic acid shows characteristic C–O stretching, in-plane and out-of-plane, and O–H bending bands at, 1283 cm^{-1}, 1425 cm^{-1} and 928 cm^{-1}, respectively [48]. Thus, the PBA-a/BTDA copolymer was formed from the combination of BA-a resin and BTDA via ester linkage formation as shown in scheme 5.1 which was expected to enhance crosslink density in the resulting hybrid polymer network. Previously studied in anhydride-cured epoxy resin systems [50], the ester linkage formation has also been reported. FT-Raman analysis revealed that curing propagation mainly occurs by polyesterification between epoxide and anhydride groups. The decrease of epoxide ring breathing vibration at 1260 cm^{-1} and anhydride ring followed by means of 1860 cm^{-1} result in the relative increase of new band observed at 1734 cm^{-1} due to ester group formation upon cure [50].

5.1.2 Network formation by thermal cure of PBA-a/BTDA copolymers

After thermal cure stages, a transparent brown PBA-a and red brown PBA-a/BTDA copolymer samples were obtained. The appearances of the cured PBA-a/BTDA copolymer samples are shown in Fig. 5.2. We can see that a PBA-a sample of about 100 μm thick is rather brittle, and can not be bent further than as shown in Fig. 5.2(a). Whereas the homogeneous samples of all the PBA-a/BTDA copolymers of the same thickness as illustrated Fig. 5.2(b)-5.2(d) showed a remarkable improvement in their flexibility as recently reported in our patent [51]. The flexibility enhancement of the PBA-a/BTDA copolymer samples maybe due to additional ester linkages, structurally flexible functional group, formed in the polybenzoxazine network as a result described in benzoxazine containing polyester by Tuzun et al [49]. In addition, the great flexibility showed a similar trend for the PBA-a/BTDA copolymers in Fig. 5.2(b)-5.2(d) with that of the commercial polyimide films such as Kapton films [52] and UPILEX-s film [53].

5.1.3 Dynamic mechanical properties

The Storage modulus that provides the material stiffness of the PBA-a/BTDA copolymer samples at a glassy state region reflecting their molecular rigidity is depicted in Fig. 5.3. From this figure, we can clearly see that the storage modulus of the PBA-a/BTDA copolymers was higher than that of the neat PBA-a and the values increased with the BTDA contents. The room temperature modulus at 25^{o}C of the copolymers exhibited the values in the ranges of 2.63-2.94 GPa whereas that of the neat PBA-a was about 2.57 GPa. We can see that the storage modulus of the PBA-a/BTDA copolymers is approximately the same as that of the polyimide film systems (i.e. in the range 2.3-3.0 GPa) such as *s*-BPDA/ODA, ODPA/ODA, PMDA/ODA [54], or fluorinated polyimide [55]. However, some of polyimide films, i.e., UPILEX-s, show tensile modulus as high as 9.1 GPa at 25^{o}C and 42% for ultimate elongation [53]. From the same figure, it was obvious that the modulus in the rubbery plateau of the PBA-a/BTDA copolymer samples also increased with the content of the BTDA. This result suggested that an addition of the BTDA resulted in a substantial enhancement in crosslink density of the PBA-a/BTDA copolymers from additional ester linkage as explained in the previous section. For a tight network structure i.e. rubbery plateau modulus greater than 10^{7} Pa such as in our case, the non-Gaussian character of the polymer network becomes more and more pronounced and the equation from theory of rubbery elasticity is no longer applicable. The approximate relation expressed in the equation below proposed by Nielsen [56, 57] is thus preferred and is reported to better describe the elastic properties of dense network e.g. in epoxy systems [58-60]. As a consequence, a crosslink density of these copolymer networks, ρ_x, can be estimated from a value of the equilibrium shear storage modulus in the rubbery region (G'_e) which equals to $\frac{E'_e}{3}$ as followed

$$\log\left[\frac{E'_e}{3}\right] = 7.0 + 293\left(\rho_x\right) \tag{5.1}$$

Where E'_e (dyne/cm^{2}) is an equilibrium tensile storage modulus in rubbery plateau, ρ_x (mol/cm^{3}) is crosslink density which is the mole number of network chains per unit volume of the polymers.

The calculated crosslink density clearly increased with an increase in BTDA in the copolymers as shown in Fig. 5.4. In theory, higher crosslink density of the polymer network can lead to higher storage modulus and glass transition temperature (T_g). In addition, the increase in modulus may be due to various kinds of possible hydrogen bonds between hydroxyl or amine groups in polybenzoxazine and the carbonyl group or hydroxyl group in carboxylic acid. Moreover, in Fig. 5.4, as the BTDA contents in the PBA-a/BTDA copolymers increased, the obtained slope of the storage modulus in the glassy state against temperature was less steep. This is due to the lower degree of molecular mobility of the more rigid PBA-a/BTDA copolymers compared to the PBA-a at the corresponding temperature. In other words, enhancement in thermal stability of PBA-a/BTDA systems was observed comparing with the neat PBA-a.

All PBA-a/BTDA copolymer samples are homogeneous and transparent, implying that no phase separation domain formed at the scale exceeding the wavelength of visible light. To verify the miscibility or co-cross-linking of the copolymers, the PBA-a/BTDA copolymer samples were subjected to thermal analysis by examining T_g characteristic. From an inset of Fig. 5.4, the T_g of PBA-a determined from the maximum of loss modulus curve in DMA experiment was about 178^{o}C and the value was found to be substantially enhanced by blending with the BTDA. All of the fully cured PBA-a/BTDA copolymer samples showed only single T_g ranging from 207^{o}C to 263^{o}C. This characteristic confirmed a presence of a single phase material in these copolymers. Additionally the copolymer of BA-a:BTDA at a mol ratio of 1.5:1 exhibited a maximum value in T_g. From the results, the optimal network formation reaction of the copolymer clearly required greater moles of benzoxazine monomers than those of the BTDA i.e. not a 1:1 molar ratio. This is likely due to an ability of the benzoxazine monomers to react among themselves (self-polymerizability) besides their ability to react with the dianhydrides. As a consequence, the consumption of the benzoxazine monomers tended to be greater than that of the dianhydrides in order to form a perfect network.

5.1.4 Nanoindentation behavior

Local hardness on surface, which is generally investigated as one of the most important factor that relates to wear resistance of a material, can be characterized using nanoindentation. The measurement is a powerful tool for probing mechanical property of a material in small volume. Fig 5.5 depicts surface hardness (H) at room temperature (25^{o}C) of PBA-a/BTDA copolymer samples as a function of BTDA content. From the results, we can see that the hardness of the PBA-a/BTDA copolymer samples initially increased with the BTDA contents in a range of 4:1 to 1.5:1 mol ratios (BA-a:BTDA) and then decreased gradually with further addition of the BTDA. The ultimate hardness (465±7.7 MPa) for the copolymer sample of BA-a:BTDA at a mol ratio of 1.5:1 exhibits 43% increment compared to the neat PBA-a (326±11.5 MPa). This significant improvement in hardness of the PBA-a/BTDA copolymers was attributed to a greater molecular rigidity from the presence of the BTDA in the PBA-a. The result was consistent with the enhancement in the glass transition temperature and the glassy state modulus of the copolymer with the amount of the BTDA discussed previously. Furthermore, a relationship between the hardness and the T_g values for the copolymers was illustrated as an inset in Fig. 5.5. A fairly good linear relationship between the hardness value at room temperature and the T_g between 178^{o}C and 263^{o}C was observed in the form of the following equation,

$$H = kTg + C \tag{5.2}$$

where C = -82.27 MPa and k = 0.92 MPa/K, the regression coefficient being 0.9249. This type of correlation was also found and reported by Fakirov et al. [61] in the system of amorphous polymers,i.e., polyester.

However, in regard to the limitations of the relationship between hardness and T_g in Eq. (5.2), it seems worth recalling that it is derived from data obtained from measurements carried out at room temperature (25^{o}C). It is to be expected that the constant C will count on the temperature of relative measurement to T_g of the samples. This implies that to obtain a more fundamental relationship, one has to perform measurements at various temperatures and produce a T_g-scaled law of wider applications as suggested by Fakirov et al., also [61].

5.1.5 Thermal stability investigation

TGA curves of the neat PBA-a and PBA-a/BTDA copolymers are depicted in Fig. 5.6 and the degradation temperatures (T_d) at 5% weight loss under nitrogen atmosphere of the copolymers with different BTDA contents are displayed in Fig. 5.7. As seen in the Fig. 5.7, the T_d of the copolymer was shifted to a higher value than that of the neat PBA-a. The presence of the BTDA, therefore, helps enhance the T_d of the neat PBA-a. The maximum T_d of 364^{o}C belonged to the copolymer sample of BA-a:BTDA at mol ratio 1.5:1 while the T_d of the BTDA and the neat PBA-a was measured to be about 317^{o}C and 339^{o}C, respectively. The formation of an additional ester linkage between the carbonyl group in the BTDA and hydroxyl group of the neat PBA-a was found to effectively improve the degradation temperature of the resulting PBA-a/BTDA copolymers. In addition, the higher crosslink density and the presence of an aromatic structure of the BTDA in the PBA-a could possibly suppress segmental decomposition via gaseous fragments thus providing an observed enhancement in T_d of the samples.

Char yield values, the percent residue at 800^{o}C, of the PBA-a/BTDA copolymer samples are also determined from the TGA thermograms in Fig. 5.6. A remarkable improvement of char yield was clearly observed in the copolymers i.e. the char yields of all copolymers showed the values significantly greater than that of the neat PBA-a. In particular, the cured copolymer sample of BA-a:BTDA at the optimal mol ratio of 1.5:1 was found to render an ultimate char value compared to other compositions i.e. as high as 61% which was disclosed in our patent [36], while those of the neat PBA-a and the BTDA were 38% and 2.5%, respectively. Similar substantial enhancement in char yield formation was also reported in the PI/PBA-a hybrid systems [22] PBA-a/SPI systems [62]. However, the char yield at 800^{o}C under nitrogen atmosphere of some of benzoxazine containing polyester systems [49], i.e. poly(benzoxazine-carboxyterephthalate), was reported with less than 48% compared to that of the copolymer sample of BA-a:BTDA = 1.5:1 mol ratio sample. In principle, the higher char residue of the copolymer of BA-a:BTDA at the mol ratio of 1.5:1 should provide a sample with enhanced flammability. Char yield of a material can be used to estimate limiting oxygen index (LOI) according to Van Krevelen and Hoftyzer equation [63,64]. Thus polybenzoxazine and the PBA-a/BTDA copolymers can be classified in the self-extinguishing category.

5.2 Effect of dianhydride types on thermomechaical properties of polybenzoxazine modified with dianhydrides

5.2.1 Curing behavior by thermal cure of PBA-a:dianhydride copolymers

Bishenol-A-aniline based benzoxazine resin (BA-a) containing BTDA type aromaticcarboxylic dianhydride at BA-a:BTDA = 1.5:1 mol ratio was selected to examine the curing reaction by differential scanning calorimetry (DSC) as displayed in Fig. 5.8 From the DSC thermograms as line (a) in Fig. 8, after vacuum drying at 80^{o}C, BA-a:BTDA mixture showed endothermic peak at 200^{o}C which corresponded to boiling point of NMP solvent (Bp = 202^{o}C). This endothermic peak decreased with an increase of heat treatment temperature, and completely disappeared after heat treatment at 150^{o}C as line (b) in Fig. 5.8. This implied that the NMP solvent was completely removed from the BA-a:BTDA mixture at this heat treatment stage. Furthermore, the BA-a:BTDA mixture possessed an exothermic peak at 245^{o}C as line (e) in Fig. 5.8. The area under the exothermic peak was observed to decrease as the cure temperature increased, and completely disappeared after curing at 240^{o}C. This suggested that the fully cured stage of BA-a:BTDA = 1.5:1 mol ratio was achieved at up to 240^{o}C heat treatment. Additionally, we obtained similar fully cured samples of BA-a:PMDA = 1.5:1 mol ratio as line (f) in Fig. 5.8 and BA-a:s-BPDA = 1.5:1 mol ratio as line (g) in Fig. 5.8 after the same heat treatment up to 240^{o}C.

After thermal curing at elevated temperature up to 240^{o}C, the obtained thickness of the transparent PBA-a:PMDA, PBA-a:s-BPDA, and PBA-a:BTDA films was about 100 μm as shown in Fig. 5.9(b)-(d). Interestingly, all of PBA-a:PMDA, BA-a:s-BPDA, and BA-a:BTDA copolymer films exhibited greatly improved toughness compared to the neat PBA-a (Fig. 5.9(a)) as can be seen in Fig. 5.9(b)-5.9(d). The flexibility enhancement of all copolymer samples due to additional ester linkages, structurally flexible functional group, formed in the PBA-a network as a result quoted in previous publications [49,65]. Furthermore, the tensile properties, e.g. tensile modulus, tensile strength and elongation at break, are displayed in Table 5.1. From the table, we can see that the tensile modulus of all copolymer films were slightly higher than that of the neat PBA-a. Interestingly, tensile strength and elongation at break of the neat PBA-a were found to increase with an addition of PMDA or s-BPDA or BTDA dianhydrides. Especially, the tensile strength of PBA-a:aromatic carboxylic dianhydride copolymer films were observed to be about three times greater than that of the neat PBA-a. This behavior was attributed to ester linkage formation in copolymer structures.

5.2.2 Fourier transform infrared spectroscopy investigation

Chemical structures of BA-a, PBA-a, dianhydride modifiers, and their network formation reactions between the PBA-a and those dianhydride modifiers were studied by FTIR spectroscopic technique. The FTIR spectra of BA-a resin and the PBA-a are previously reported in details [22,66,67]. Characteristic absorption bands of the BA-a resin were found at 1232 cm^{-1} assigned to C–O–C stretching mode of oxazine ring whereas the band around 1497 cm^{-1} and 947 cm^{-1} were attributed to the tri-substituted benzene ring. After the curing phenomenon proceeded, an infinite three dimensional network was formed from benzoxazine ring opening by the breakage of C–O bond and then the benzoxazine molecule transformed from a ring structure to a network structure. During this process, the backbone of benzoxazine ring, the tri-substituted benzene ring around 1497 cm^{-1}, became tetra-substituted benzene ring centered at 1488 cm^{-1} and 878 cm^{-1} which led to the formation of a phenolic hydroxyl group-based polybenzoxazine (PBA-a) structure. In addition, an indication of ring opening reaction of the BA-a resin upon thermal treatment could also be observed from the appearance of a broad peak about 3300 cm^{-1} which was assigned to the hydrogen bonding of the phenolic hydroxyl group formation. The chemical transformation of BA-a:PMDA, BA-a:s-BPDA, and BA-a:BTDA at 1.5:1 mol ratio upon thermal curing was investigated and the resulting spectra are shown in Figs 5.10(a)-5.10(c). The important characteristic infrared absorptions of the neat PBA-a structure were clearly observed as above mentioned. On the other hand, the aromatic carboxylic dianhydride, i.e. PMDA, s-BPDA and BTDA, may be identified by a distinctive carbonyl band region. From the Fig. 5.10(a)-5.10(c), the spectra of all aromatic carboxylic dianhydrides provided the strong carbonyl characteristic absorption peaks with component in the 1860 cm^{-1} and 1780 cm^{-1} region. Moreover, all dianhydrides also showed a strong C–O stretching band in range of 1300-1100 cm^{-1} [48,65]. After fully cured stage, the new absorption bands of PBA-a:PMDA, PBA-a:s-BPDA, and PBA-a:BTDA copolymers at 1.5:1 mol ratio was observed. The phenomenon was ascribed to the appearance of carbonyl stretching bands of ester linkage [68]. From the PBA-a:aromatic carboxylic dianhydride spectra in Fig. 5.10(a)-5.10(c), we can see that the carbonyl stretching bands of aromatic carboxylic dianhydride at 1860 cm^{-1} and 1780 cm^{-1} completely disappeared. It was suggested that the reaction between the phenolic hydroxyl group of the PBA-a and the anhydride group of the aromatic carboxylic dianhydrides could occur to form ester linkage as evidenced by the observed peak in the spectrum at 1730 cm^{-1}. In general, IR spectra for esters exhibit an intense band in the range 1750-1730 cm^{-1} of its C=O stretching band. This peak varies slightly depending on the functional groups attached to the carbonyl with exemplification of a benzene ring or double bond in conjugation with the carbonyl which will bring the wavenumber down about 30 cm^{-1}. Furthermore, the carboxylic acid occurred after thermal curing of the PBA-a: aromatic carboxylic dianhydride mixture can also be followed by monitoring a band at 1650-1670 cm^{-1} [69] and 1613 cm^{-1} [49] due to C=O stretching. In addition, carboxylic acid shows characteristic C–O stretching, in-plane and out-of-plane, and O–H bending bands at 1320-1210 cm^{-1}, 1440-1395 cm^{-1} and 960-900 cm^{-1}, respectively [48,70]. As a consequence, we proposed a reaction model of these PBA-a:aromatic carboxylic dianhydride copolymers as shown in Scheme 5.2. The reaction mechanism was similar to the esterification of di-(2-ethylhexyl) phthalate and hydroxyl group of allyl alcohol [71] as well as the reaction between BTDA dianhydride and hydroxyl group of 2-hydroxyethyl acrylate [72]. Moreover, the ester linkage formation in anhydride-cured epoxy resin systems has also been reported [47,50]. FT-Raman analysis revealed that curing propagation of the epoxy-anhydride system mainly occurs by polyesterification between hydroxyl group of the ring-opened epoxide and anhydride groups. The decrease of epoxide ring at 1260 cm^{-1} and anhydride ring at 1860 cm^{-1} resulted in a relative increase of a new band observed at 1734 cm^{-1} due to ester group formation upon cure [73].

5.2.3 Dynamic mechanical properties of PBA-a:diandydride copolymers

Viscoelastic properties of PBA-a:PMDA, PBA-a:s-BPDA, and PBA-a:BTDA copolymer films at a mole ratio of 1.5:1 were evaluated and storage modulus (E'), loss modulus (E'') and tanδ are illustrated in Figs. 5.11-5.13. Generally, the storage modulus demonstrates the deformation resistances of the material when external force is applied sinusoidally. The E' at room temperature (25^{o}C) of the PBA-a:aromatic carboxylic dianhydride copolymer systems shown in Fig. 5.11 exhibited values of 3.02 GPa for PBA-a:PMDA, 3.42 GPa for PBA-a:s-BPDA, and 2.94 GPa for PBA-a:BTDA, which are higher than that of the neat PBA-a i.e. 2.57 GPa. We can see that the storage modulus of all PBA-a:aromatic carboxylic dianhydride copolymers is approximately equal to that of typical polyimide films with a reported value in a range of 2.3-3.0 GPa such as in *s*-BPDA/ODA, ODPA/ODA, PMDA/ODA polyimides [54], fluorinated polyimide [55].

Fig. 5.12 displays T_g which shows the dimension stability, from the maximum point of a loss modulus curve, of the PBA-a:aromatic carboxylic dianhydride copolymers, i.e. PBA-a:PMDA, PBA-a:s-BPDA, and PBA-a:BTDA at a fixed mol ratio of 1.5:1. From the figure, PBA-a and its copolymers showed only single T_g which suggested all the PBAa:aromatic carboxylic dianhydride copolymer films were a homogeneous network and no phase separation occurred. The ultimate T_g value of the neat PBA-a was determined to be about 178^{o}C and that of the copolymers, i.e. PBA-a:PMDA, PBA-a:s-BPDA, and PBAa:BTDA, was found to be 300^{o}C, 270^{o}C, and 263^{o}C, respectively. That is the T_g value of PBA-a was significantly enhanced by an incorporation of all aromatic carboxylic dianhydrides. In addition, we can clearly see that the T_g of the copolymers is in the order of PBA-a:PMDA > PBA-a:s-BPDA > PBA-a:BTDA which is a similar trend as that found in aromatic carboxylic dianhydride-based polyimide films derived from those dianhydrides i.e. PMDA, s-BPDA, BTDA mixed with DADE [74] and with ODA [75]. This observed behavior is attributed to the nature of the stiffness/bulkiness of the dianhydride moieties and the bridging group in the dianhydrides which strongly affects T_g of the copolymers. From our result, it was found that T_g values of aromatic carboxylic dianhydride modified with polybenzoxazine were decreased according to the increase of structural flexibility of selected dianhydrides. As expected, the PBA-a:PMDA film showed the highest T_g due to the rigid pyromellitimide unit while the PBA-a:s-BPDA and the PBA-a:BTDA exhibited the lower T_g than that of the PBAa:PMDA due to the presence of a more flexibility bridging group, i.e., biphenyl and benzophenone units in a dianhydride structure [76,77]. Moreover, an enhanced crosslink density via ester linkage between phenolic hydroxyl group of PBA-a and anhydride group of dianhydride as depicted in FTIR spectra results in further T_g improvement of the copolymers.

Crosslink density values of the PBA-a and its copolymers i.e. PBA-a:PMDA, PBA-a:s-BPDA, and PBA-a:BTDA at an equal mole ratio of 1.5:1, calculated from equation (5.3) are 3981 mol/cm^3, 8656 mol/cm^3, 7664 mol/cm^3 and 7630 mol/m^3, respectively. It is evident that the crosslink density of the neat PBA-a was greatly enhanced by an addition of PMDA, s-BPDA or BTDA, corresponding to an enhancement in their T_g values discussed previously. An effect of crosslink density which is one key parameter on T_g of aromatic carboxylic diandydride modified PBA-a network can be accounted for using Fox-Loshaek equation [78].

$$Tg = Tg(\infty) - \frac{k}{M_n} + k_x \rho_x \tag{5.3}$$

where $Tg(\infty)$ is glass transition temperature of infinite molecular weight linear polymer, k and k_x are numerical constants, M_n is number average molecular weight which equals infinity in a crosslinking system (therefore, this term, $\frac{k}{M_n}$, can be neglected), (x is the crosslink density. From the equation, the higher the crosslink density, the greater the T_g of the copolymers, which was in excellent agreement with our DMA results.

Loss tangent (tan δ) of the PBA-a and their copolymers of various aromatic carboxylic dianhydride types is illustrated in Fig. 5.13. A peak height of tan δ of PBA-a:PMDA, PBA-a:s-BPDA, and PBA-a:BTDA at an equal mol ratio of 1.5:1 tended to decrease while the peak position of their copolymers clearly shifted to higher temperature. The results suggested that an increase in the crosslink density caused a restriction of the chain's segmental mobility in aromatic carboxylic dianhydride modified polybenzoxazine copolymers thus a more elastic nature of the copolymer films compared to the PBA-a. In addition, the width-at-half-height of tan δ curves was found to be broader in their PBA-a copolymers, which indicated a more heterogeneous network in the resulting copolymers due to a hybrid polymer network formation. Moreover, the obtained transparent copolymer films and the single tan δ peak observed in each copolymer suggested no macroscopic phase separation in these copolymer films.

5.2.4 Thermal Stability of PBA-a:Dianhydride Copolymers

Thermal stability of the PBA-a and their copolymers including PBA-a:PMDA, PBA-a:s-BPDA, and PBA-a:BTDA was investigated by thermogravimetric analysis (TGA). Fig. 5.14 compares TGA thermograms of the PBA-a and its copolymers in nitrogen atmosphere. From the figure, we can see that the degradation temperature (T_d) reported at 10 percent weight loss of the neat PBA-a was 361°C while the T_d of the copolymers increased in the order of PBAa:PMDA (426^{o}C) > PBA-a:s-BPDA (422^{o}C) > PBA-a:BTDA (410^{o}C). In other words, the order of thermal stability (T_d) with respect to aromatic skeleton of acid dianhydride component is phenylene unit > biphenyl unit > benzophenone unit. Furthermore, the T_d value of the neat PBA-a film was observed to significantly increase with an incorporation of aromatic carboxylic dianhydrides. In summary, the higher crosslink density and the presence of an aromatic structure of these aromatic carboxylic dianhydrides could suppress segmental decomposition via gaseous fragments of the neat PBA-a thus providing an observed improvement in T_d of the samples.

Another interesting feature in the TGA thermograms is an amount of carbonized residue or char yield at 800^{o}C of all samples shown in Fig. 5.14. The char yields of those copolymer films provided a value as high as 60% which is much greater than that of the neat PBA-a, i.e. 38%, implying that these copolymers possess excellent thermal stability. The high char yield value of these aromatic carboxylic dianhydride-modified polybenzoxazines in nitrogen could also be attributed to their greater aromatic content unit in the molecular structure [74,79] and enhanced crosslink density of the resulting copolymers. In principle, the greater the char yield, the higher the flame retardancy of the polymer. Therefore, these copolymers tended to provide a sample with potentially substantial improvement in their flame retardancy which was highly useful in some applications such as aviation, automotive, and electronic industries. Recently, polyimide derived from 1,4-bis(4-amino-2-trifluoromethylphenoxy) benzene systems studied by Li et al. [80] exhibited a char yield at 10% weight loss of 49% at 800^{o}C under nitrogen atmosphere which was attributed to the presence of high fluorine contents in the polymer backbone. In our research, the high char yields of aromatic carboxylic dianhydride modified PBA-a films did not require any presence of fluorine moieties in these copolymers. In addition, char yield's copolymers were also higher than that of the commercial polyimide films such as Kapton® H film (53%) and UPILEX® S film (48%) [81]. However, it is found that the improved char yield of aromatic carboxylic dianhydride-modified polybenzoxazine copolymer films is as high as that of polyimides derived from similar dianhydrides such as PMDA, s-BPDA/MCDEA and PMDA, s-BPDA/DAM [82].

5.3 High performance composites based on carbon fiber and dianhydride-modified benzoxazine resin systems

5.3.1 Effect of carbon fiber contents on properties of carbon fiber-reinforced PMDA-modified polybenzoxazine composites

5.3.1.1 Density of carbon fiber-reinforced PBA-a:PMDA composites at various carbon fiber contents

One of the quantification methods to evaluate the maximum packing of the carbon fiber-reinforced PMDA-modified polybenzoxazine composites can be evaluated by density measurement [83]. The maximum packing density of the composites was defined by the maximum actual density value, corresponding to the theoretical density. The actual density at room temperature calculated using Eq. (4.1) of the carbon fiber composites based on bisphenol-A/aniline benzoxazine resin (BA-a) at 1.5 mol and PMDA at 1 mol (BA-a:PMDA =1.5:1 mol) with a function of carbon fiber content is depicted in Fig. 5.15 and the theoretical densities of the carbon fiber composites are based on the density of carbon fiber of 1.75 g/cm^3 and the density of PMDA-modified bisphenol-A/aniline polybenzoxazine (PBA-a:PMDA copolymer) of 1.26 g/cm^3. From the figure, we can see that the actual density of all composites insignificantly reduced to be lower than the theoretical density. This characteristic may be due to the presence of a few voids as a defect which often occurs in the composite prepared by the solvent cast technique. Based on the result, the carbon fiber-reinforced PBA-a:PMDA composite at 65% by weight of carbon fiber provided the actual density value nearby the theoretical density of the composites than the other carbon fiber fraction.

5.3.1.2 Flexural properties of carbon fiber-reinforced PBA-a:PMDA composites at various carbon fiber contents

Flexural properties such as flexural strength and modulus of PMDA-modified polybenzoxazine composed of BA-a = 1.5 mol and PMDA = 1 mol reinforced with carbon fiber at different carbon fiber contents ranging from 60 to 80% by weight are shown in Table 2. From the table, the flexural strength represented an ability of materials to absorb maximum force at rapture of the composite increased with increasing carbon fiber content and reached to the highest flexural strength value, i.e. 652 MPa at 65% by weight of carbon fiber (57% by volume). In case of flexural modulus as seen in the Table 5.2, the car bon fiber composite showed the flexural modulus increased to be approximately 65 GPa with an incorporation of carbon fiber content at 65% by weight, and then the flexural modulus value slightly decreased at higher carbon fiber content. However, the flexural modulus and strength values, i.e. 61-64 GPa and 439-625 MPa, respectively, of the resulting carbon fiber composites were still high than 56.45% by volume carbon fiber-reinforced bisphenol-A based epoxy composites having 35 GPa for the flexural modulus and 365 MPa for flexural strength. [84].

5.3.1.3 Dynamic mechanical analysis (DMA) of carbon fiber-reinforced PBA-a:PMDA composites at various carbon fiber contents

Recently, DMA operated under fixed frequency over a range of temperature has grown as useful analytical techniques for the characterization of polymeric materials, such as homopolymers, copolymers, and composites [85,86]. The evaluation is based on the determination of the temperature dependence of the dynamic moduli, stress relaxation, mechanical loss, and damping phenomena. In this work, the effect of carbon fiber content on thermomechanical properties as dynamic moduli and mechanical loss of the PMDA-modified PBA-a matrix composed of BA-a = 1.5 mol and PMDA = 1 mol reinforced with various CF contents are depicted in Figs. 5.16-5.17.

Fig. 5.16 illustrates the storage modulus (E') as a function of temperature ranging from 30 to 300^{o}C of PMDA-modified PBA-a composed of BA-a = 1.5 mol and PMDA = 1 mol reinforced with difference carbon fiber contents ranging from 60 to 80% by weight. From the figure, the storage modulus (E') related to the stiffness of the composites expectedly increases with an increasing amount up to 65% by weight of carbon fiber. Beyond 75% by weight of carbon fiber, the storage modulus value slightly decreases. In addition, the storage modulus at 35^{o}C of the resulting carbon fiber composites having a carbon fiber content of 65% by weigh has a value up to 45.3 GPa which is very high compared to that of 70% by weight carbon fiber-reinforced bisphenol-A epoxy composite with a storage modulus value of 15 GPa [84]. Furthermore, the curve in transition region of the resulting carbon fiber composites is observed to be less steep when the fiber content is increased. This may be due to content of the carbon fiber which greatly restricts the motion of the polymer matrix molecules and imparts higher thermal stability to the composites.

Glass transition temperature (T_g) of PMDA-modified PBA-a composites reinforced with different carbon fiber contents ranging from 60 to 80% by weight can be obtained from the maximum point on the loss modulus curve as presented in Fig. 5.17 The T_g values of carbon fiber composites were determined as 234^{o}C, 237^{o}C, 235^{o}C, 230^{o}C, and 229^{o}C for the composite composed of 60 to 80wt% carbon fiber contents, respectively. It is clearly seen that the highest T_g was observed in carbon fiber composite based on 65% by weight of carbon fiber.

5.3.2 Effects of PMDA contents on properties of carbon fiber-reinforced PBA-a:PMDA composites

5.3.2.1 Thermomechanical properties of 65% by weight carbon fiber-reinforced PBA-a:PMDA composites at various PMDA mol ratios

Thermomechanical properties of the 65% by weight carbon fiber-reinforced PBA-a composite and the 65% by weight carbon fiber-reinforced PBA-a modified with PMDA composites at five mol ratios between BA-a and PMDA = 4:1, 3:1, 2:1, 1.5:1 and 1:1 are investigated. Storage modulus (E') values of the above composites as a function of temperature are shown in Fig. 5.18 From the figure, the storage modulus of 65% by weight of carbon fiber-reinforced PBA-a:PMDA composites at room temperature (35^{o}C) exhibited values in the range of 43-46 GPa, which are slightly higher than that of the 65% by weight of carbon fiber-reinforced PBA-a composite, i.e. 41 GPa. This observation indicated that the addition of PMDA can help improve the storage modulus of the carbon fiber-reinforced PBA-a:PMDA composites. This could be related to more benzene ring in PMDA molecular structure which enhances rigidity of the carbon fiber-reinforced PBA-a:PMDA composites. Moreover, the highest storage modulus of the PBA-a:PMDA reinforced with 65% by weight of carbon fiber content was observed to be 46 GPa which is clearly higher than that of 60% by volume of carbon fiber-reinforced 8,8'-bis(3,4-dihydro-3-pheny-2H-1,3-benzoxazine (abbreviated as 22Pa) composite with a value of 10 GPa [6].

Glass transition temperature (T_g) of the 65% by weight carbon fiber-reinforced PBA-a composite and the 65% by weight carbon fiber-reinforced PBA-a modified with PMDA composites at various mol ratios of PMDA are depicted in Fig. 5.19 The T_g determined from the maximum of loss modulus curve from dynamic mechanical analysis (DMA) of the 65% by weight carbon fiber-reinforced PBA-a composites was found to be about 183^{o}C while all of the PMDA-modified PBA-a composites reinforced with 65% by weight of carbon fiber showed the T_gs in the range of 203^{o}C to 237^{o}C. Moreover, it can be noticed that the highest T_g, i.e. 237^{o}C, observed from DMA thermograms belonged to the 65% by weight-carbon fiber-reinforced composite composed of BA-a:PMDA = 1.5:1 mol. From the results, the T_g value substantially enhanced with the incorporation of PMDA into the composites. This phenomenon is due to the presence of greater aromatic content and the increased crosslink density via ester linkage between hydroxyl group of PBA-a and anhydride group of PMDA in the copolymer structures [87].

Loss tangent (tanδ) of 65% by weight carbon fiber-reinforced PBA-a and 65% by weight carbon fiber-reinforced PMDA-modified PBA-a composites at various mol ratios of PMDA are illustrated in Fig. 5.20 We can see that a magnitude of tan δ decreased with an addition of PMDA and the peak shifted to high temperature. The results suggested that an increase in the crosslink density caused a restriction of the chain's segmental mobility in PBA-a:PMDA matrix thus a more elastic nature compared to the PBA-a. In addition, the incorporation of stiff fibers reduced the tanδ peak height by restricting the movement of polymer molecules.

5.3.2.2 Thermal stability of 65% by weight carbon fiber-reinforced PBA-a:PMDA composites at various PMDA mol ratios

Thermal stability, thermal degradation temperature (T_d) and char yield, of the 65% by weight carbon fiber-reinforced PBA-a and the 65% by weight carbon fiber-reinforced PBA-a:PMDA composites at various PMDA contents was evaluated by TGA at the programmed temperature range of 35^{o}C to 1000^{o}C. The TGA curves of all above composites are shown in Fig. 5.21 The thermal degradation temperatures at 10% weight loss (T_{d10}) of the 65% by weight carbon fiber-reinforced neat PBA-a composite was observed to be 404^{o}C whereas the 65% by weight carbon fiber-reinforced PMDA-modified PBA-a composites at various mol ratio between BA-a:PMDA = 4:1, 3:1, 2:1, 1.5:1 and 1:1 was ranging from 458^{o}C to 498^{o}C. However, the 65% by weight carbon fiber-reinforced PMDA-modified PBA-a composites exhibited higher degradation temperatures than that of the PBA-a:PMDA copolymer matrix. It is due to the effect of high degradation temperature of the reinforcing material as the carbon fiber. Furthermore, the greater T_d of the composites with higher amount of the PMDA fraction in the PBA-a:PMDA copolymer matrix. This is possibly due to the enhanced crosslink density of the PBA-a with an addition of PMDA as mentioned previously [87].

Another important feature in the TGA thermograms is the amount of carbonized residues or char yield at 800^{o}C of all composites which are related to the flammability of materials. The char yield was found to be 75.7% for the 65% by weight carbon fiber-reinforced neat PBA-a composite while the char yield of the 65% by weight carbon fiber-reinforced PBA-a modified with PMDA composites at various PMDA mol ratios systematically increased from 80.7% to 82.2%.

5.3.2.3 Limiting oxygen index (LOI) of 65% by weight carbon fiber-reinforced PBA-a:PMDA composites at various PMDA mol ratios

Ignitability and fire resistivity of composites can be characterized by a limiting oxygen index (LOI). The relative flammability is determined by adjusting the concentration of oxygen. The LOI value is the lowest oxygen gas concentration that must be present in an oxygen/nitrogen mixture for a material to burn. Table 5.3 indicates the LOI values of the 65% by weight carbon fiber-reinforced PBA-a composite and the 65% by weight carbon fiber-reinforced PBA-a:PMDA composites at various PMDA contents. From the figure, the LOI values of all carbon fiber-reinforced PBA-a:PMDA copolymers was found in range of 32.5-49.5 while that of the PBA-a reinforced with 65% by weight carbon fiber were 26. Therefore, the incorporation of the PMDA into the polybenzoxazine shows a significant effect on promoting the flame retardance of the carbon fiber composites. This is due to the fact that the char formed during combustion can act as a protective layer to prevent the oxygen diffusion to the surface. Consequently, more oxygen is needed for combustion. Interestingly, the LOI values of our carbon fiber composites are significantly higher than that of novel 9,10-dihydro-9-oxy-10-phosphaphenanthrene-10-oxide (DOPO)-based flame retardants in carbon fibre epoxy composites, i.e. 70% by weight carbon fiber-reinforced epoxy having LOI = 45.3-47.7 [88].

5.3.2.4 UL-94 vertical test of 65% by weight carbon fiber-reinforced PBA-a:PMDA composites at various PMDA mol ratios

UL-94 results of the 65% by weight carbon fiber-reinforced PMDA-modified PBA-a composites at various mol ratio between BA-a:PMDA = 4:1, 3:1, 2:1, 1.5:1, and 1:1 are presented in Table 5.4. Normally, the standard requirements of the sample thickness should be at least 3 mm. In our investigation, the carbon fiber composite thickness was prepared at 1 mm for having a more severe condition for the UL-94 vertical flame test. As the result from Table 5.4, the 65% by weight carbon fiber-reinforced PBA-a composite is classified as V-1 in the UL-94 vertical flame test which were higher than that of 70% by weight carbon fiber-reinforced epoxy (RTM6) composite (3 mm) classified as horizontal burning (HB), the lowest UL-94 classification. Interestingly, all 65% by weight-reinforced PBA-a:PMDA composites showed total after flame time (t_1+t_2 for the 5 specimens) to be less than 50 seconds which can be classified as V-0 in the UL-94 vertical flame test, the maximum flame resistant class of UL-94 vertical rating. As exemplification, the photographs of samples after the UL-94 vertical flame test are shown in Fig. 5.22(a)-(f).

Furthermore, an increasing of PMDA content resulted in reduced burning time, suggesting that an addition of the PMDA into the PBA-a matrix of the carbon fiber composites can help improve the fire resistance of the composite. This result is in good agreement with our previous work [68] reported that the char yield value of polybenzoxazine modified with dianhydrides copolymers were much higher than that of the neat PBA-a. In principle, the higher char residue of the copolymer can provide a sample with enhanced flammability because char formation can inhibit volatile products from diffusing to the flame and shield the polymer surface from heat and air [89].

5.3.2.5 Flexural properties of 65% by weight carbon fiber-reinforced PBA-a:PMDA composites at various PMDA mol ratios

Generally, the strength, modulus and mode of failure of fiber-reinforced composite depend on properties of constituents and interfacial interaction between the fiber and the matrix. However, the critical controlling mechanism identified for the composite quality was fiber interfacial wetting. A property that can indicate the fiber interfacial wetting of a considering carbon fiber-reinforced polybenzoxazine modified with PMDA is the bending characteristics.

Flexural properties of a composite are very important for structural applications, as it is comprised of both the tensile and compressive strength components of the composites. During flexural testing, upper part is dominated by compressive force and the lower part by tensile force in the longitudinal direction. It is reported that tensile response of the composite (rather than the compressive) has a critical influence on flexural strength [66]. Flexural properties of the 65% by weight carbon fiber-reinforced PBA-a and the 65% by weight-reinforced PMDA-modified PBA-a composites at mol ratios between BA-a:PMDA = = 4:1, 3:1, 2:1, 1.5:1, and 1:1 were examined. In Fig. 5.23, flexural strength values of the 65% by weight-reinforced PMDA-modified PBA-a composites were observed to be in the range of 637 MPa to 652 MPa. The values are slightly higher than the flexural strength value of the 65% by weight-reinforced PBA-a composite was determined to be 636 MPa. However, the flexural strength of carbon fiber composites in this work was found to be higher than that of 70% by weight carbon fiber-reinforced bisphenol-A epoxy composites with a published value of 488 MPa [90].

Moreover, the flexural modulus values of the 65% by weight-reinforced PMDA-modified PBA-a composites at various PMDA mol ratios depicted in Fig. 5.24 were also observed to slightly increase with an incorporation of PMDA into the PBA-a matrix having values ranging from 61 GPa to 65 GPa and the values are also higher than that of the 65% by weight-reinforced PBA-a composite, i.e. 55 GPa. The enhancement in the composite's flexural properties with PMDA addition was possibly due to the improved interfacial adhesion between the carbon fiber and the copolymer matrix with increasing PMDA content. In addition, the flexural modulus of the 65% by weight-reinforced PBA-a modified with PMDA composites showed a maximum value at a composite composed of BA-a:PMDA = 1.5:1 mol. It may possible due to an increase aromatic in structure of PMDA. The tendency is in good agreement with the results from DMA mentioned above.

5.3.2.6 Fracture surface of carbon fiber composites based on PBA-a modified with PMDA

Wettability of the PBA-a:PMDA copolymer matrix on the carbon fiber and interfacial adhesion between the fiber and the copolymer matrix have been inspected using scanning electron microscopic (SEM) technique. The micrographs show phase information and fracture characteristics reflecting the reasons why the mechanical properties have been changed and in turn determining the mechanical properties of polymeric composites.

The surface morphology of the carbon fiber and the fractured surfaces from flexural specimen test of the carbon fiber composites using a PBA-a copolymer matrix at a mol ratio between BA-a:PMDA = 1.5:1 are illustrated in Fig. 5.25 From Fig. 5.25(a), SEM micrograph indicates the relative smooth, defect-frees carbon fiber and also reveals the fibers' cylindrical morphology with a diameter about 8 microns. Furthermore, the surface fracture in the weft region and in the warp region of the 65% by weight-reinforced PBA-a:PMDA composites is displayed in Fig. 5.25(b) and Fig. 5.25.(c), respectively. From Fig. 5.25(b), the fracture surface in the weft region of the carbon fiber is extensively embedded with the PBA-a:PMDA copolymer. This implies that cohesive failure occurred in the PBA-a:PMDA copolymer matrix region due to the significant interfacial adhesion between the carbon fiber and the copolymer matrix. In addition, in Fig. 5.25(c), the pull-out length is short. This phenomenon confirmed that the carbon fibers were potentially adhered by the PBA-a:PMDA copolymer matrix, as can be seen from the pieces of matrix attached to the fiber. The results from the SEM micrographs agree well with the observed enhancement in mechanical properties of these composites.

Table 5.1 Tensile properties of PBA-a and aromatic carboxylic dianhydride-modified PBA-a copolymers

Samples (mole ratio)	Modulus (GPa)	Strength (MPa)	Elongation (%)
PBA-a	2.10	25	1.9
PBA-a:PMDA (1.5:1)	2.60	78	5.4
PBA-a:s-BPDA (1.5:1)	2.68	95	6.6
PBA-a:BTDA (1.5:1)	2.50	88	6.0

Table 5.2 Flexural properties of carbon fiber (CF)-reinforced PBA-a:PMDA composites at various carbon fiber contents.

Sample (wt%)	Flexural Strength (MPa)	Flexural Modulus (GPa)
CF/PBA-a:PMDA (60/40)	526 ± 18.68	61 ± 1.02
CF/PBA-a:PMDA (65/35)	625 ± 10.20	64 ± 0.99
CF/PBA-a:PMDA (70:30)	483 ± 18.46	63 ± 0.41
CF/PBA-a:PMDA (75/25)	449 ± 28.31	62 ± 0.68
CF/PBA-a:PMDA (80/20)	439 ± 11.32	62 ± 1.06

Note PBA-a:PMDA copolymer based on BA-a = 1.5 mol and PMDA = 1 mol

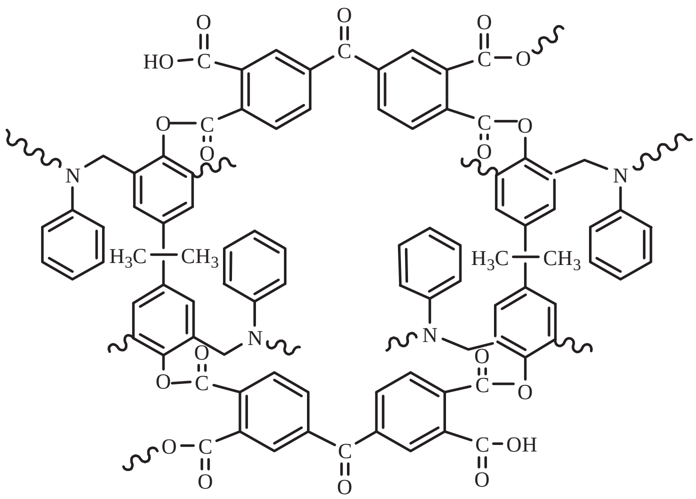
Table 5.3 The Limiting oxygen index (LOI) of the 65wt% carbon fiber-reinforced PBA-a:PMDA composites.

Samples	65wt% carbon fiber-reinforced PBA-a:PMDA composites at various mol ratio PBA-a:PMDA					
	1:0	4:1	3:1	2:1	1.5:1	1:1
LOI values	26.0	32.5	33	44	47	49.5

Table 5.4 UL-94 flame test of the 65wt% carbon fiber-reinforced PBA-a:PMDA composites at various PMDA mole ratios.

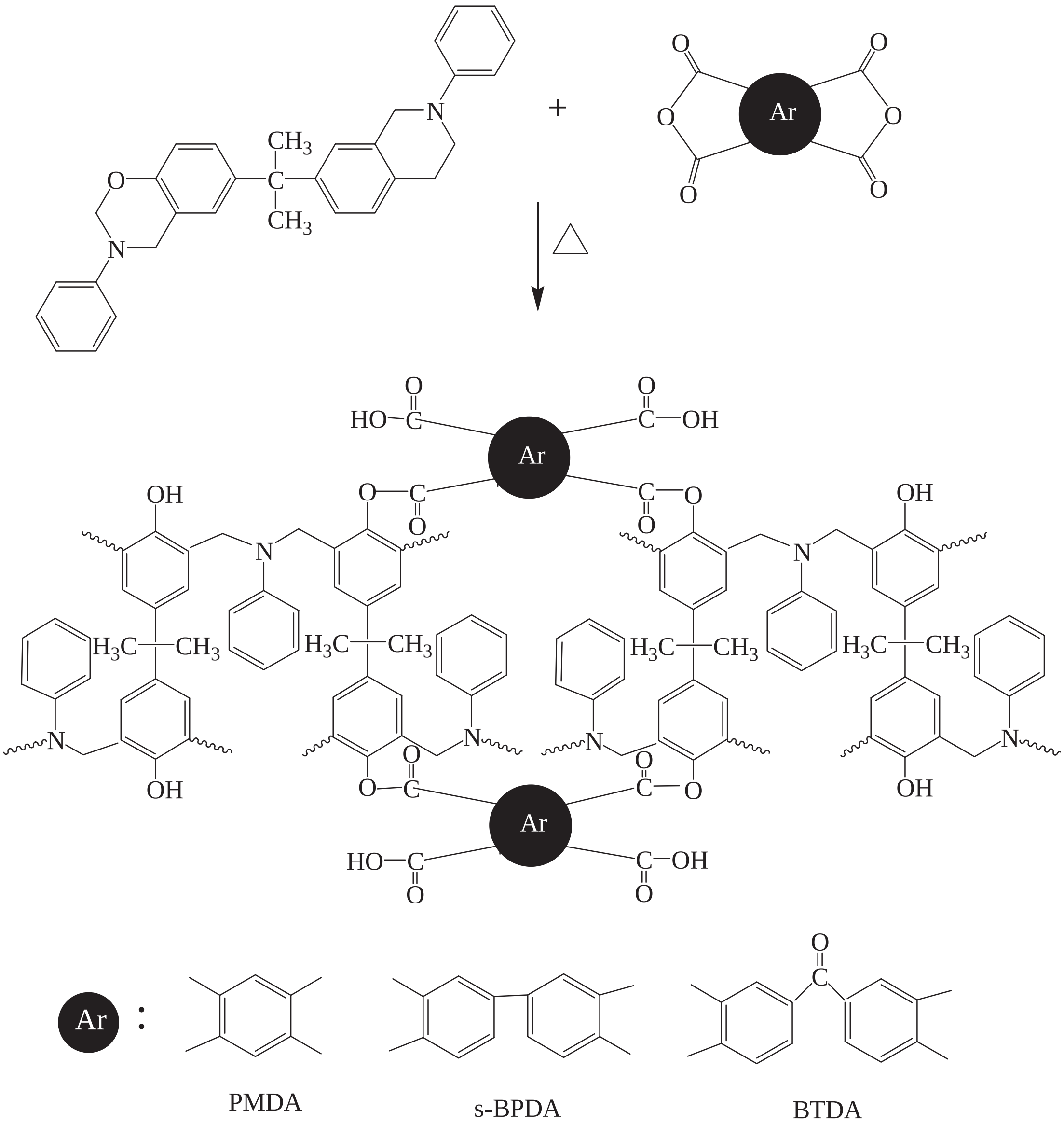
Criteria Conditions	CF/PBA-a:PMDA (mole ratio)					
	1:0	4:1	3:1	2:1	1.5:1	1:1
- Afterflame time for each individual specimen t1 or t2 (s)	12.0, 4.5	4.8, 3.5	1.9, 5.1	0.4, 3.4	0.4, 2.8	0, 0.8
- Total afterflame time for any condition set (s) (t1 + t2 for the 5 specimens)	82.7	41.9	31.1	23.5	16.2	4.1
- Afterflame plus afterglow time for each individual specimen after the second flame application (t2 + t3) (s)	4.5	3.5	5.1	3.4	2.8	0.8
- Afterflame or afterglow of any specimen up to the holding clamp	No	No	No	No	No	No
- Cotton indicator ignited by flaming particales of drops	No	No	No	No	No	No
UL-94 Classification	**V-1**	**V-0**	**V-0**	**V-0**	**V-0**	**V-0**

Note -Vertical flame test of 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios. (Thickness:~1mm.)



PBA-a/BTDA Copolymer

Scheme 5.1 A possible copolymerization between PBA-a and BTDA.



Scheme 5.2 Model reaction of dianhydride-modified polybenzoxazine copolymers.

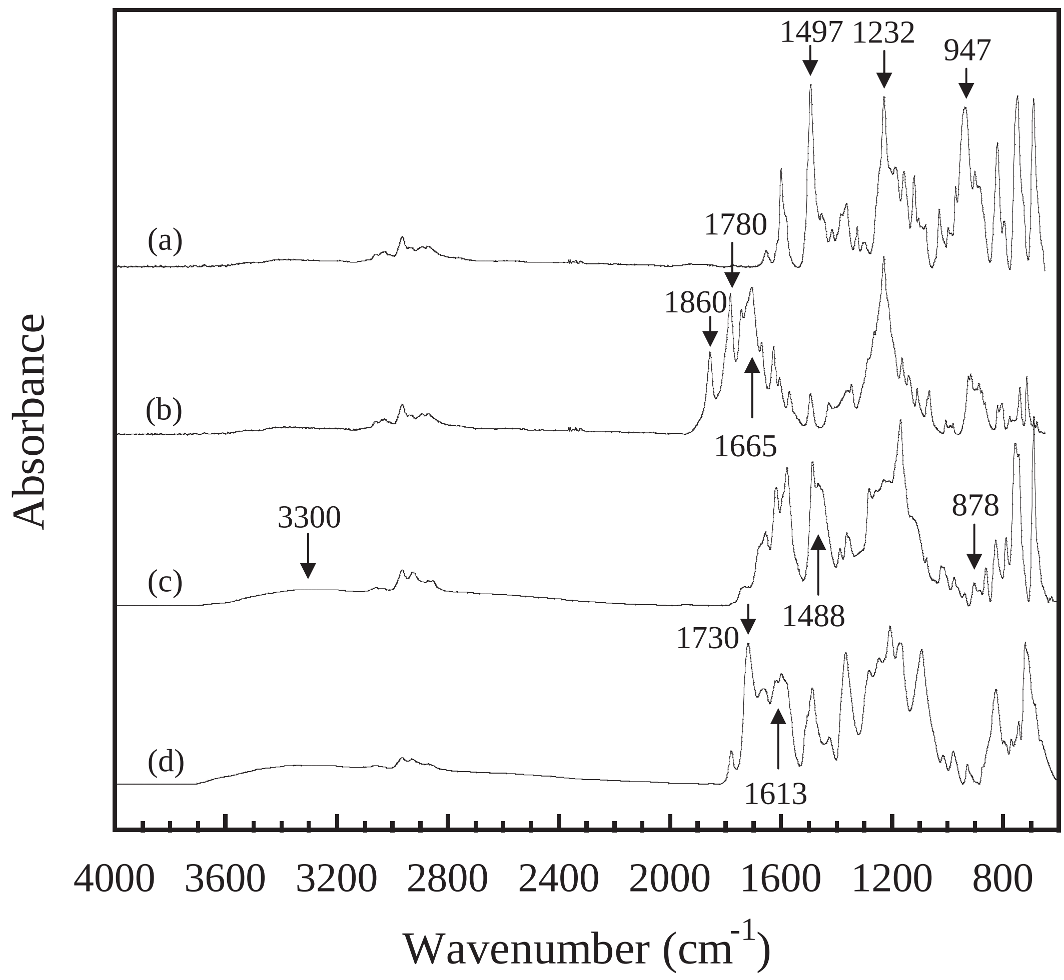


Fig. 5.1 IR spectra: (a) BA-a resin, (b) BTDA, (c) PBA-a, (d) BA-a:BTDA = 1.5:1 mol ratio

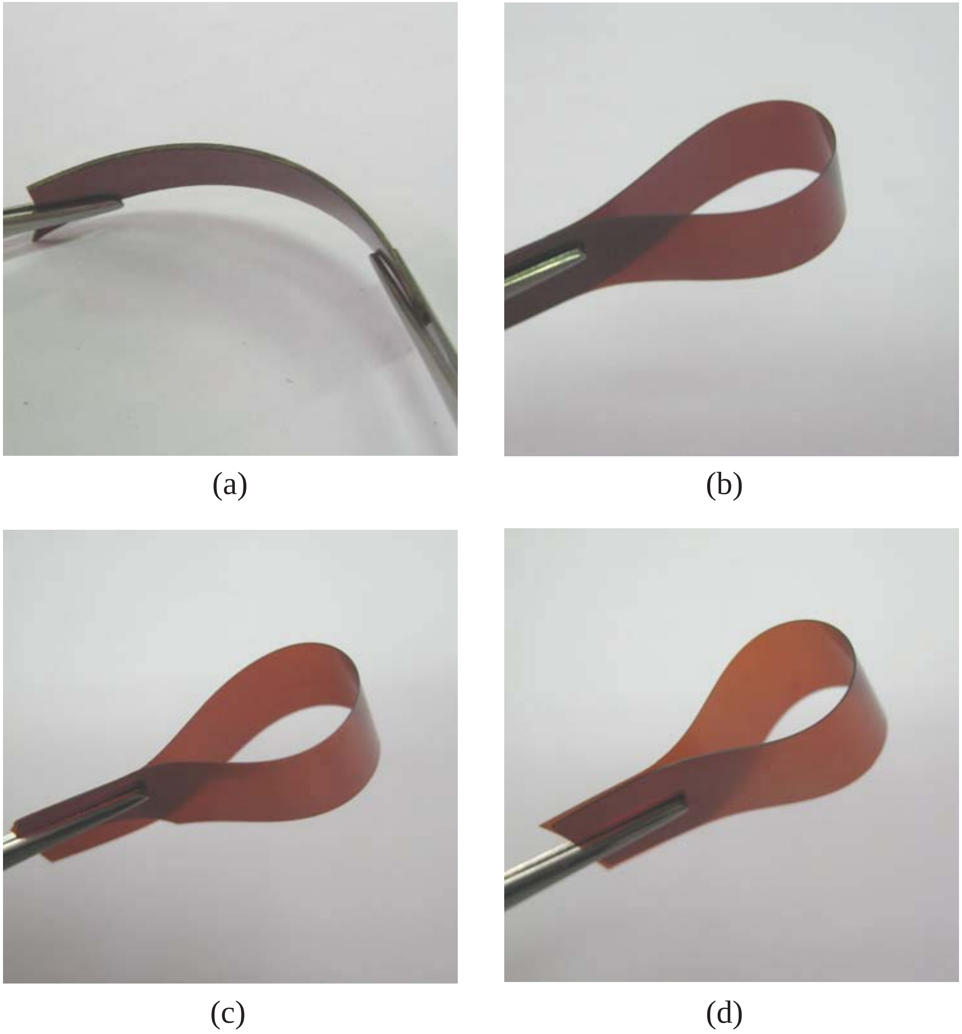


Fig. 5.2 Appearance of the fully cured PBA-a/BTDA copolymers at various BTDA mol ratio: (a) PBA-a, (b) BA-a/BTDA 4:1, (c) BA-a/BTDA 3:1, (d) BA-a/BTDA 1.5:1.

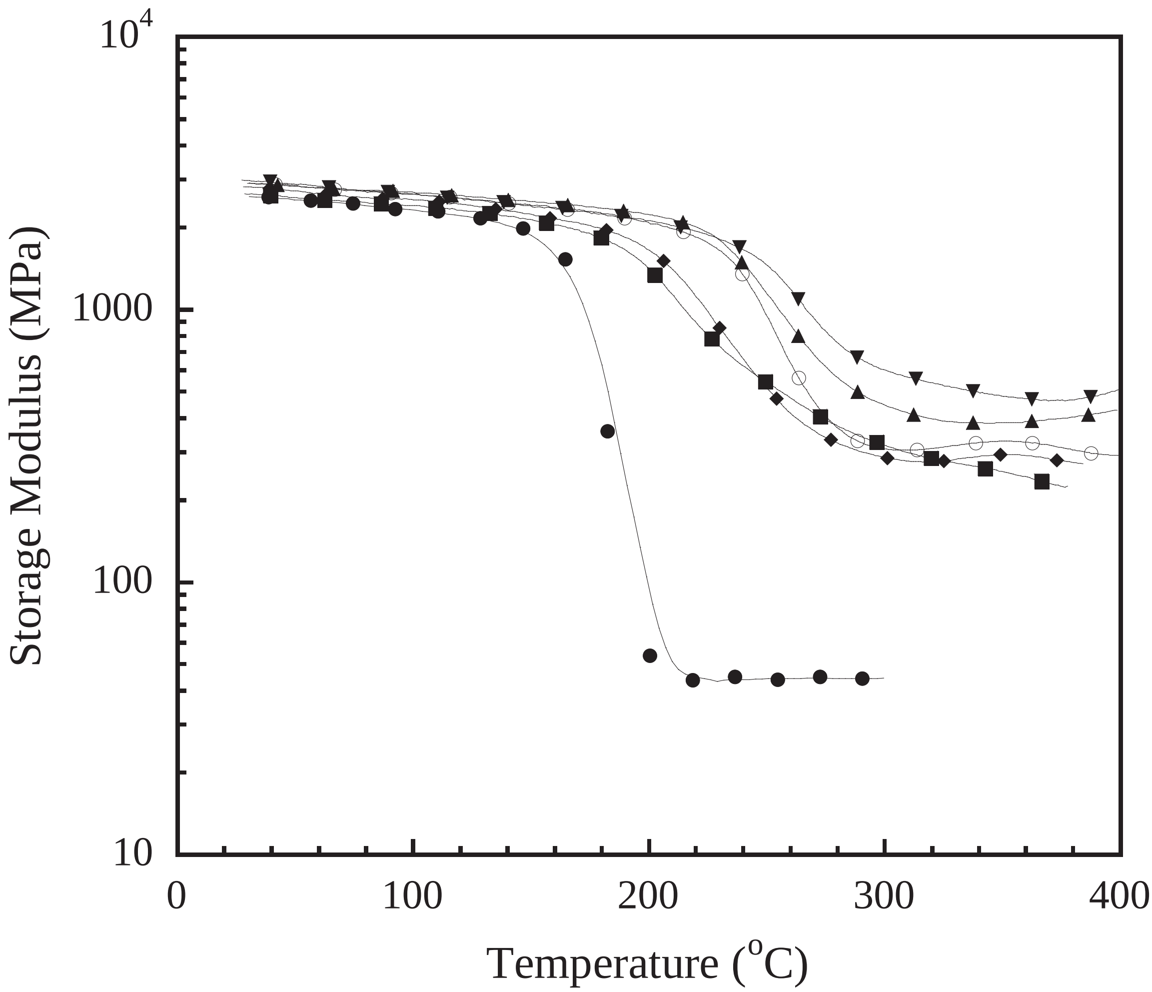


Fig. 5.3 Storage and loss modulus of PBA-a/BTDA copolymers as a function of temperature at different BTDA mole ratio: (●) PBA-a, (■) BA-a/BTDA 4:1, (♦) BA-a/BTDA 3:1, (▲) BA-a/BTDA 2:1, (▼) BA-a/BTDA 1.5:1, (○) BA-a/BTDA 1:1.

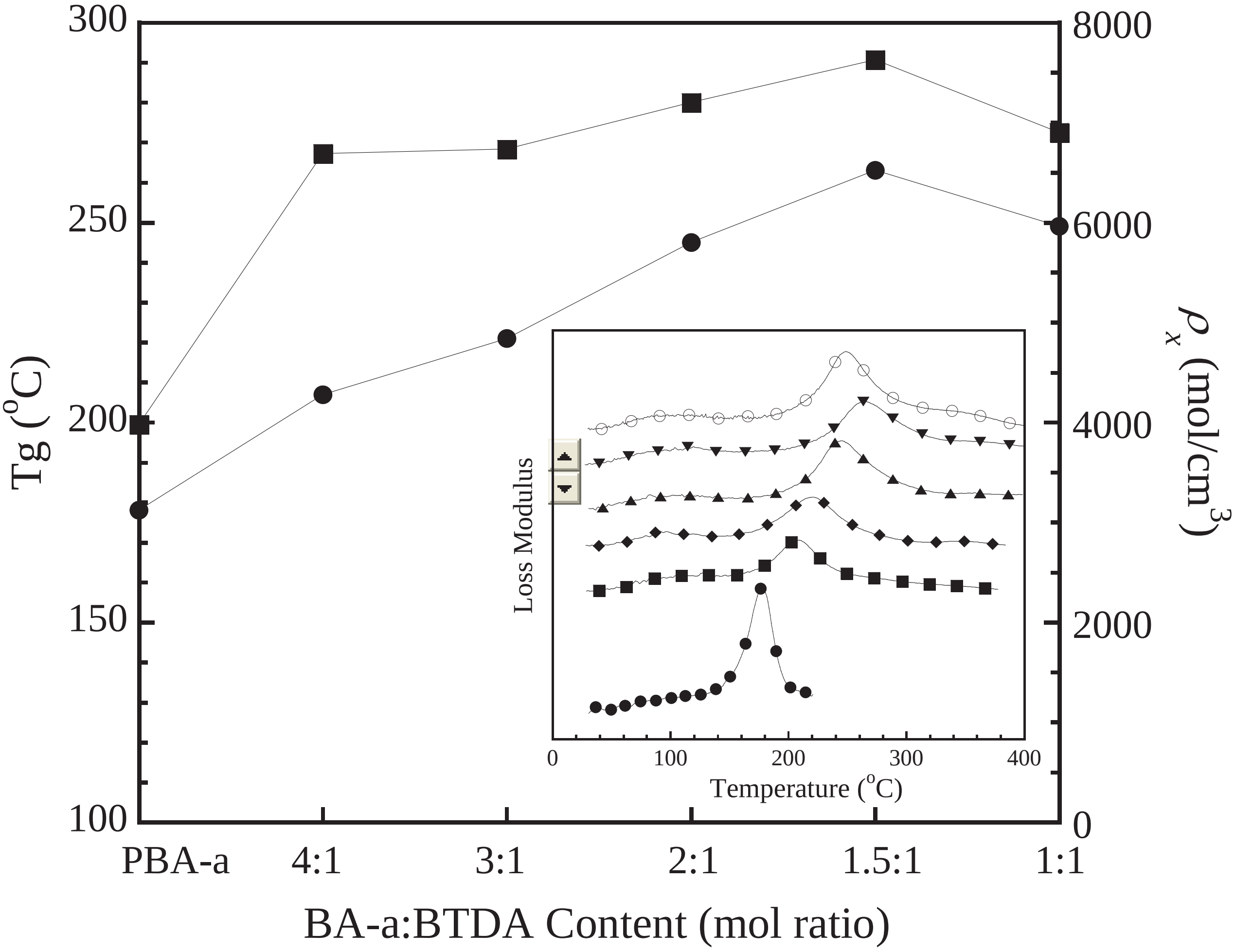


Fig. 5.4 Crosslink density (ρ_x) and glass transition temperature (Tg) at various BTDA mol ratio: (●) Tg, (■) ρ_x..

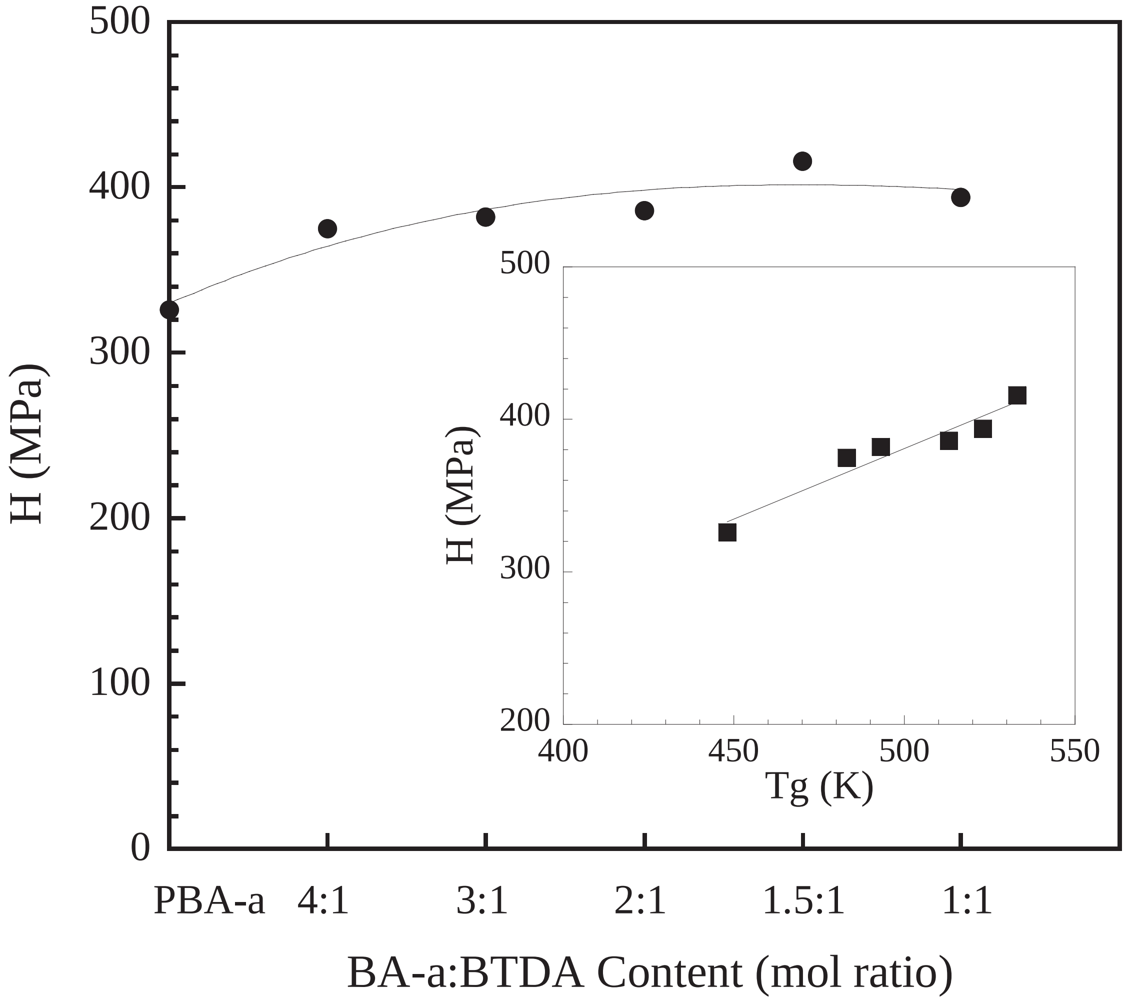


Fig. 5.5 Room temperature-measured microhardness (H) of PBA-a/BTDA copolymers at different BTDA mole ratio (●), and Relationship between the room temperature-measured microhardness (H) and T_g (■).

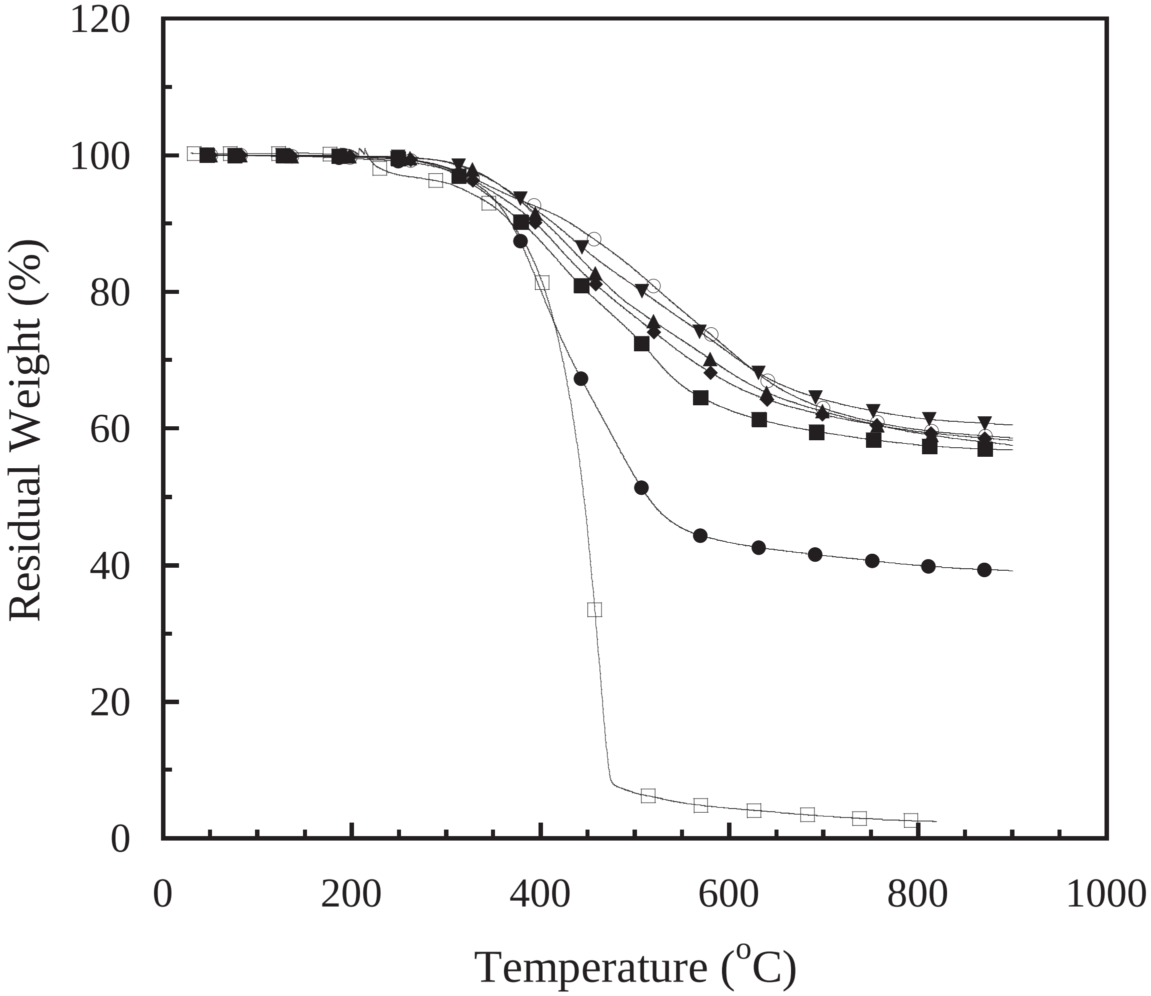


Fig. 5.6 TGA experiments of PBA-a/BTDA copolymers as a function of temperature at different BTDA mole ratio: (●) PBA-a, (■) BA-a/BTDA 4:1, (♦) BA-a/BTDA 3:1, (▲) BA-a/BTDA 2:1, (▼) BA-a/BTDA 1.5:1, (○) BA-a/BTDA 1:1, (□) BTDA.

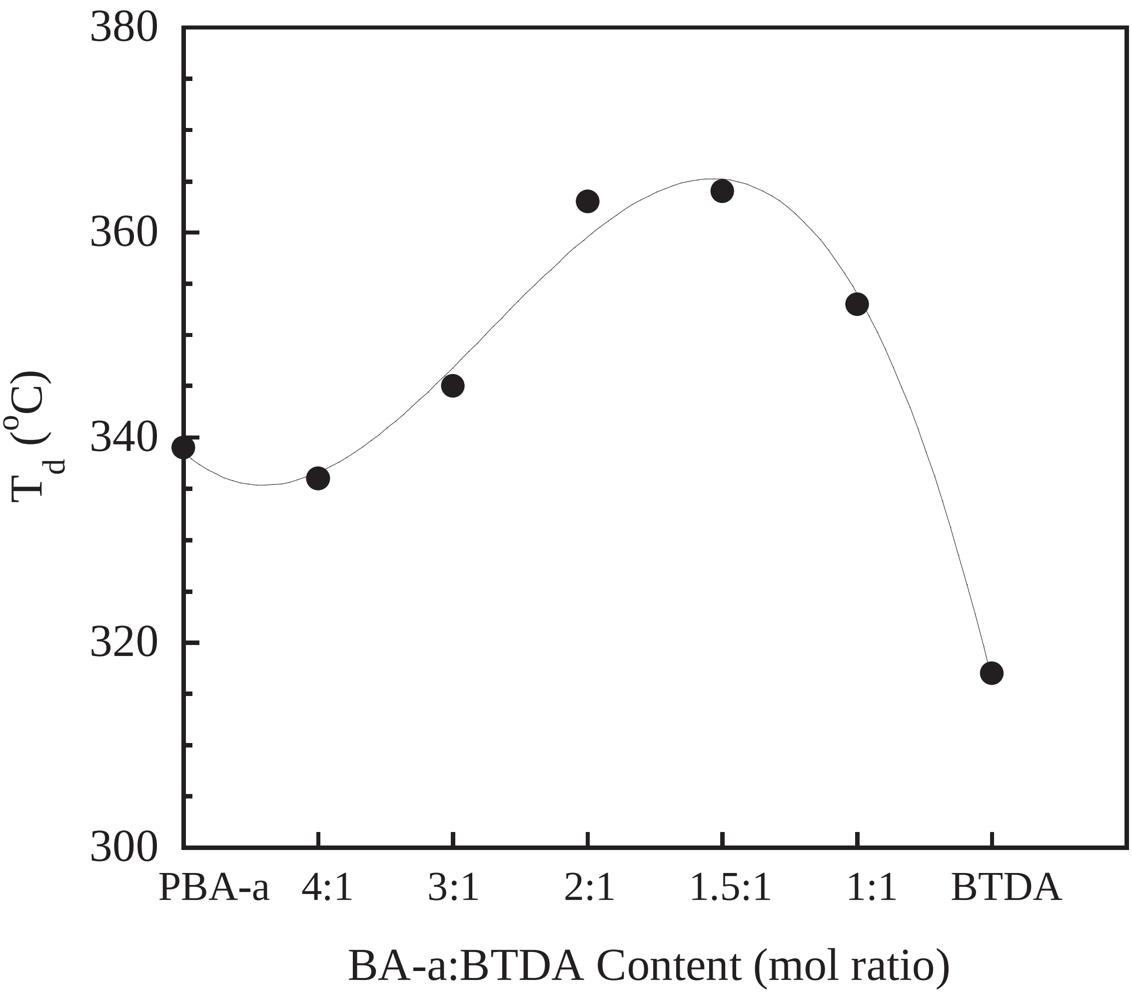


Fig.5.7 Degradation temperature at 5% weight loss under nitrogen atmosphere of PBA-a/BTDAcopolymers as a function of BTDA content.

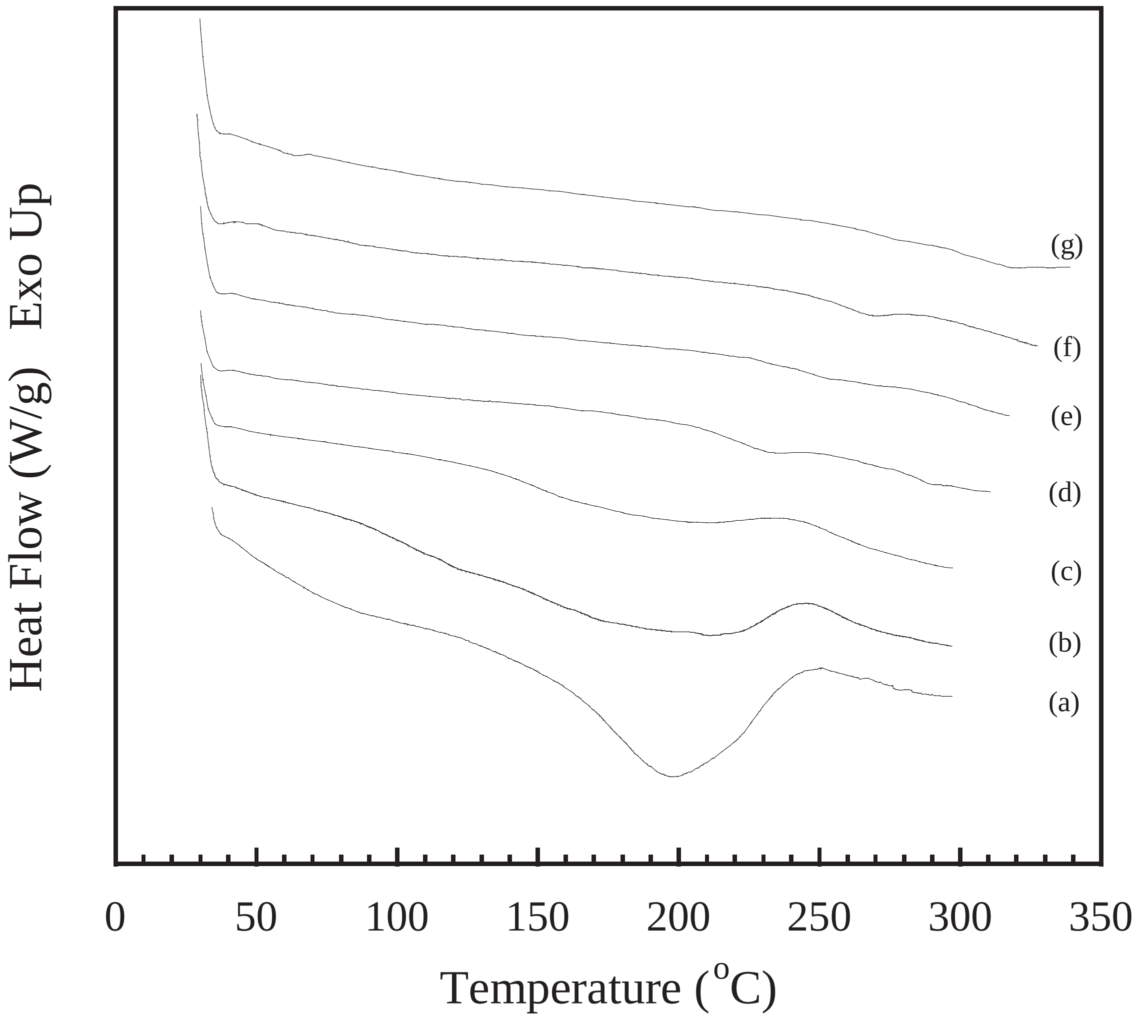
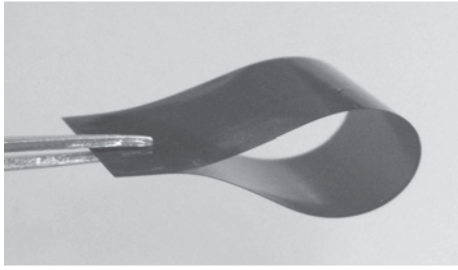
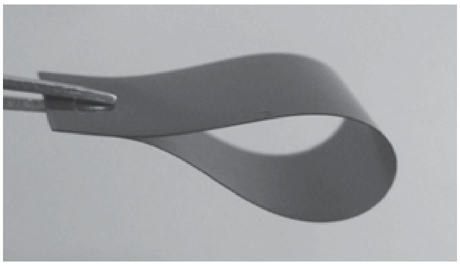


Fig. 5.8 DSC thermograms of the benzoxazine blending with BTDA at 1.5:1 mole ratio at various curing conditions: (a) 60°C, 80°C/24h (b) 60°C, 80°C/24h + 150°C/1h (c) 60°C,80°C/24h + 150°C, 170°C/1h (d) 60°C, 80°C/24h + 150°C, 170°C/1h + 190°C, 210°C/2h (e) 60°C, 80°C/24h + 150°C, 170°C/1h + 190°C, 210°C, 230°C/2h + 240°C/1h (f) 60°C, 80°C/24h + 150°C, 170°C/1h +190°C, 210°C, 230°C/2h + 240°C/1h (BA-a:s-BPDA = 1.5:1 mol ratio), (g) 60°C, 80°C/24h + 150°C, 170°C/1h + 190°C, 210°C, 230°C/2h + 240°C/1h (BA-a:PMDA = 1.5: 1 mol ratio).

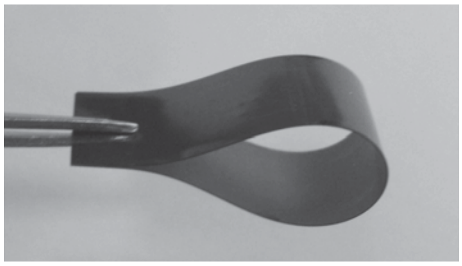
(a)



(b)



(c)



(d)

Fig. 5.9 Photographs of aromatic carboxylic dianhydride modified PBA-a films: (a) PBA-a, (b) PBA-a:PMDA, (c) PBA-a:s-BPDA, (d) PBA-a:BTDA.

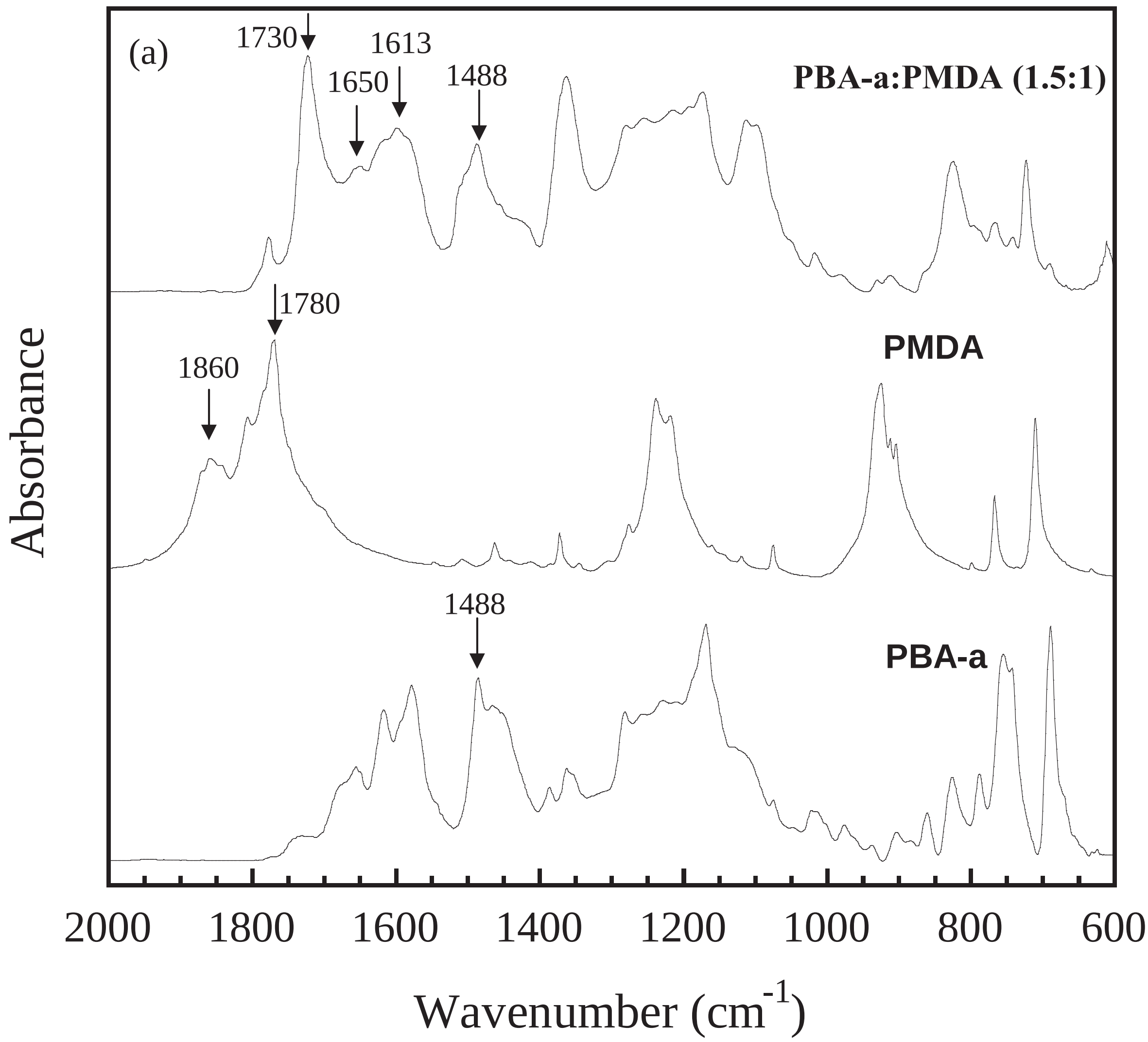


Fig. 5.10(a) FTIR spectra of PBA:PMDA = 1.5:1 mol.

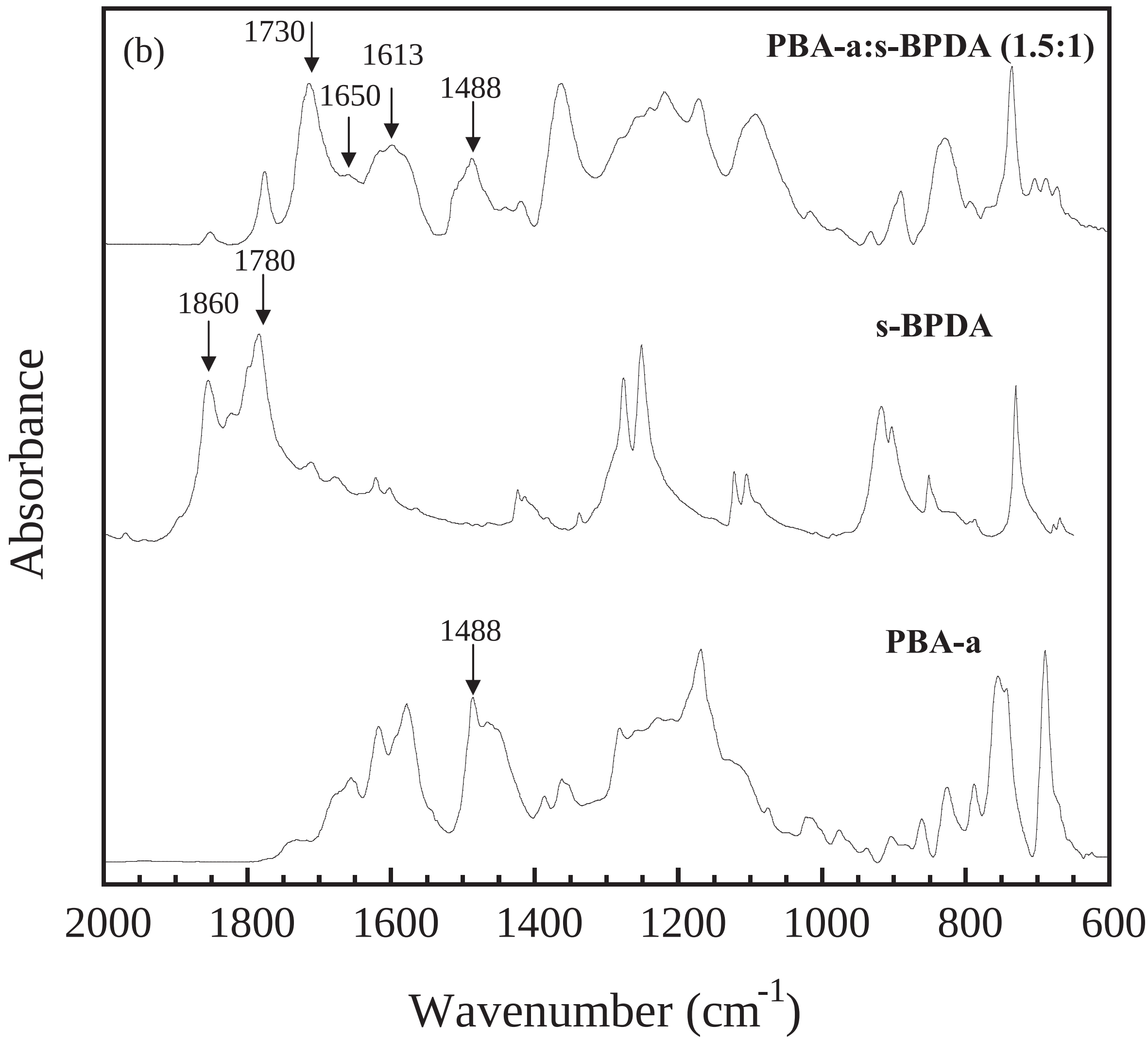


Fig. 5.10(b) FTIR spectra of PBA-a:s-BPDA = 1.5:1 mol.

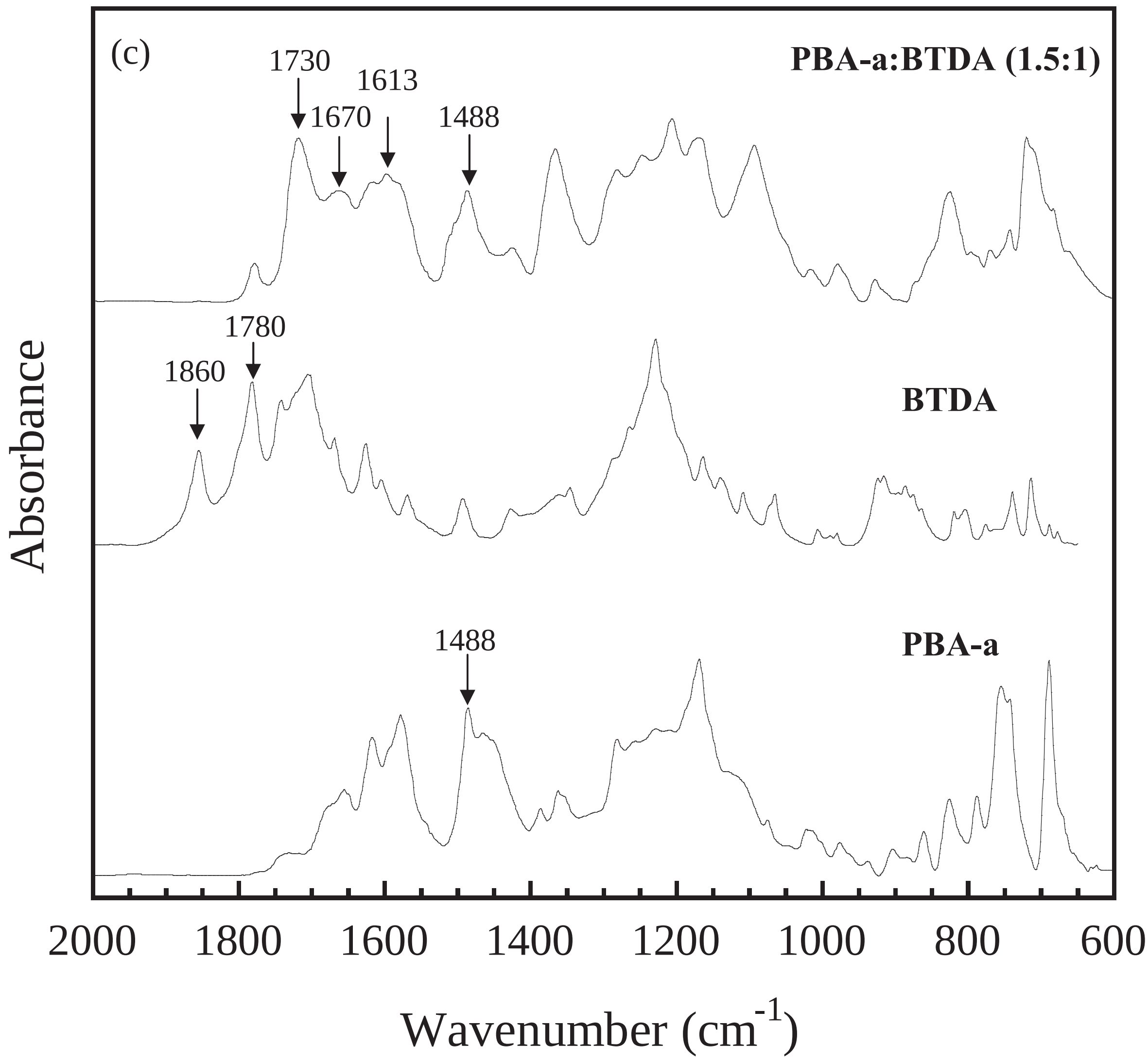


Fig. 5.10(c) FTIR spectra of PBA-a:BTDA = 1.5:1 mol.

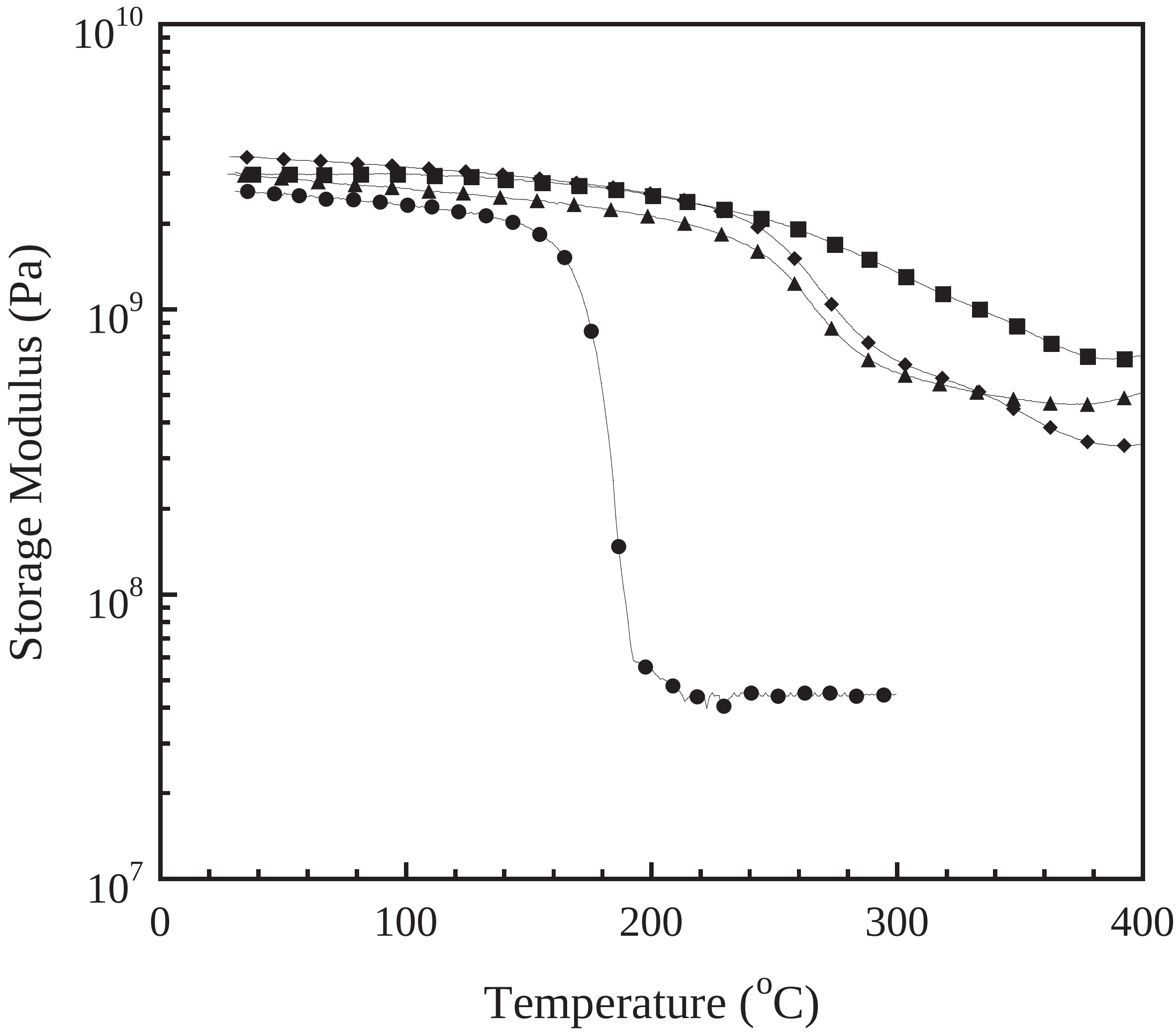


Fig. 5.11 Storage modulus of aromatic carboxylic dianhydride modified PBA-a films: (●) PBA-a, (■) PBA-a:PMDA, (♦) PBA-a:s-BPDA, (▲) PBA-a:BTDA.

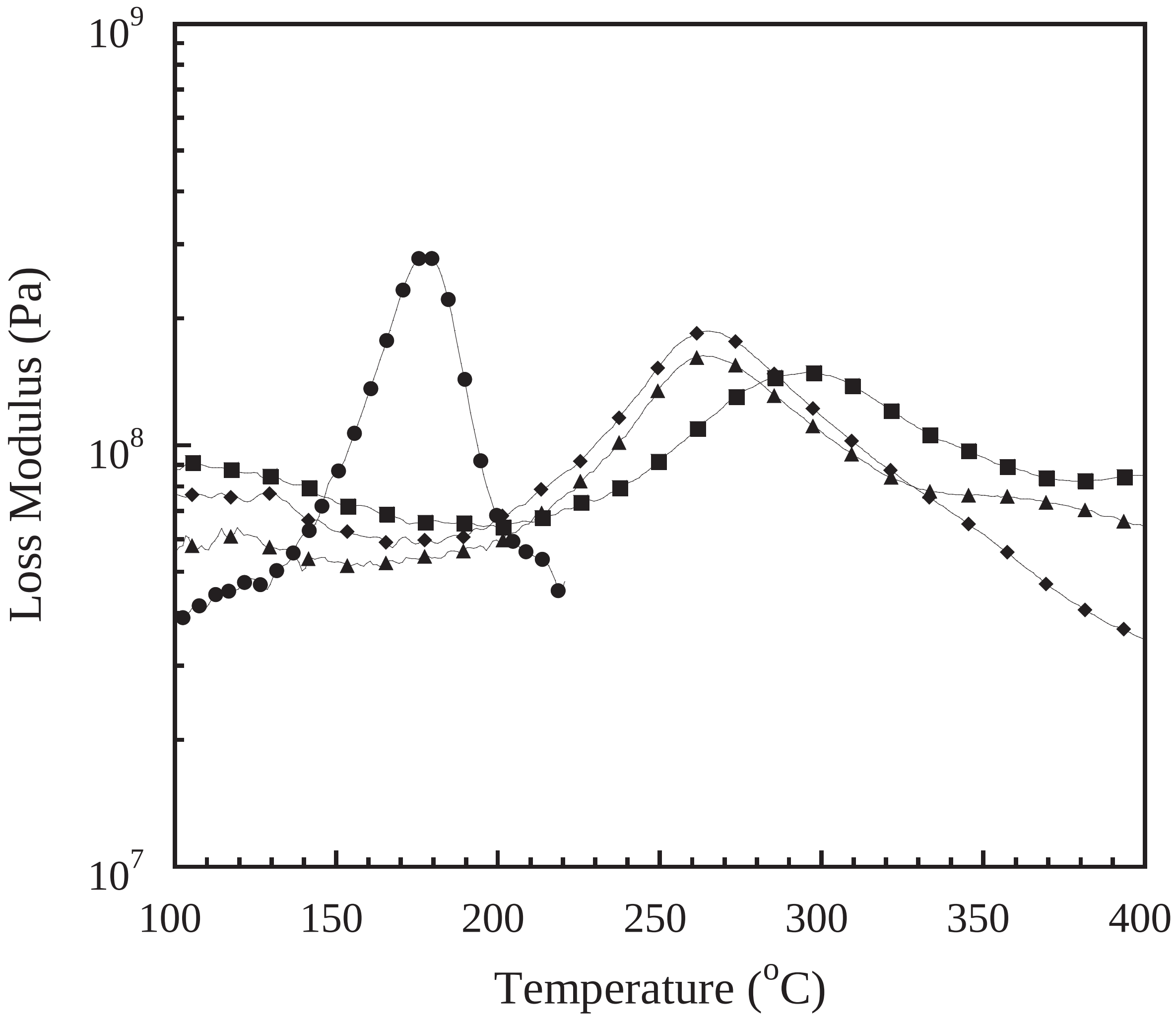


Fig. 5.12 Loss modulus of aromatic carboxylic dianhydride modified PBA-a films:

(●) PBA-a, (■) PBA-a:PMDA, (♦) PBA-a:s-BPDA, (▲) PBA-a:BTDA.

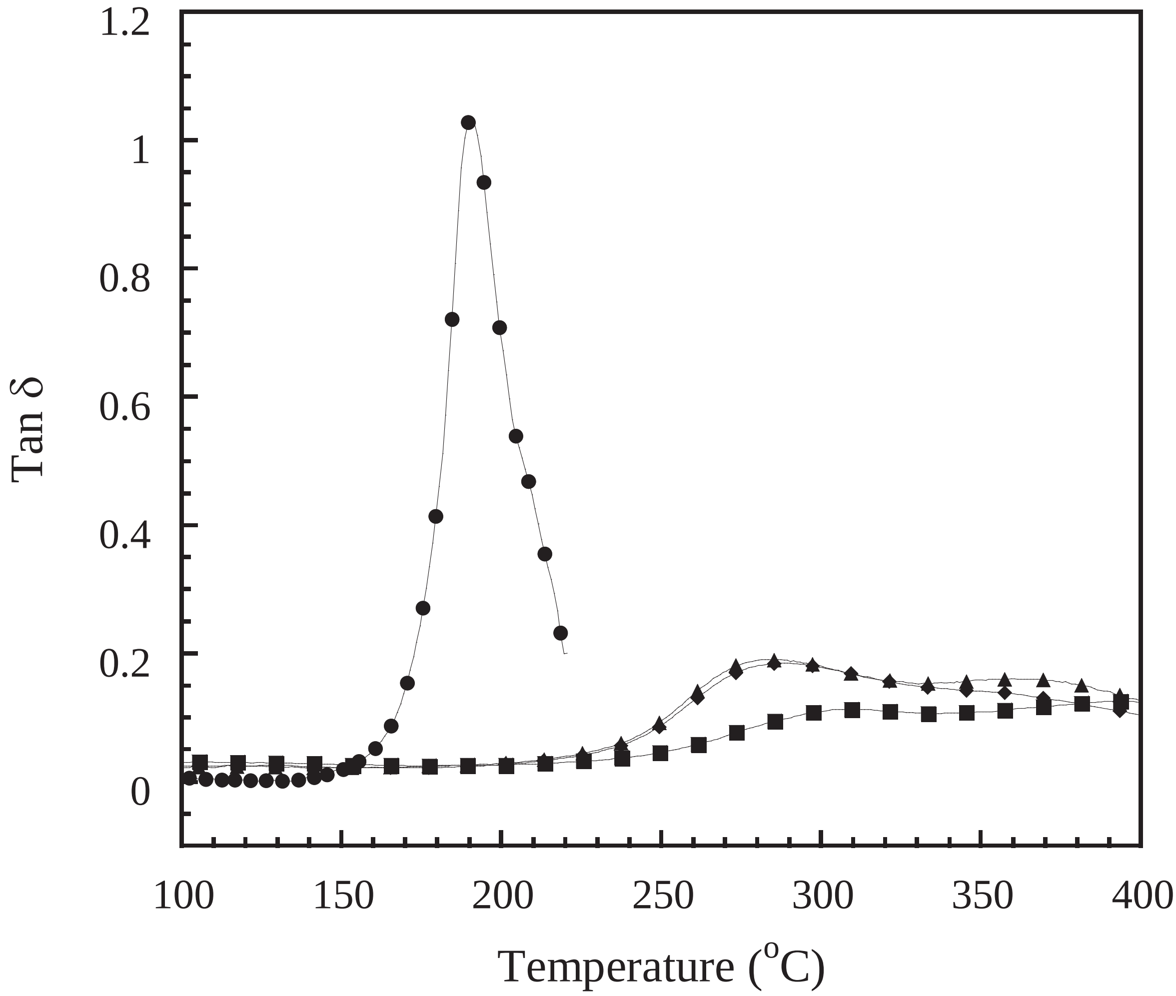


Fig. 5.13 Loss tangent of aromatic carboxylic dianhydride modified PBA-a films: (●) PBA-a, (■) PBA-a:PMDA, (♦) PBA-a:s-BPDA, (▲) PBA-a:BTDA.

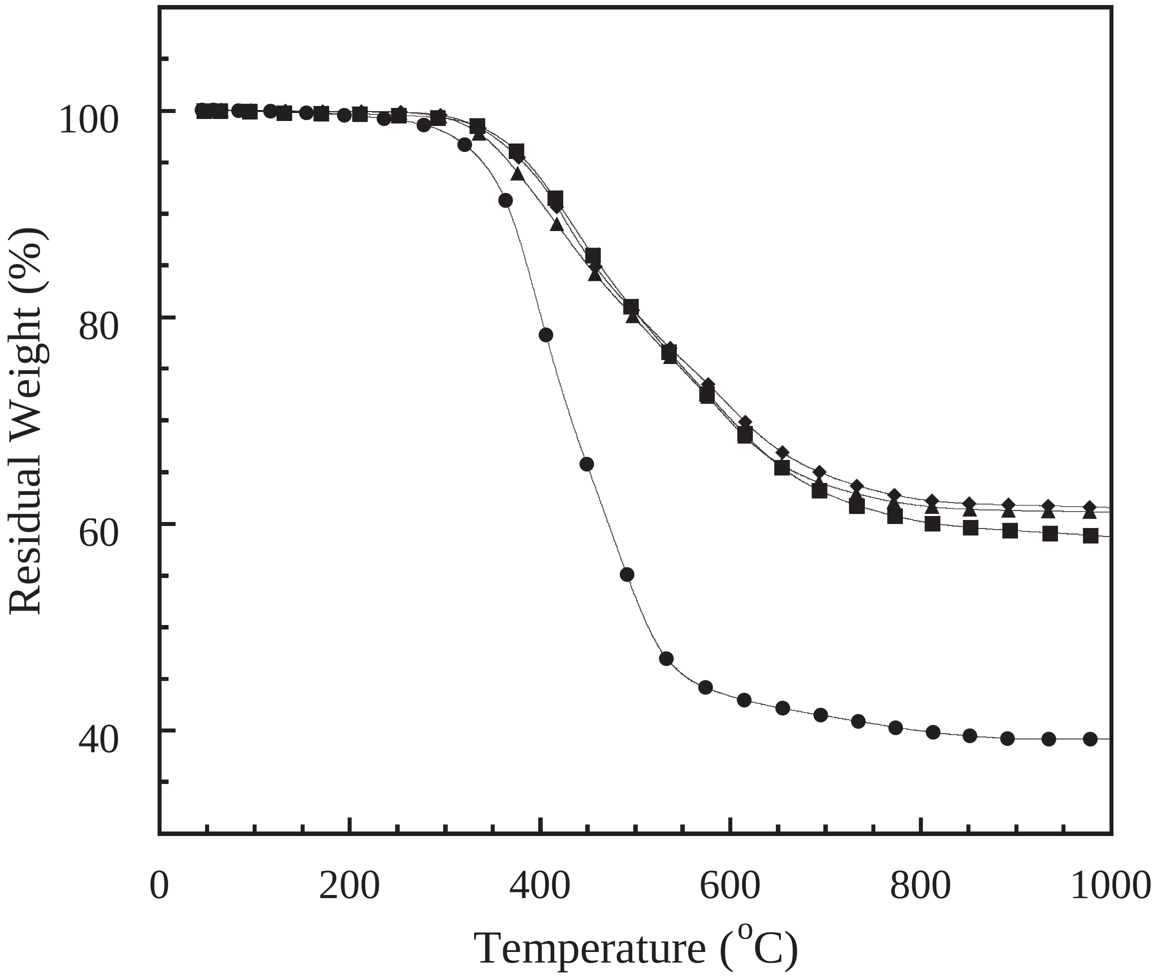


Fig. 5.14 Thermal degradation of aromatic carboxylic dianhydride modified PBA-a films: (●) PBA-a, (■) PBA-a:PMDA, (♦) PBA-a:s-BPDA, (▲) PBA-a:BTDA.

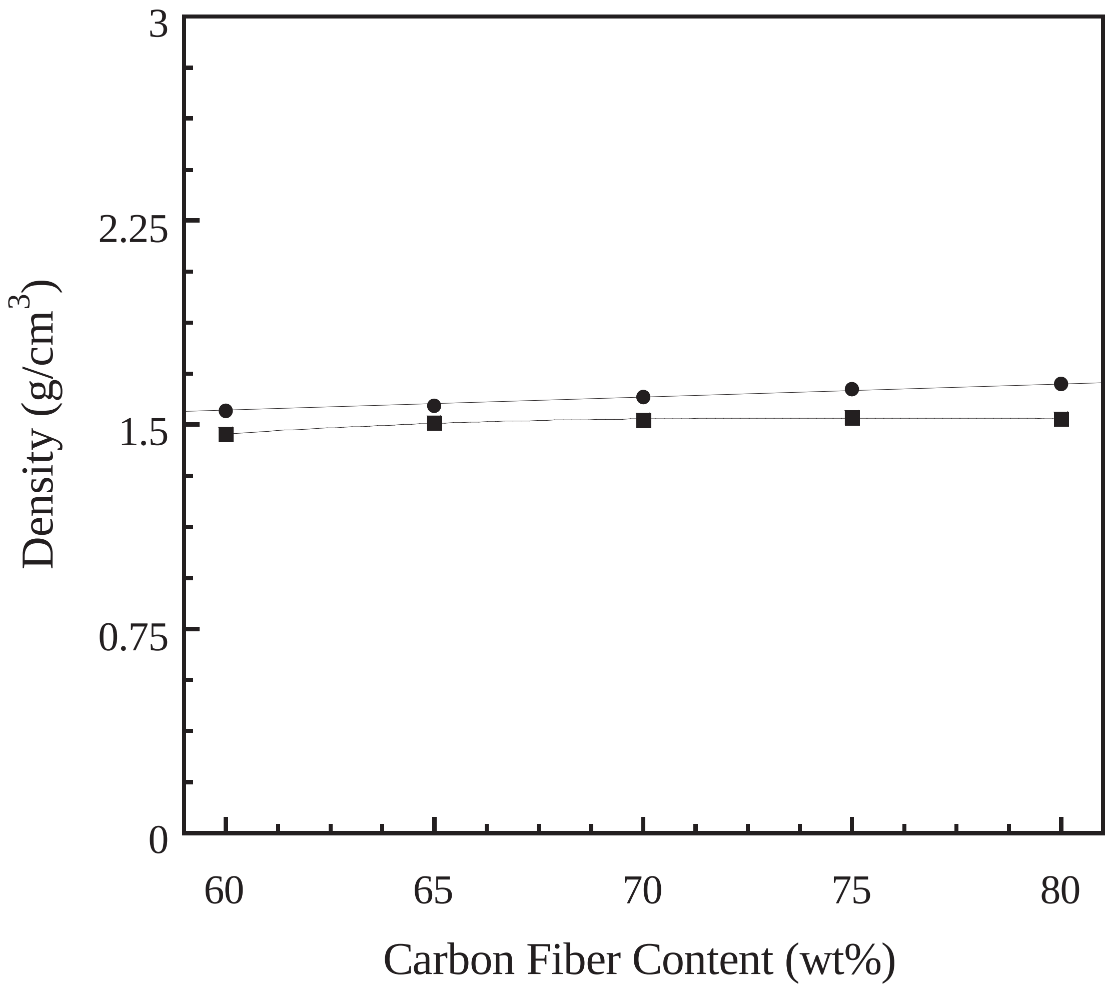


Fig. 15 The maximum packing density of CF-reinforced PBA-a:PMDA composites at various fiber contents. (●) theoretical density and (■) actual density.

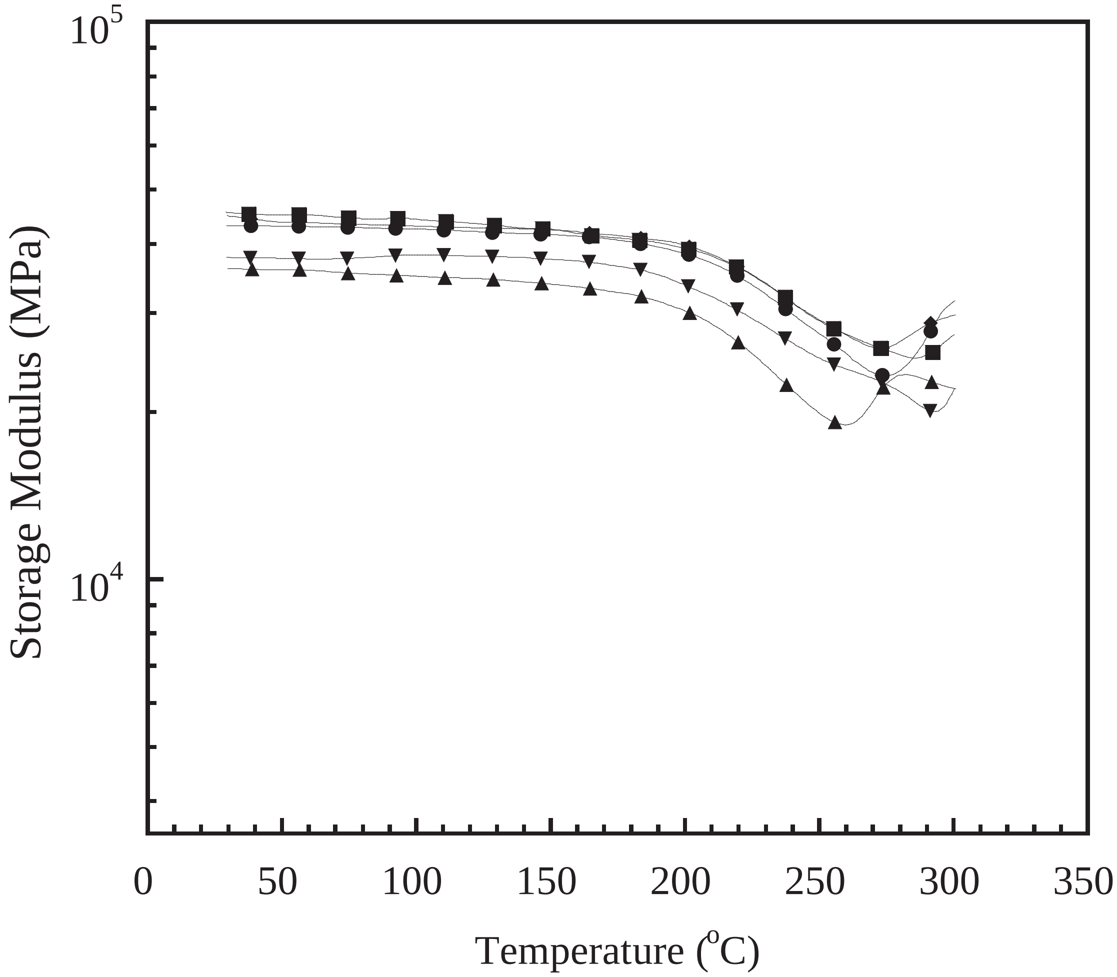


Fig. 16 Storage modulus of carbon fiber (CF)-reinfored PBA-a:PMDA composites as a function of temperature at various carbon fiber contents. (●) CF/ PBA-a:PMDA = 60/40, (■) CF/ PBA-a:PMDA = 65/35, (◆) CF/ PBA-a:PMDA = 70/30, (▲) CF/ PBA-a:PMDA = 75/25, (▼) CF/ PBA-a:PMDA = 80/20.

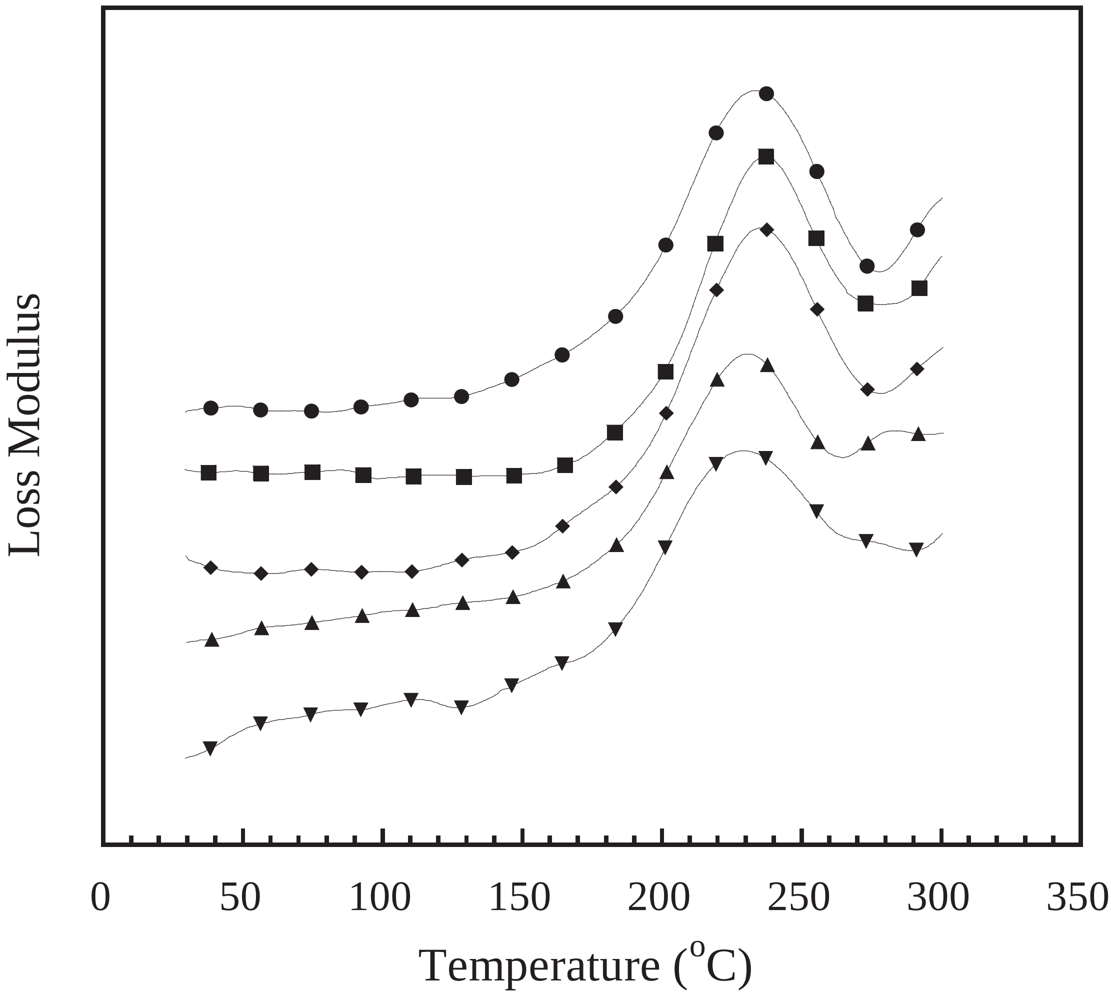


Fig. 17 Loss modulus of CF-reinfored PBA-a:PMDA composites as a function of temperature at various carbon fiber contents. (●) CF/ PBA-a:PMDA = 60/40, (■) CF/ PBA-a: PMDA = 65/35, (◆) CF/ PBA-a:PMDA = 70/30, (▲) CF/ PBA-a:PMDA = 75/25, (▼) CF/ PBA-a:PMDA = 80/20.

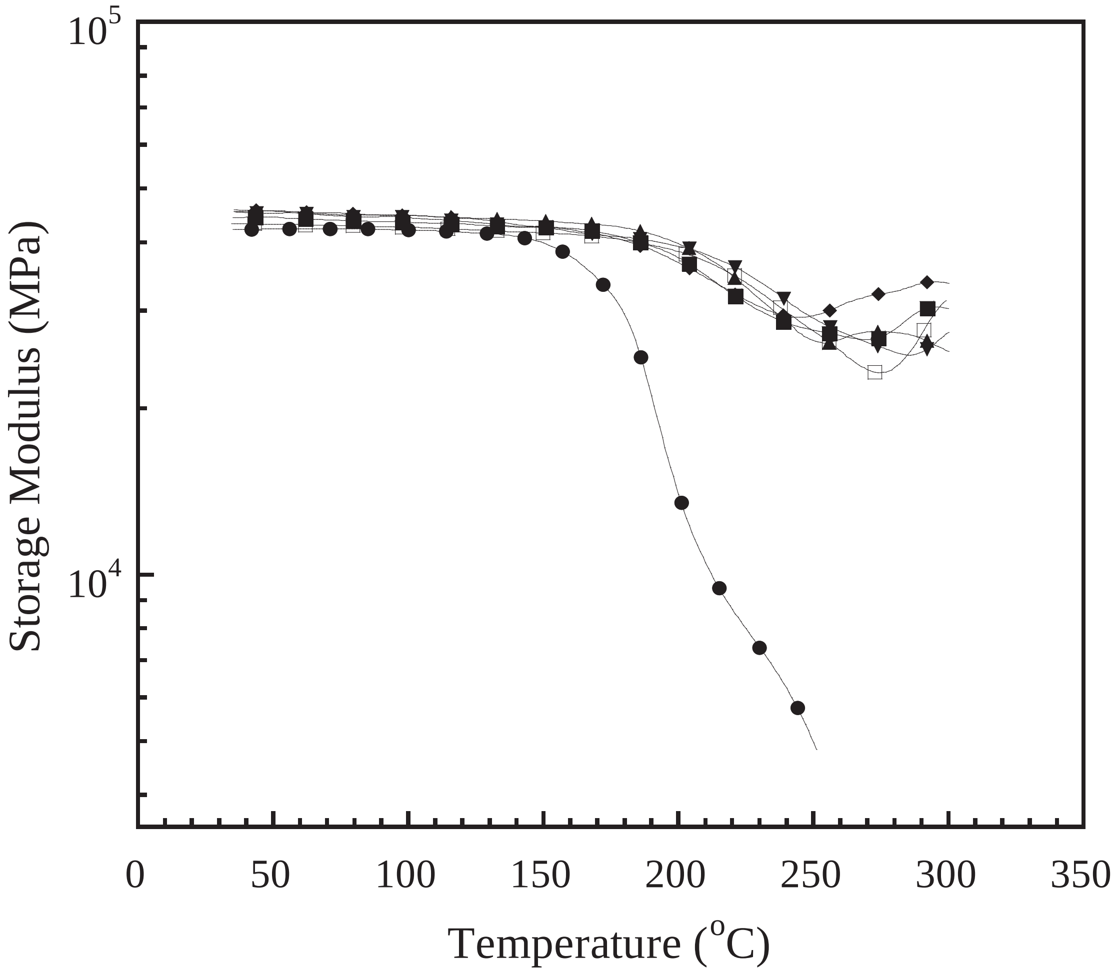


Fig. 18 Storage modulus of 65wt% CF-reinfored PBA-a:PMDA composites as a function of temperature at various PMDA mole ratios. (●) CF/PBA-a, (■) CF/ PBA-a:PMDA = 4:1,(◆) CF/ PBA-a:PMDA = 3:1, (▲) CF/PBA-a: PMDA = 2:1,(▼) CF/PBA-a:PMDA = 1.5:1, (□) CF/PBA-a:PMDA = 1:1.

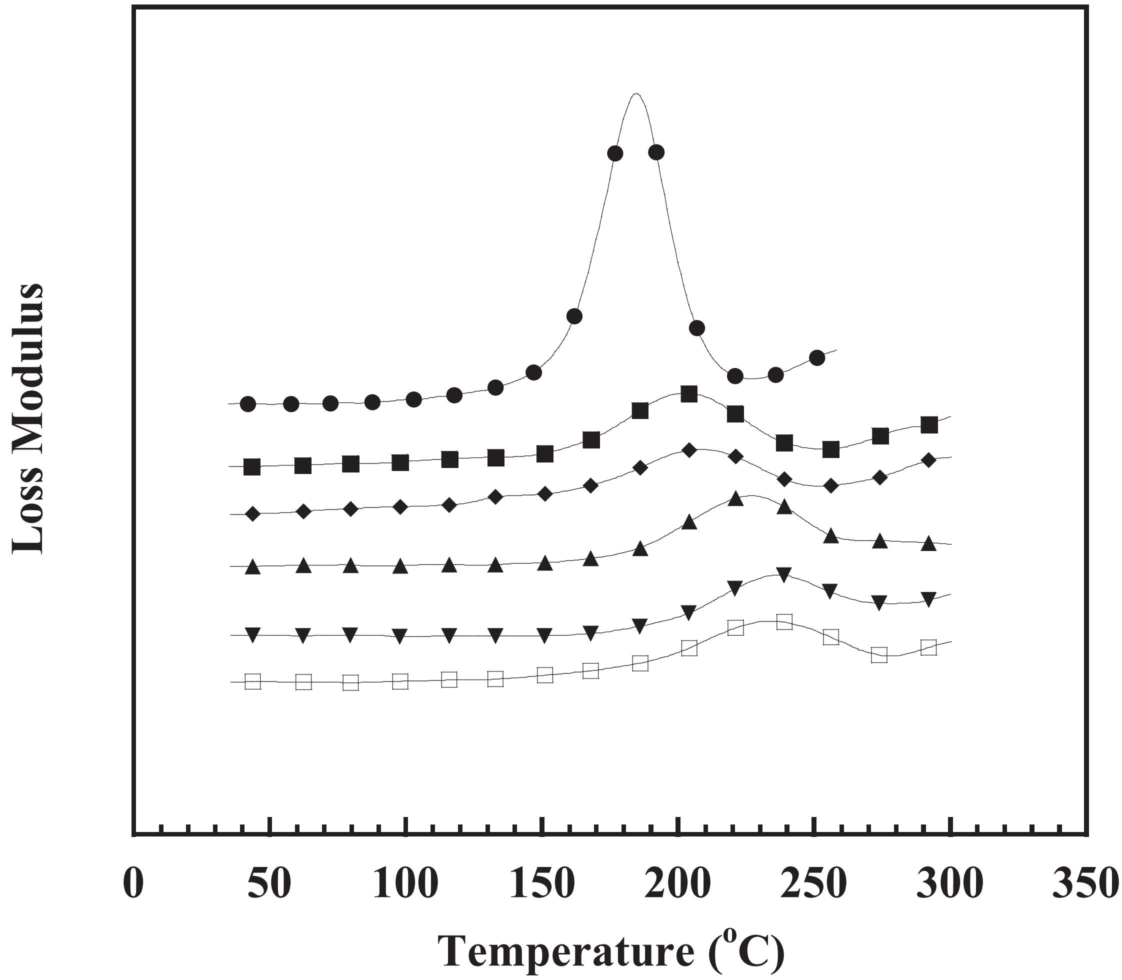


Fig. 19 Loss modulus of 65wt% CF-reinfored PBA-a:PMDA composites as a function of temperature at various PMDA mole ratios. (●) CF/PBA-a, (■) CF/ PBA-a:PMDA = 4:1,(◆) CF/ PBA-a:PMDA = 3:1, (▲) CF/PBA-a: PMDA = 2:1,(▼) CF/PBA-a:PMDA = 1.5:1, (□) CF/PBA-a:PMDA = 1:1.

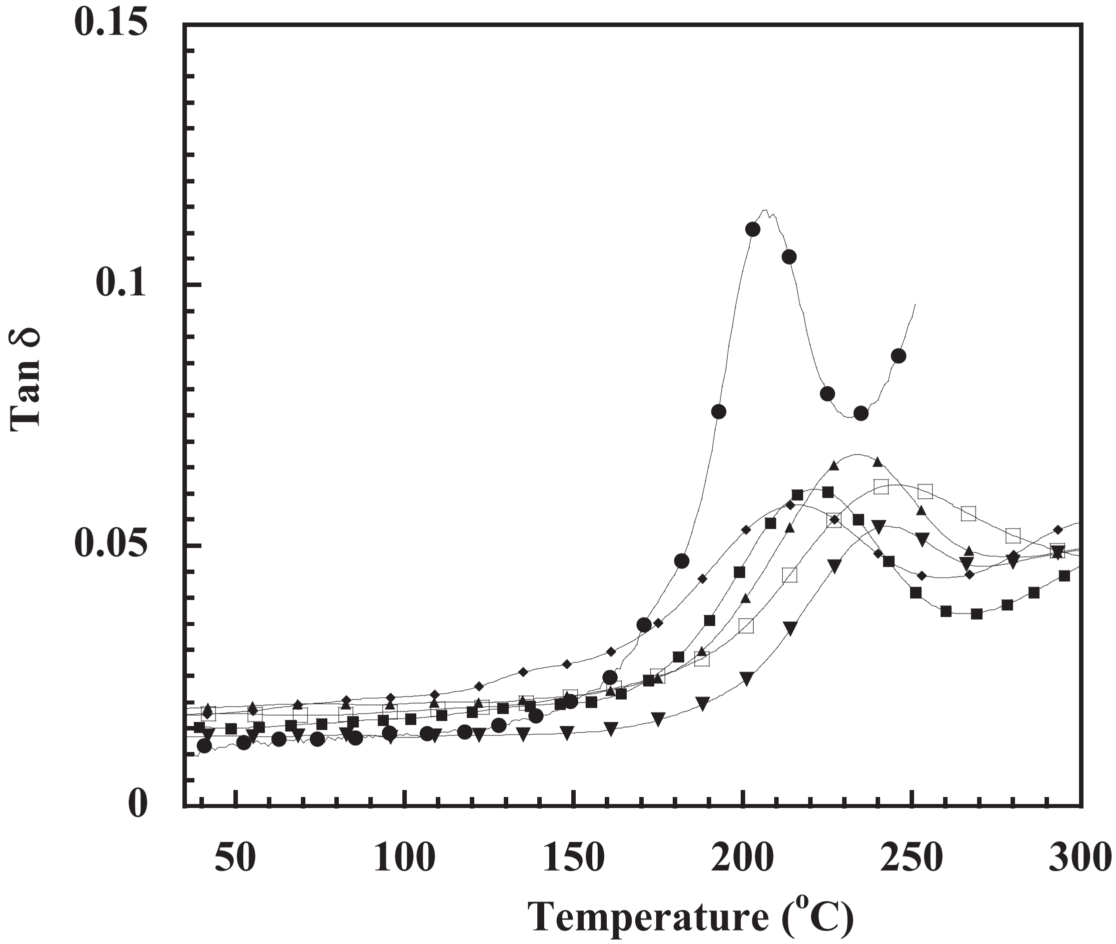


Fig. 20 Loss tangent of 65wt% CF-reinfored PBA-a:PMDA composites as a function of temperature at various PMDA mole ratios. (●) CF/PBA-a, (■) CF/ PBA-a:PMDA = 4:1,(◆) CF/ PBA-a:PMDA = 3:1, (▲) CF/PBA-a: PMDA = 2:1,(▼) CF/PBA-a:PMDA = 1.5:1, (□) CF/PBA-a:PMDA = 1:1.

.

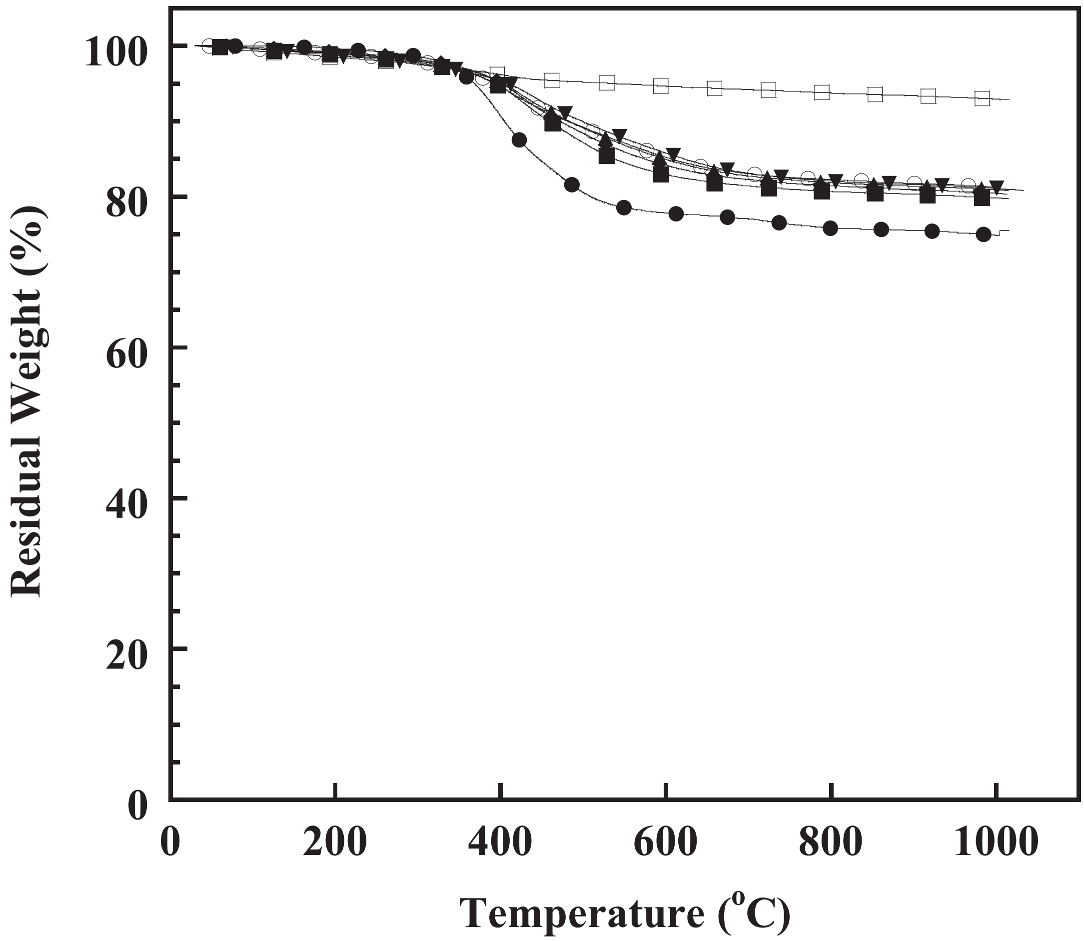
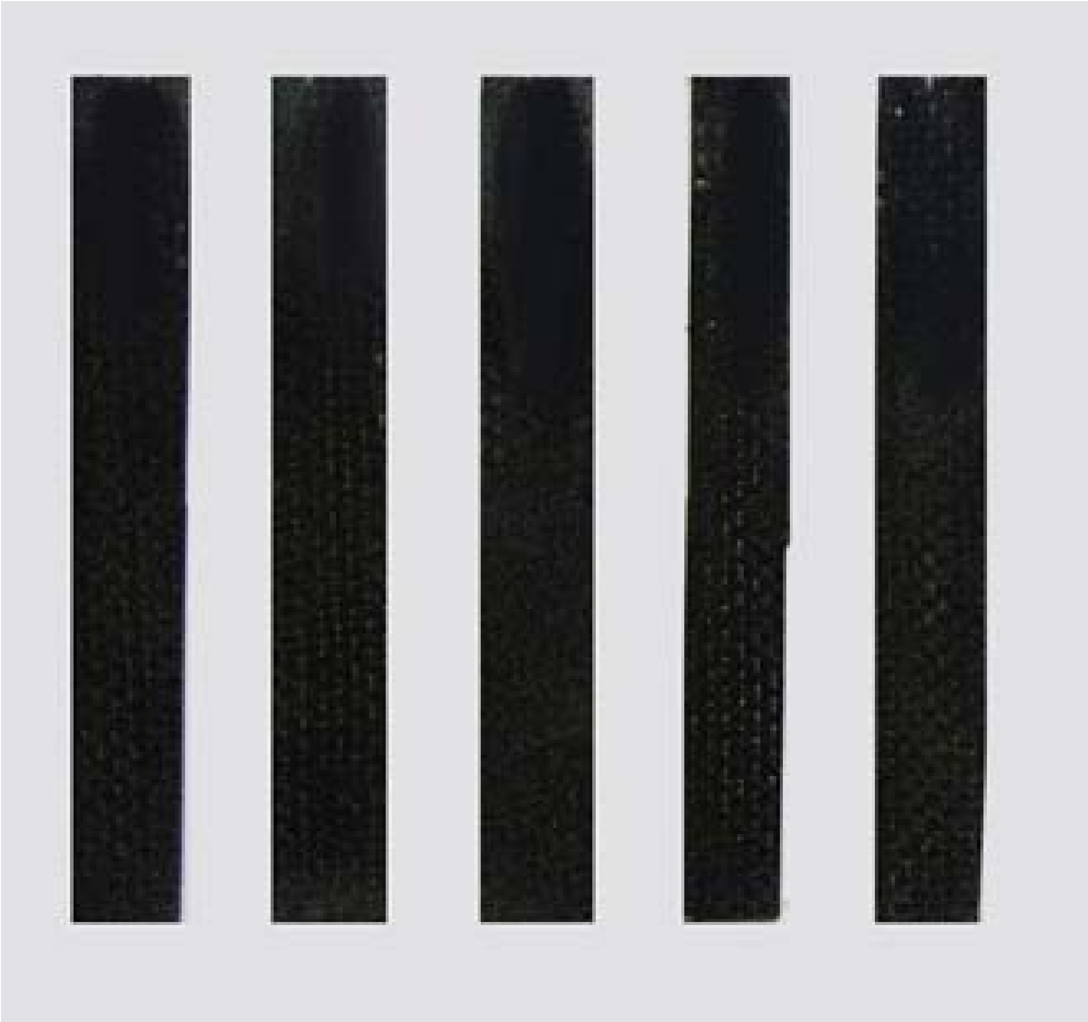
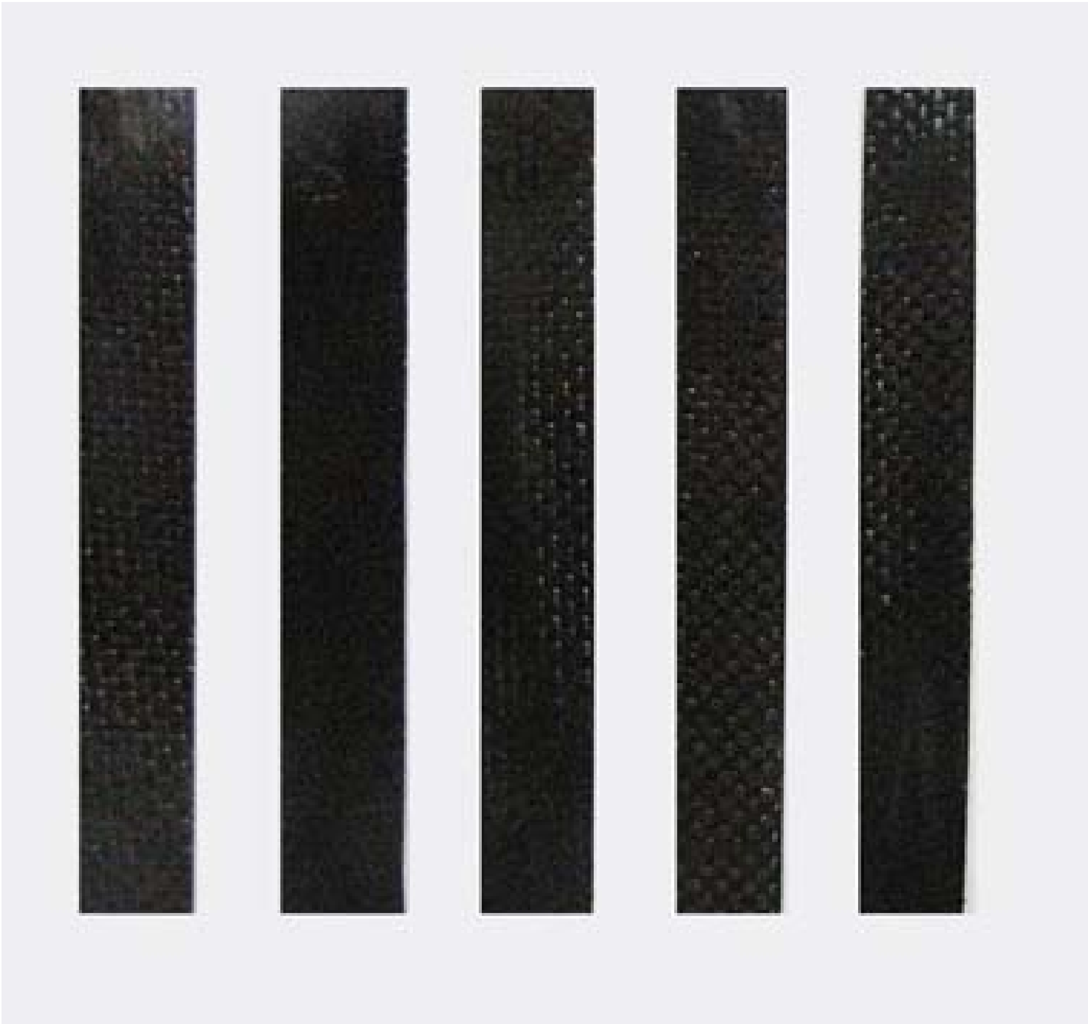


Fig.21 TGA thermograms of (□) carbon fiber and 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios. (●) CF/PBA-a, (■) CF/ PBA-a:PMDA = 4:1, (◆) CF/ PBA-a:PMDA = 3:1, (▲) CF/PBA-a:PMDA = 2:1, (▼) CF/PBA-a: PMDA = 1.5:1, (○) CF/PBA-a:PMDA = 1:1.



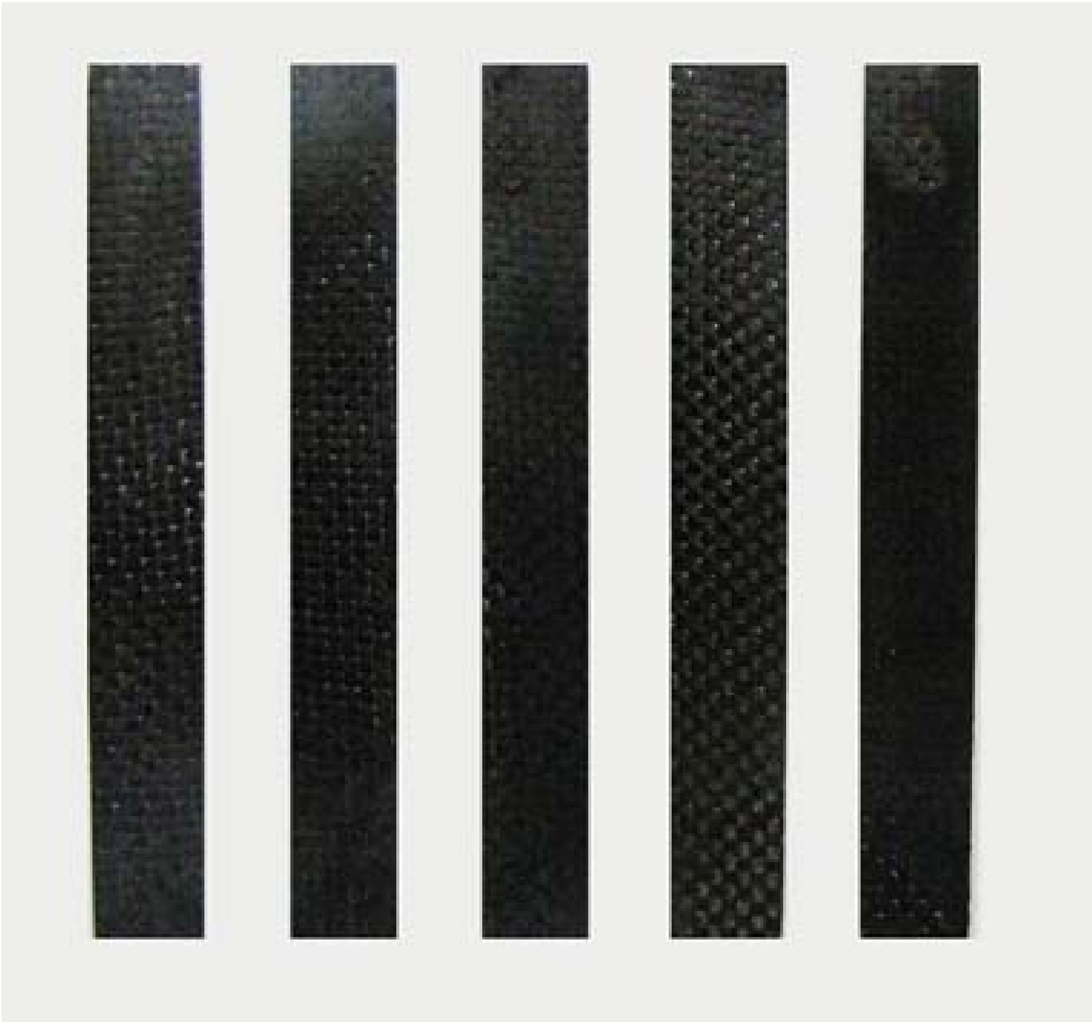
V-1

Fig. 22(a) UL-94 vertical flame test of 65wt% CF-reinforced neat PBA-a composites.



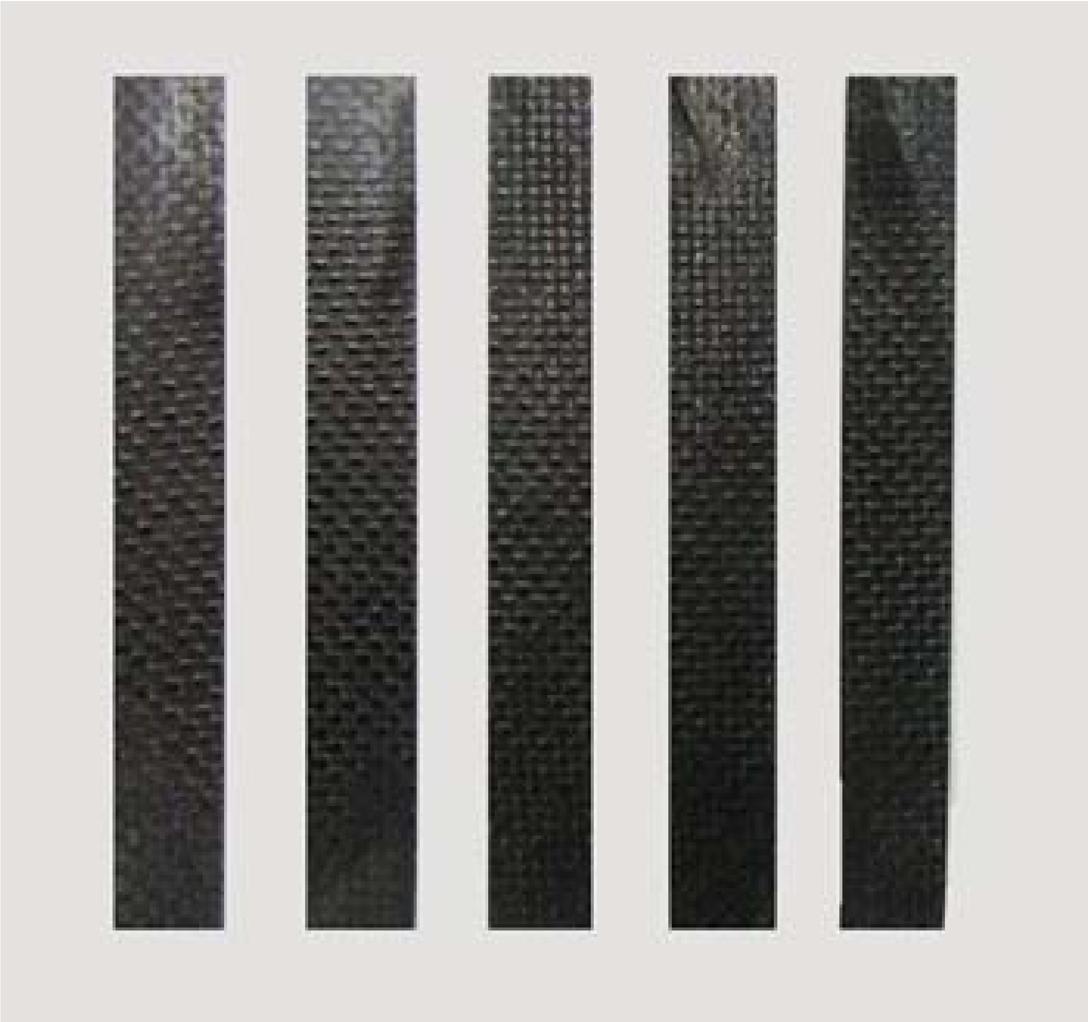
V-0

Fig. 22(b) UL-94 vertical flame test of 65wt% CF-reinforced PBA-a:PMDA (4:1) composites.



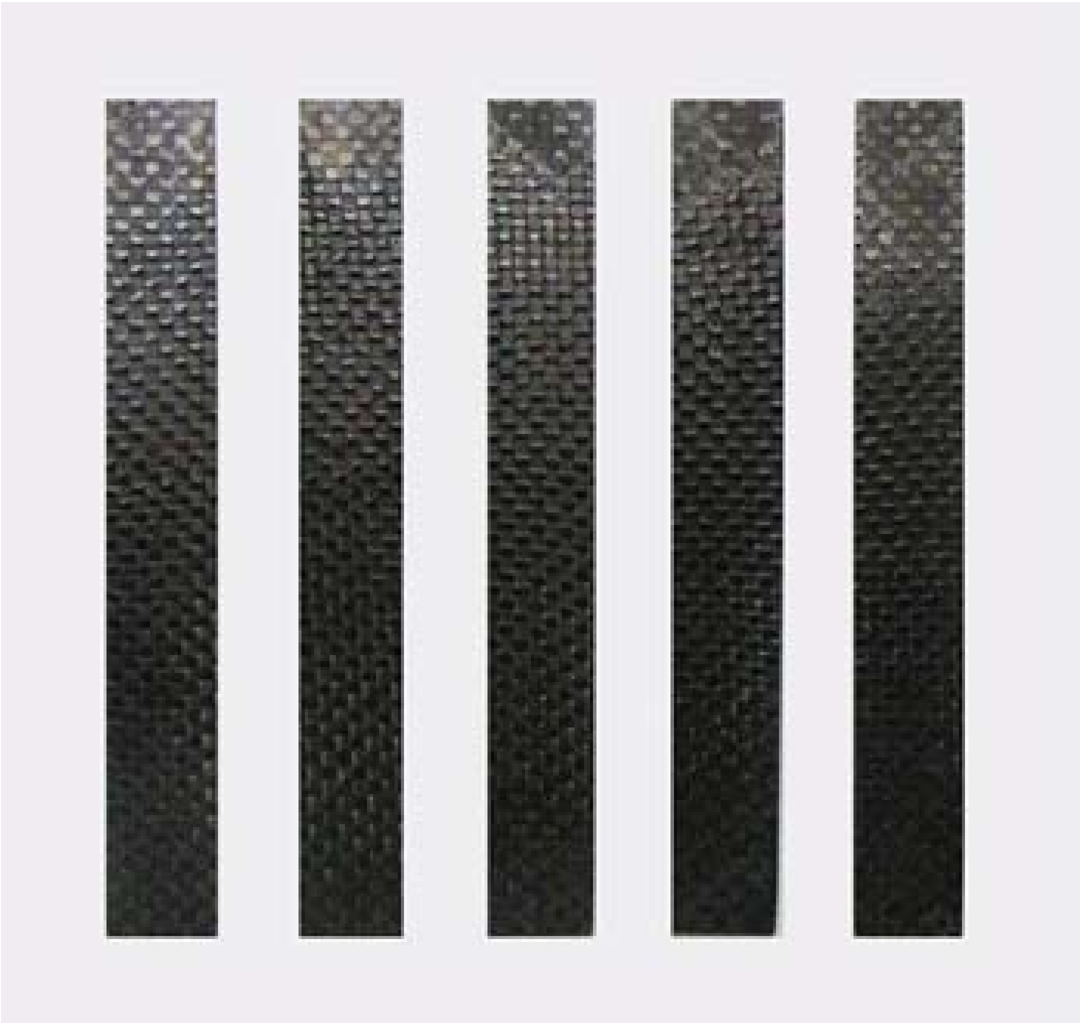
V-0

Fig. 22(c) UL-94 vertical flame test of 65wt% CF-reinforced PBA-a:PMDA (3:1) composites.



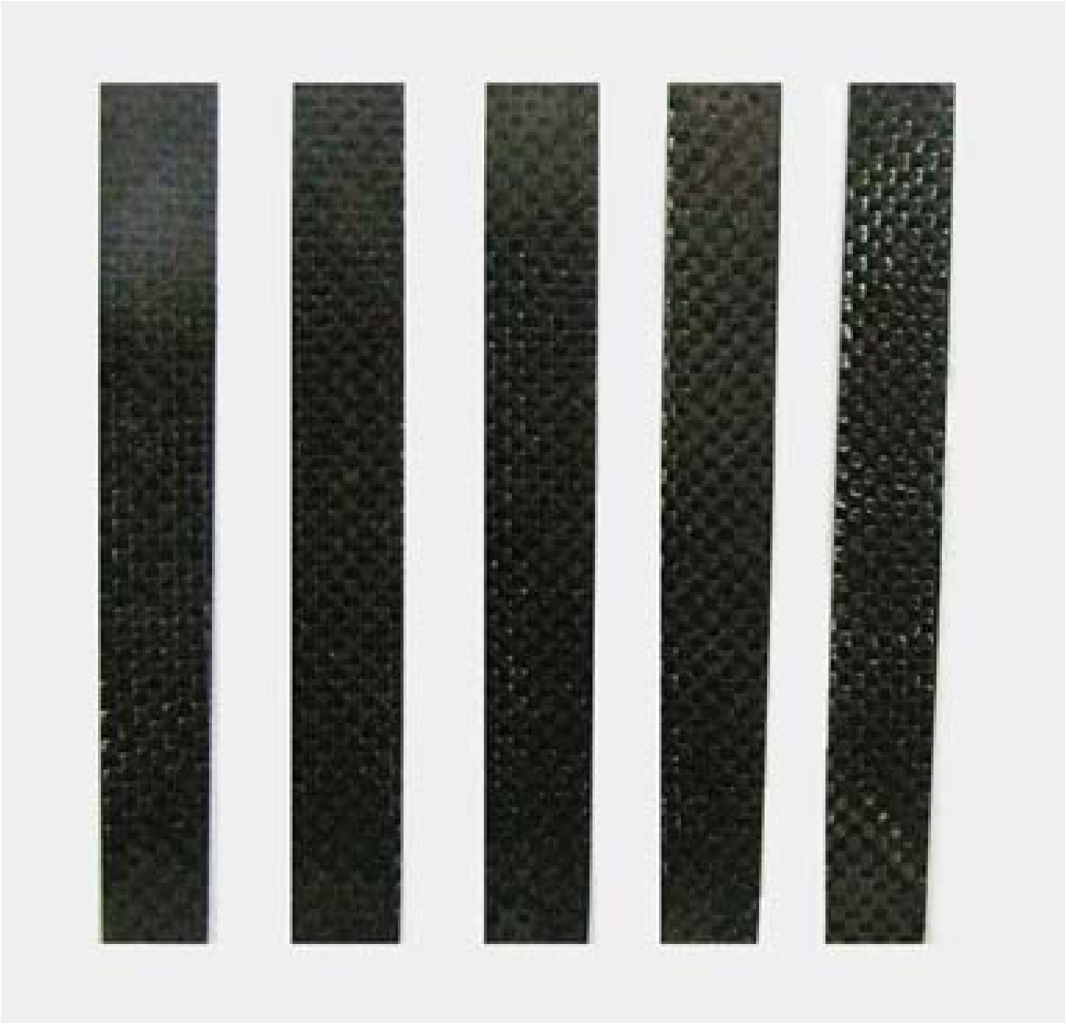
V-0

Fig. 22(d) UL-94 vertical flame test of 65wt% CF-reinforced PBA-a:PMDA (2:1) composites.



V-0

Fig. 22(e) UL-94 vertical flame test of 65wt% CF-reinforced PBA-a:PMDA (1.5:1) composites.



V-0

Fig. 20(f) UL-94 vertical flame test of 65wt% CF-reinforced PBA-a:PMDA (1:1) composites.

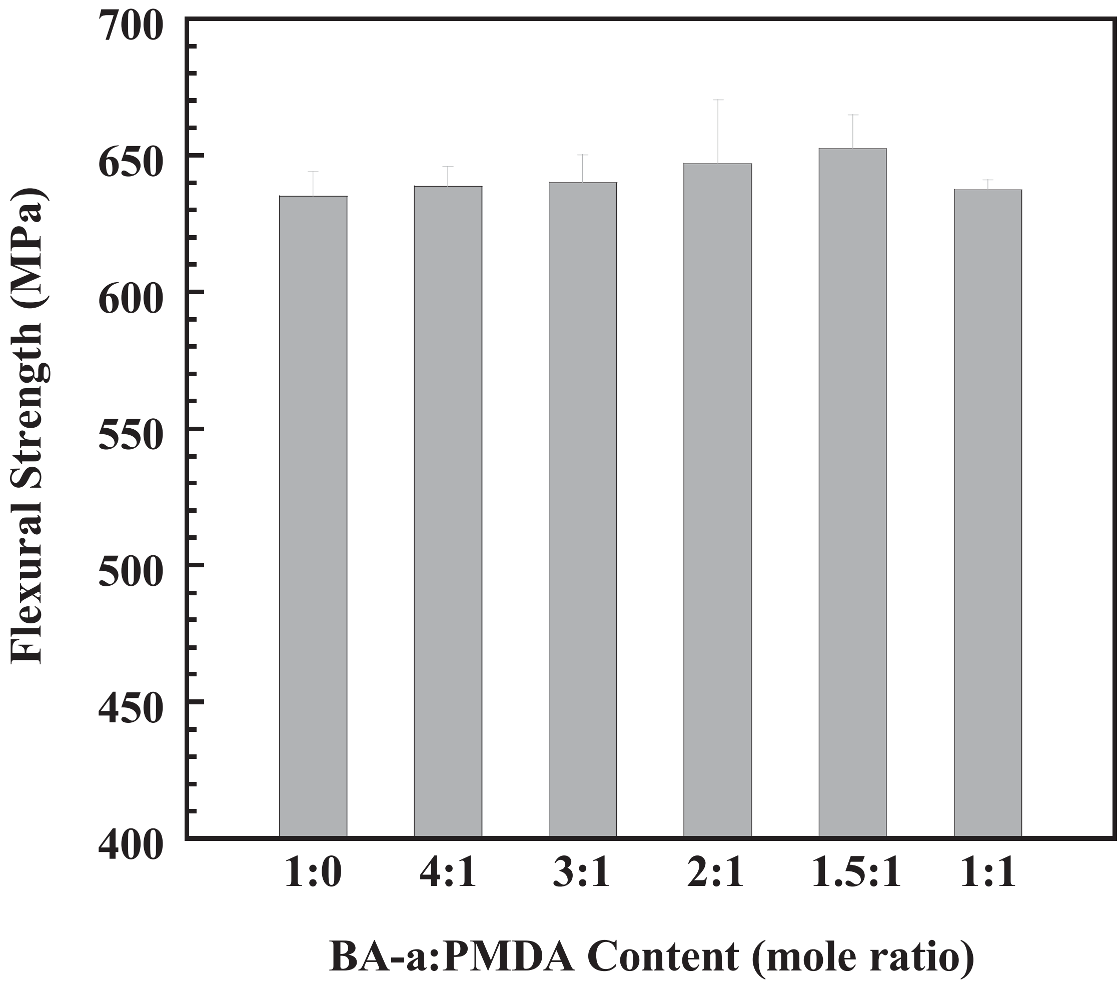


Fig. 23 Flexural strength of 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios.

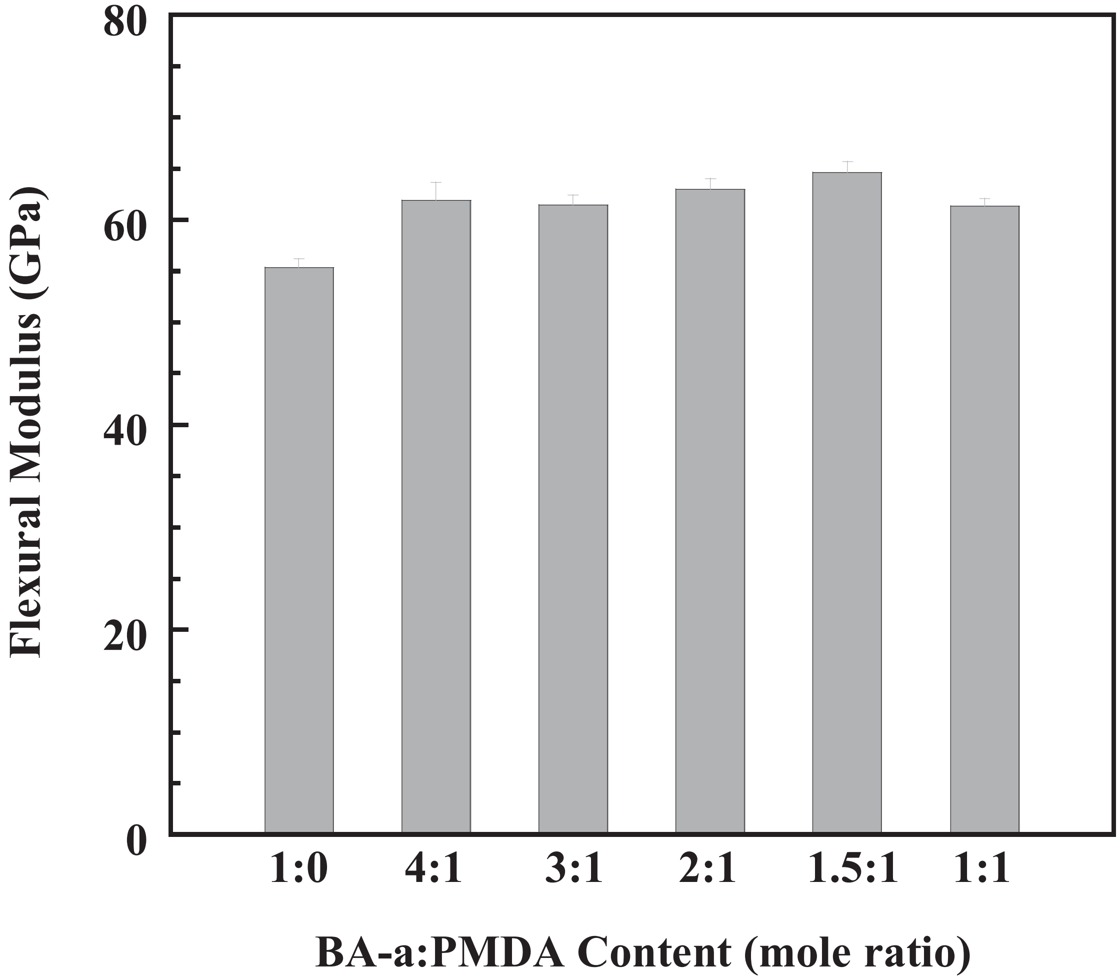
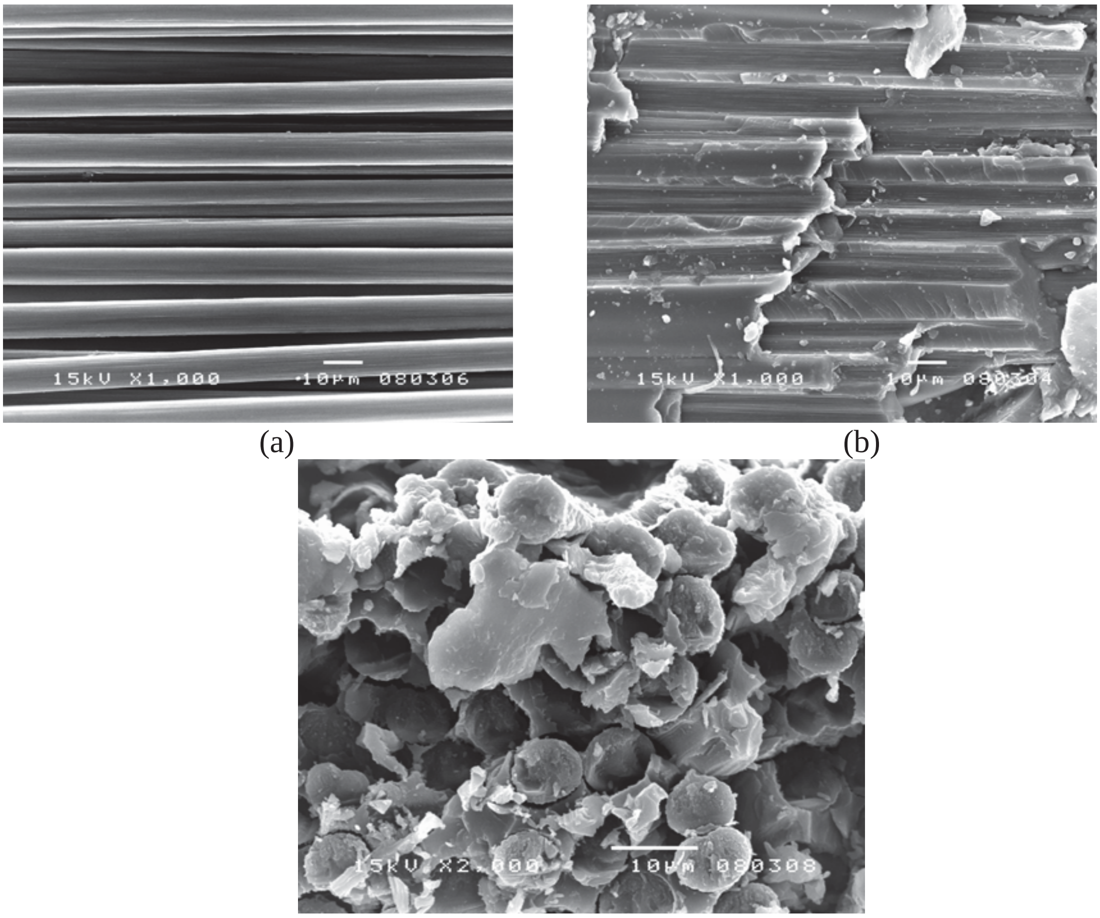


Fig. 24 Flexural strength of 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios.



(a) (b)

(c)

Fig. 25 SEM micrographs (a) carbon fiber morphology (b) fractured surface of CF/PBA-a:PMDA = 1.5:1 composite in weft region (c) fractured surface of CF/PBA-a:PMDA = 1.5:1 composite in warp region.

Conclusions

The copolymers of bisphenol-A-aniline based polybenzoxazine (PBA-a) modified with dianhydride showed significant enhancement in their mechanical and thermal properties compared to those of the neat PBA-a. FTIR spectroscopy revealed that the ester linkage occurred from a reaction of hydroxyl group of PBA-a and anhydride group of BTDA. DMA experiment showed an enhancement in crosslink density of the obtained copolymers resulting in an increase in the corresponding glass transition temperature. Moreover, an incorporation of BTDA into PBA-a resulted in higher surface hardness compared to the neat PBA-a. The thermal decomposition temperature and weight residue at 800^{o}C also remarkably increased with an incorporation of the BTDA. Therefore, the presence of BTDA into PBA-a to form PBA-a/BTDA copolymers was found to improve the reliability of the polymer hybrids.

A series of bisphenol-A-aniline type polybenzoxazine (PBA-a) containing aromatic carboxylic dianhydride copolymers as transparent films was prepared. Networks of aromatic carboxylic dianhydride modified PBA-a copolymer films were formed by a reaction between hydroxyl groups of the PBA-a and the anhydride group of dianhydride as revealed by FTIR spectroscopy. The obtained copolymers exhibited excellent toughness, excellent thermal stability, and good mechanical properties. Glass transition temperature of the neat PBA-a was substantially enhanced by blending with the aromatic carboxylic dianhydrides. The effect of types of dianhydrides on T_g was found to be as follows: PBA-a:PMDA > PBA-a:s-BPDA > PBA-a:BTDA. Furthermore, degradation temperature and char yield at 800^{o}C of the copolymer films were also improved with an incorporation of the aromatic carboxylic dianhydrides. The copolymers may be considered as potential candidates for high temperature materials with enhanced mechanical integrity as a matrix of advanced composite materials.

The effects of carbon fiber (CF) and PMDA contents on flammability, mechanical, and thermal properties of CF-reinforced bisphenol A-aniline based polybenzoxazine (PBA-a) modified with PMDA composites can be summarized as follows. The maximum packing density of carbon fiber in PBA-a:PMDA composites belonged to 65% by weight with the highest mechanical properties, i.e. flexural modulus and strength, thermal property as glass transition temperature (T_g) and flammability. The incorporation of PMDA into benzoxazine resin based on bisphenol-A and aniline (BA-a) can be achieved relatively flammability. Limiting oxygen index (LOI) values of the 65% by weight carbon fiber-reinforced

PBA-a:PMDA composites substantially increased with increasing PMDA content compared with the 65% by weight-reinforced PBA-a. Importantly, all 65% by weight carbon fiber-reinforced PBA-a:PMDA composites as thin as 1 mm passed the highest V-0 classification of UL-94 vertical flame test. Furthermore, the highest T_g value of the composite consisted of BA-a:PMDA = 1.5:1 mol was approximately 237^{o}C. The degradation temperature (T_{d10}) and char yield at 800^{o}C of the 65% by weight carbon fiber-reinforced PBA-a:PMDA composites was remarkably higher than those of the 65% by weight carbon fiber-reinforced-PBA-a composite. The increase of PMDA content was found to enhance the char yield of the composites up to 82% for the molar ratio of BA-a:PMDA = 1.5:1 reinforced with 65% by weight carbon fiber. In addition, the flexural modulus and strength of the 65% by weight carbon fiber-reinforced PBA-a:PMDA composites increased with increasing PMDA. The modulus and strength under flexure mode of the 65% by weight carbon fiber-reinforced PBA-a:PMDA = 1.5:1 mol was recorded as 65 GPa and 652 MPa, respectively, compared to the 65% by weight carbon fiber-reinforced PBA-a composite which displayed the values of the flexural modulus and strength to be 55 GPa and 635 MPa, respectively. Scanning electron micrographs showed good fiber-matrix interfacial adhesion as observed tight interfaces between the carbon fiber and the copolymer matrix.

References

1. F.U. Buehler and J.C. Seferis, Composites, **31**, 741 (2000).
2. H. Ishida and T. Chaisuwan, Polym Compos, **24**, 597 (2003).
3. J. Jang and H. Yang, Compos Sci Tech, **60**, 457 (2000).
4. J. Delmonte, Technology of carbon and graphite fiber composites, New York: Van Nostrand Reinhold, 1981.
5. R.E. Shalin, Polymer matrix composites, London: Chapman&Hall, 1995.
6. S. Shen and H. Ishida, Polym Compos, **17**, 710 (1996).
7. X. Ning and H. Ishida, J Polym Sci Polym Chem, **32**, 1121 (1994).
8. H. Ishida and D.J. Allen, J Polym Sci Polym Phys, **34**, 1019 (1996).
9. C.P.R. Nair, Prog Polym Sci, **29**, 401 (2004).
10. H. Ishida and D.P. Sander, J Polym Sci Polym Phys, **38**, 3289 (2000).
11. H. Ishida and D.P. Sander, US Patent 6160079 (2000).
12. H. Ishida and D.P. Sander, Macromolecules, **33**, 8149 (2000).
13. H. Ishida and D.P. Sander, Polymer, **42**, 3115 (2001).
14. G.P. Cao, W.J. Chen and X.B. Liu, Polym Degrad Stabili, **93**, 739 (2008).
15. M. Sponton, G. Lligadas, J.C. Ronda, M. Galia and V. Cadiz, Polym Degrad Stabili, **94**, 1693 (2009).
16. T. Uyar, Z. Kouncu, H. Ishida and J. Hacaloglu, Polym Degrad Stabili, **93**, 2096 (2008).
17. M. Sponton, J.C. Ronda, M. Galia and V. Cadiz, Polym Degrad Stabili, **93**, 2158 (2008).
18. S. Rimdusit, S. Pirstpindvong, W. Tanthapanichakoon and S. Damrongsakkul, Polym Eng Sci, **45**, 288 (2005).
19. H. Kimura, Y. Murata, A. Matsumoto, K. Hasegawa, K. Ohtsuka and A. Fukuda, J Appl Polym Sci, **74**, 2266 (1999).
20. H. Kimura, A. Matsumoto, H. Sugito, K. Hasfgawa, K. Ohtsuka and A. Fukuda, J Appl Polym Sci, **79**, 555 (2001).
21. H. Ishida and S. Ohba, J Appl Polym Sci, **101**, 1670 (2006).
22. T. Takeichi, Y. Guo and S. Rimdusit, Polymer, **46**, 4909 (2005).
23. K.S. Santhosh Kumar, C.P. Reghunadhan Nair and K.N. Ninan, Euro Polym J, **45**, 494 (2009).

24. T. Takeichi, Y. Saito, T. Agag, H. Muto and T. Kawauchi, Polymer, **49**, 1173 (2008).
25. T.T. Serafini, P. Delvings and G.R. Lightsey, J Appl Polym Sci, **16**, 905 (1972).
26. H. Ishida, U.S. Patent 5543516 (1996).
27. H. Ishida and T. Agag, Handbook of benzoxazine resins. Elsevier, New York (2011).
28. X. Ning and H. Ishida, Macromolecules, **33**, 2893 (2000).
29. M.K. Ghosh and K.L. Mittal, Polyimides fundamentals and application. New York: Marcel Dekker, 1996.
30. H. Itatani, M. Kashima, M. Matsuda, H. Yoshimoto and H. Yamanoto, U.S. Patent 3940426 (1976).
31. J.G. Lavin, Fiber fracture: Carbon fiber, United Kingdom: Elsevier Science, 2002.
32. Zoltek Corporation. Continuous carbon fiber tow [Online]. 2010. Available from: http:// www.zoltek.com [2011, April 15].
33. CJ Composites Technology. Plain weave carbon fiber fabric [Online]. 2010. Available from: http:// cjcompositestechnology.com/carbon-fiber-fabric/3k-plain-weave-carbon-fiber-fabric-50 [2011, April 15].
34. Nanjing Huanyu Carbon Fiber Technology. Carbon fiber application [Online]. 2010. Available from: http://image.made-in-china.com/6f3j00m MJECNTInQku/ Carbon-fiber-for-racing-car.jpg [2011, April 15].
35. Dave, P. $34,000 Carbon Fiber Monocoque Framed F1 Bicycle [Online]. 2010. Available from: http://www.carbonfibergear.com/wp-content/uploads/2010 /03/2-beru-factor-001-carbon-fiber-bike.jpg [2011, April 15].
36. S. Yashpal, Carbon Fiber Cello from Luis and Clark [Online]. 2009. Available from: http://blog.360dgrs.nl/wp-content/uploads/luis-and-clark-carbon-fiber-cello_tlu6y_52.jpg [2011, May 9].
37. Outdoor gear. Franklin 17001f4 uniforce large carbon fibre multi-use work glove black [Online]. 2009. Available from: http://liquid.homelinux.org/img/1/22913/1.jpg [2011, April 15].
38. X. Ning and H. Ishida, J Polym Sci Polym Phys, **32**, 921 (1994).
39. S. Rimdusit and H. Ishida, Polymer, **41**, 7941 (2000).
40. S. Rimdusit and H. Ishida, Rheol Act, **41**, 1, 2002.
41. X. Zhao, Y.F. Li, S.J. Zhang, Y. Shao and X.L. Wang, Polymer, **48**, 5241 (2007).
42. J. Jang and H. Yang, J Mater Sci, **35**, 2297 (2000).

43. S. Rimdusit, P. Jongvisuttisun, C. Jubsilp and W. Tanthapanichakook, J Appl Polym Sci, **111**, 1225 (2009).

44. T. Takeichi, Y. Guo and T. Agag, J Polym Sci Polym Chem, **38**, 4165 (2000).

45. W.Y. Chiang and S.C. Chan, J Appl Polym Sci, **43**, 1827 (1991).

46. T.K. Ahn, M. Kim and S. Choe, Macromolecules, **30**, 3369 (1997).

47. V. Trappe, W. Burchard and B. Steinmann, Macromolecules, **24**, 4738 (1991).

48. B.H. Stuart, Infrared spectroscopy: fundamentals and applications. Chichester:John Wiley & Son, Inc.; 2004. pp. 71-79.

49. A. Tuzun, B. Kiskan, N. Alemdar, A.T. Erciyes and Y. Yagci, J Polym Sci Polym Chem, **48**, 4279 (2010).

50. R. Jain, V. Choudhary and A.K. Narula, J Appl Polym Sci, **105**, 3802 (2007).

51. S. Rimdusit and Jubsilp, Thailand Patent pending. Issue number 0701003695 (2007).

52. P.M. Hergenrother, . In : Kroschwitz JI, editor. High performance polymers and composites : Heat-resistant polymersNew York: John Wiley & Sons, 1991. p. 374.

53. Available from: http://www.ube.com/content.php?pageid=81 accessed on 29/12/10.

54. S. Rimdusit, W. Benjapan, S. Assabumrungrat and T. Takeichi, Polym Eng Sci, **47**, 489 (2007).

55. C. Wang, X. Zhao, G. Li and J. Jiang, Polym Degrad Stability, **94**, 1746 (2009).

56. L.E. Nielsen, J Macromol Sci Rev Macromol Chem, **3**, 69 (1969).

57. L.E. Neilsen and R.F. Landel, Mechanical properties of polymer and composites. New York: Marcel Dekker, 1994.

58. H. Ishida and Y.H. Lee, Polymer, **42**, 6971 (2001).

59. G. Levita, S. De Petris, A. Marchetti and A. Lazzeri, J Mater Sci, **26**, 2348 (1991).

60. D.C.C. Lam and A.C.M. Chong, Mater Sci Eng A – Struct, **281**, 156 (2000).

61. S. Fakirov, F.J. Balta Calleja and M. Krumoval, J Polym Sci Polym Phys, **37**, 1413 (1999).

62. S. Tiptipakorn, S. Damrongsakkul, S. Ando, K. Hemvichian and S. Rimdusit, Polym Degrad Stabili, **92**, 1265 (2007).

63. D.W. Vankrevelen and P.J. Hoftyzer, Properties of polymers. New York: Elsevier, 1976. p. 529.

64. R. Jain, A.K. Narula and V. Choudhary, J Appl Polym Sci, **106**, 3327 (2007).

65. C. Jubsilp, T. Takeichi, and S. Rimdusit, Polym Degrad Stabili, **96**, 1047 (2011).

66. H. Ishida and H.Y. Low, Macromolecules, **30**, 1099 (1997).

67. H. Ishida and Y. Rodriguez, J. Appl. Polym. Sci., **58**, 1751 (1995).

68. M. Konieczny, H. Xu, R. Battaglia, S.L. Wunder, and W. Volksen, *Polymer*, **38**, 2969 (1997).

69. F.A. Settle, *Handbook of Instrumental Techniques for Analytical Chemistry*, Prentice Hall, Inc., New Jersey (1997).

70. N.B. Colthup, L.H. Daly, and S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, Inc., London (1990), p. 310.

71. H.A. Wittcoff, B.G. Reuben and J.S. Plotkin, *Industial Organic Chemicals*, 2nd ed., Wiley-interscience, Hobogen N.J. (2004).

72. W.Y. Chiang and S.C. Chan, *J. Appl. Polym. Sci.*, **43**, 1827 (1991).

73. J. Rocksa, L. Rintoula, F. Vohwinkelc, and G. Georgea, *Polymer*, **45**, 6799 (2004).

74. H. Inoue, H. Okamoto, and Y. Hiraoka, *Radiat. Phys. Chem*., **29**, 283 (1987).

75. S. Tamai, A. Yamaguchi, and M. Ohta, *Polymer*, **37**, 3683 (1996).

76. C.P. Yang, S.H. Hsiao and K.L. Wu, Polymer, **44**, 7067 (2003).

77. K.L. Wang, W.T. Liou, D.J. Liaw and S.T. Huang, Polymer, **49**, 1538 (2008).

78. J.E. Mark, ed., *Physical Properties of Polymer Handbook*, Springer, New York (1996).

79. T.L. Grubb, V.L. Ulery, T.J. Smith, G.L. Tullos, H. Yagci, L.J. Mathias, and M. Langsam, *Polymer*, **40**, 4279 (1999).

80. H. Li, J. Liu, K. Wang, L. Fan and S. Yang, Polymer, **47**, 143 (2006).

81. T.L. Grubb, V.L. Ulery, T.J. Smith, G.L. Tullos, H. Yagci, L.J. Mathias, and M. Langsam, *Polymer*, **40**, 4279 (1999).

82. R.H. Vora, *Mater. Sci. Eng. B*, **168**, 71 (2010). 47

83. H. Ishida and S. Rimdusit, Thermochim Acta, **320**, 177 (1998).

84. F.H. Chowdhury, M.V. Hosur and S. Jeelani, Mater Sci Eng A, **421**, 298 (2006).

85. P. Ghosh, N.R. Bose, B.C. Mitra and S. Das, J Appl Polym Sci, **64**, 2467 (1997).

86. D. Ray, B.K. Sarkar, S. Das and A.K. Rana, Comput Sci Technol, **62**, 911 (2002).

87. C. Jubsilp, B. Ramsiri and S. Rimdusit, Polym Eng Sci, (2012), doi:10.1002/pen.23107

88. B. Perret, B. Schartel, K. StoB, M. Ciesielski, J. Diederichs, M. Doring, J. Kramer and V. Altstadt, Eur Polym J, **47**, 1081 (2011).

89. V. Cadiz, J.C. Ronda, G. Lligadas and M. Glia, Handbook of benzoxazine resins. Oxford UK: Elsevier (2011).

90. Y. Zhou, F. Pervin, S. Jeelani and P.K. Mallick, J Mater Process Tech, 198, 445 (2008).

Outputs from this research

1. ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

1.1 . **C. Jubsilp,** T. Takeichi, and S. Rimdusit, “Property Enhancement of polybenzoxazine Modified with Dianhydride ”, *Polym. Degrad. Stabili.*, **96** (2011), 1047-1053.

1.2 **C. Jubsilp,** B. Ramsiri, and S. Rimdusit, “Effect of Aromatic Carboxylic Dianhydride on Thermomechanical Properties of Polybenzoxazine-Dianhydride Copolymers”, *Polym. Eng. Sci.*, DOI: 10.1002/pen.23107

1.3 S. Rimdusit**,** B. Ramsiri, **C. Jubsilp,** and I. Dueramae, “Characterization of Polybenzoxazine Modified with Isomeric Biphenyltetracarboxylic Dianhydrides” *Accepted to eXPRESS Polymer Letters Vol.6, No.x (2012) x–x.*

1.3 S. Rimdusit, S. Tiptipakorn, **C. Jubsilp**, and T. Takeichi, “Polybenzoxazine Alloys and Blends: Some Unique Properties and Applications” *Accepted to Reactive and functional polymers (2012).*

2. การนำผลงานวิจัยไปใช้ประโยชน์

เชิงวิชาการ

เป็นการผลิตบุคลากรที่มีทักษะด้านงานวิจัยโดยมีนิสิตระดับปริญญาโท สาขาวิศวกรรมเคมี (จุฬาลงกรณ์มหาวิทยาลัย) จำนวน 1 คน และนิสิตระดับปริญญาตรีจำนวน 4 คน สำเร็จการศึกษาจากผลงานวิจัยนี้

3. การเสนอผลงานในที่ประชุมวิชาการระดับนานาชาติ

3.1 **C. Jubsilp,** T. Takeichi, and S. Rimdusit, “Degradation Kinetic of Polybenzoxazine Modified with Aromatic Tetracarboxylic Dianhydride” Proceeding of 3rd International Symposium on Network Polymers (Symposium BAEKELAND 2011), <u>Oral presentation</u>, Toyohashi, Japan, 11-14 September 2011.

3.2 **C. Jubsilp**, S. Rimdusit, and I. Dueramae, “Effects of Aromatic Tetracarboxylic Dianhydride Type on Degradation Kinetic of Polybenzoxazine Copolymers” Proceeding of 6th- Pure and Applied Chemistry International Conference (PACCON 2012), <u>Oral Presentation</u>, Chiang Mai, Thailand, 11-13 January 2012.

3.3 C. Panyawanitchakun, **C. Jubsilp**, and S. Rimdusit, “Characterization of High Performance PMDA-Modified Polybenzoxazine Composites Reinforced with Carbon

Fiber" Proceeding of 6th- Pure and Applied Chemistry International Conference (PACCON 2012), Oral Presentation, Chiang Mai, Thailand, 11-13 January 2012.

3.4 S. Rimdusit, B. Ramsiri, and **C. Jubsilp,** "Effects of Aromatic Dianhydrides on Thermomechanical Property Enhancement of Polybenzoxazine" Proceeding of 6th- Pure and Applied Chemistry International Conference (PACCON 2012), Oral Presentation, Chiang Mai, Thailand, 11-13 January 2012.

3.5 S. Rimdusit, C. Panyawanichakun, and **C. Jubsilp**, "High Performance PMDA-Modified Polybenzoxazine Composites Reinforced with Carbon Fiber" Proceeding of MAMIP2012 Asian International Conference on Materials, Minerals and Polymers, Oral Presentation, Penang, Malaysia, 23-24 March 2012.

4. Manuscript

C. Jubsilp, C. Panyawanitchakun, and S. Rimdusit, "Flammabiliby and Thermomechaical Properties of Dianhydride-Modified Polybenzoxazine Composites Reinforced with Carbon Fiber" *Manuscript will be submitted to Journal of Applied Polymer Science, 2012*

"

Reprints or manuscripts

Appendices

APPENDIX A

Effects of Carbon Fiber Contents on Properties of Carbon Fiber-reinforced PBA-a:PMDA Composites

Appendix A-1 The maximum packing density and void content of CF-reinforced PBA-a:PMDA (1.5:1 mol) composites.

Carbon fiber content (wt%)	Theoretical density (g/cm^3)	Actual density (g/cm^3)	Void content (%)
60	1.55	1.46 $\pm$ 0.01	5.5 $\pm$ 0.73
65	1.57	1.51 $\pm$ 0.01	4.1 $\pm$ 0.86
70	1.6	1.52 $\pm$ 0.007	5.1 $\pm$ 0.52
75	1.63	1.53 $\pm$ 0.01	6.1 $\pm$ 0.69
80	1.65	1.52 $\pm$ 0.007	7.8 $\pm$ 0.51

Appendix A-2 The storage modulus (E') at 35^{o}C and the glass transition temperature (Tg, loss modulus), of CF-reinforced PBA-a:PMDA (1.5:1 mol) composites at various carbon fiber contents which were determined from DMA.

Sample (wt%)	Storage modulus (E') at 35^{o}C (GPa)	$T_{g,DMA}$ (^{o}C)
CF/PBA-a:PMDA (60/40)	43.1	233
CF/PBA-a:PMDA (65/35)	45.3	237
CF/PBA-a:PMDA (70/30)	44.5	235
CF/PBA-a:PMDA (75/25)	35.9	230
CF/PBA-a:PMDA (80/20)	37.7	229

APPENDIX B

Effects of PMDA Contents on Properties of 65wt% carbon fiber-reinforced PBA-a:PMDA Composites

Appendix B-1 The storage modulus (E') at 35^{o}C and the glass transition temperature (Tg, loss modulus), of 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios which were determined from DMA.

Sample	Storage modulus (E') at 35^{o}C (GPa)	$T_{g,DMA}$ (^{o}C)
65wt% CF/PBA-a:PMDA (1:0)	41.3	183
65wt% CF/PBA-a:PMDA (4:1)	44.1	203
65wt% CF/PBA-a:PMDA (3:1)	45.6	208
65wt% CF/PBA-a:PMDA (2:1)	45.3	227
65wt% CF/PBA-a:PMDA (1.5:1)	45.3	237
65wt% CF/PBA-a:PMDA (1:1)	43.05	234

Appendix B-2 The flexural properties of 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios.

Samples CF/PBA-a:PMDA	Flexural strength (MPa)	Flexural modulus (GPa)
1:0	635 ± 8.94	55 ± 0.88
4:1	639 ± 7.03	61 ± 0.71
3:1	640 ± 10.20	65 ± 1.01
2:1	647 ± 23.27	63 ± 1.04
1.5:1	652 ± 12.59	61 ± 0.99
1:1	637 ± 13.46	62 ± 1.75

Appendix B-3 The mechanical and the thermal properties of CF/PBA-a:PMDA systems composites and other high-performance composites.

Resins	Fiber weight fraction (%)	Storage modulus (E') (GPa)	Flexural properties		$T_{g,DMA}$ (^{o}C) ()
			Strength (MPa)	Modulus (GPa)	
PBA-a:PMDA					
1:0	65	41	635	55	183
4:1	65	44	639	61	203
3:1	65	46	640	65	208
2:1	65	45	647	63	227
1.5:1	65	45	652	61	237
1:1	65	43	637	62	234
BA-a[1]	80	43	397	51	183
BA-35X[2]	N/A	8.5	550	31	240
BEP362[3]	58(vol%)	57.7	1011	71	150
SC-15 epoxy[4]	70	12	488	48.9	111
SC-15 epoxy[5]	56(vol%)	21	380	38	99
Epoxy[6]	50(vol%)	5.4	731	58	162
Phenolic[7]	50	9.5	350	6.9	N/A

[1] Ref.: Rimdusit, S., Liengvachiranon, C., Tiptipakorn, S., and Jubsilp, C. Thermomechanical characteristics of benzoxazine-Urethane copolymers and their carbon fiber-reinforced composites. J. appl. Polym. Sci. 113 (2009): 3823-3830.

[2] Ref.: Ishida, H., and Chaisuwan, T. Mechanical property improvement of carbon fiber reinforce polybenzoxazine by rubber interlayer. Polym. Compos. 24 (2003): 597-607.

[3] Ref.: Rimdusit, S., Jongvisuttisan, P., Jubsilp, C., and Tanthapanichakoon, W. Highly processable ternary systems based on benzoxazine, epoxy, and phenolic resins for carbon fiber composite processing. J. appl. Polym. Sci. 111 (2009): 1225-1234.

[4] Ref.: Zhou, Y., Pervin, F., Jeelani, S., and Mallick, P. K. Improvement in mechanical properties of carbon fabric-epoxy composite using carbon nanofibers. J. Mater. Pro. Tech. 198 (2008): 445-453.

[5] Ref.: Chowdhury, F. H., Hosu,r M. V., and Jeelani, S. Investigations on the thermal and flexural properties of plain weave carbon/epoxy-nanoclay composites by hand-layup technique. J. Mater. Sci. 42 (2007): 2690–2700.

[6] Ref.: Gabr, M. H., Elrahman, M. A., Okubo, K., and Fujii, T. A Study on mechanical properties of bacterial cellulose/epoxy reinforced by plain woven carbon fiber modi□ed with liquid rubber. Composites: Part A 41 (2010): 1263–1271.

[7] Ref.: Cho, D., and Lee, J. Effect of quasi-carbonization processing parameters the mechanical properties of quasi-carbon/phenolic composites. J. appl. Polym. Sci. 107 (2008): 3350–3357

Polymer Degradation and Stability 96 (2011) 1047–1053

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Property enhancement of polybenzoxazine modified with dianhydride

Chanchira Jubsilp [a], Tsutomu Takeichi [b], Sarawut Rimdusit [c,*]

[a] Department of Chemical Engineering, Faculty of Engineering, Srinakharinwirot University, Ongkharak, Nakhonnayok 26120, Thailand
[b] Department of Environmental and Life Sciences, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441-8580, Japan
[c] Polymer Engineering Laboratory, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

ARTICLE INFO

Article history:
Received 30 December 2010
Received in revised form
22 March 2011
Accepted 28 March 2011
Available online 5 April 2011

Keywords:
Polybenzoxazine
Thermosetting polymer
Cross-linking
Thermal property
Copolymer

ABSTRACT

A novel bisphenol-A-aniline type polybenzoxazine (PBA-a) modified with dianhydride was successfully prepared by reacting bisphenol-A-aniline based benzoxazine (BA-a) resin with 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) in 1-methyl-2-pyrrolidone (NMP) solvent. The miscible monomer mixture was easily transformed into transparent PBA-a/BTDA copolymers by thermal cure. Fourier-transform infrared spectroscopy reveals the formation of ester linkage which is a covalent interaction between hydroxyl group of the PBA-a and the carbonyl group in the dianhydride. The PBA-a/BTDA copolymers show only one glass transition temperature (Tg) with the value as high as 263 °C at BA-a:BTDA = 1.5:1 mol ratio. The value is remarkably higher than that of the unmodified PBA-a, i.e. 160 °C. In addition, the resulting PBA-a/BTDA copolymers display relatively high degradation temperature up to 364 °C and substantial enhancement in char yield with a value of up to 61% by weight. Moreover, flexibility of the PBA-a/BTDA copolymer samples is also significantly enhanced compared to the unmodified PBA-a. The obtained copolymer demonstrates high potential for those applications that require high thermal and mechanical properties with fire resistant characteristics.

1. Introduction

An improvement of polymeric material properties particularly by modification of the existing polymers to achieve high thermal stability, high char yield, and high glass transition temperature (Tg) becomes increasingly important for an advanced composite system such as in an electronic packaging industry [1,2]. Polybenzoxazines are a novel class of thermosetting polymers that combine outstanding thermal properties and flame retardance of phenolic resins with excellent mechanical performance and molecular design flexibility of epoxy resins [3–5]. The chemistry of benzoxazine synthesis offers a wide range of molecular design flexibility by using derivatives of phenol, aldehyde, or primary amine. As the polymer can be cured through ring-opening polymerization with or without a catalyst, no by-product is released during the curing process, which eliminates the formation of voids in the products. Moreover, polybenzoxazines possess several outstanding properties such as near-zero shrinkage after curing, low water absorption, and relatively high Tg even though they render relatively low cross-linking density [6–8]. To obtain high performance polybenzoxazines by utilizing its molecular design flexibility, thermal and thermo-oxidative stabilities of polybenzoxazines have been substantially improved by altering the functional group on the phenol and/or amine [9–16]. Ishida and Sanders [9–12] invented a novel class of arylamine-based bifunctional benzoxazine resin. In their benzoxazine resins, a bifunctional bisphenol-A-xylidine type benzoxazine resin (BA-35x) provided superior thermal stability to a bisphenol-A-aniline type (BA-a) and a bisphenol-A-toluidine type (BA-mt) resins. At its fully cured stage, BA-35x's Tg and degradation temperature were reported to exhibit the values much greater than those of BA-a polymer due to the regioselectivity of the benzoxazine polymerization in the aromatic amine-based polybenzoxazines. Selectively protecting or activating sites on the pendant aromatic ring toward electrophilic aromatic substitution with alkyl groups allow a series of polybenzoxazines to be developed which contain various amount of phenolic Mannich bridges, arylamine Mannich bridges, and methylene linkages. In the case of BA-a polymer, the network structure consists of largely phenolic Mannich base structures with a small amount of the arylamine rings being cross-linked by Mannich bridges. Whereas the network structures of BA-mt and BA-35x polymers also contain increasing amount of methylene-bridged species in the network structure which give rise to significantly enhanced Tg. In addition, the power of the molecular design-approach to enhance thermal properties of polybenzoxazine was further demonstrated by Cao et al. in a novel cyano functionalized polybenzoxazine (BZCN) [13]. The authors reported that the completely cured materials could achieve high char yield and high Tg. The thermally activated curing of

* Corresponding author. Tel.: +66 2 2186862; fax: +66 2 2186877.
E-mail address: sarawut.r@chula.ac.th (S. Rimdusit).

0141-3910/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2011.03.021

BZCN follows multiple curing mechanisms via the ring-opening polymerization of oxazine rings and the triazine ring-formation of cyano groups, which contribute to the stability of this polymer. More recently, thermal stability of 9,10-dihydro-9-oxa-10-phosphaphenanthrene (DOPO)-containing polybenzoxazine was reported by Sponton [14]. Thermal stability of the phosphorus-containing polybenzoxazines was evaluated by examining their degradation temperature (Td) and char yield. The Td at 5% weight loss and char yield under nitrogen atmosphere at 750 °C of the modified polybenzoxazines were reported to be 332 °C and 25%, respectively. However, disadvantages of the modification of the molecular structure of the benzoxazine resins to obtain high performance polymer include difficulty of the resin preparation, the purification process, and the high cost of raw materials used.

An ability of benzoxazine resins to form alloys with various other resins or polymers often renders a novel class of resin systems with intriguing properties [16–22]. For example, alloying between benzoxazine resin and epoxy resin is considered to be a potentially effective measure to enhance thermal or mechanical properties as well as flammability of the polymers [17–24]. Sponton et al. [16] developed a mixture of bis(m-aminophenyl)methylphosphine oxide based benzoxazine (Bz-BAMPO) and glycidylether (DGEBA). The authors reported that the Bz-BAMPO:DGEBA at 2:1 mol ratio showed Td at 5% weight loss of about 347 °C compared to 333 °C of Bz-BAMPO. Ishida and Ohba [20] reported that maleimide-functionalized benzoxazine could be copolymerized with epoxy to improve toughness and processibility without compromising their thermal properties. The resulting polymer with 10% by mol of epoxy resin (DGEBA) provided Tg with 25 °C higher than that of the obtained homopolymer. Moreover, Rimdusit et al. [17] reported that toughness of the alloys of rigid bisphenol-A-aniline type polybenzoxazine (PBA-a) and isophorone diisocyanate-based urethane prepolymers (PU) systematically increased with the amount of the PU toughener due to the addition of more flexible molecular segments in the polymer hybrids. The Tg of the PBA-a/PU alloys was found to be 220 °C which was substantially higher than that of the parent polybenzoxazine, i.e. 165 °C. In this work, polybenzoxazine obtained by thermal ring-opening polymerization of their precursors contains phenolic hydroxyl groups. These phenolic hydroxyl groups have a strong potential for reacting with NCO groups in the PU. This interaction resulted in enhancement of the cross-linked density of the polybenzoxazine. Takeichi et al. [21] revealed a performance improvement of bisphenol-A-aniline type polybenzoxazine (PBA-a) by alloying with polyimide (PI). They reported that Tg values and thermal stabilities of the alloys increased as the PI component increased. Tgs of the PBA-a:PI alloys were in a range of 186 °C–205 °C and were higher than that of the polybenzoxazine, i.e. 152 °C.

3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) is a chemical used as co-monomer for high tensile strength polyimide fibers, films and foams to provide excellent mechanical and electrical performances as well as outstanding heat insulation and fire retardant properties of the materials. In addition, polyimide based on BTDA has been extensively used as a matrix resin for advanced composites, such as PMR-15 [24–26]. Furthermore, BTDA can function as a curing agent for high performance-epoxy resins used in electric insulations, composites and powder coating [27]. Trappe et al. [28], suggested that epoxy group showed remarkable reactivity toward a number of different curing agents such as amines, phenols, acids, and acid anhydrides. The reactions between an acid anhydride and diepoxies or triepoxies lead to efficiently cross-linked materials with excellent physical properties. Moreover, for epoxy resins which contain free hydroxyl groups, the curing reaction is started by the reaction of the hydroxyl group with the anhydride to generate a monoester with a free carboxylic acid group, and this, in turn, reacts with another anhydride. In this paper, we demonstrate an ability of benzoxazine resin to react with dianhydride (BTDA) to yield novel high performance thermosetting copolymers. The modification is very simple and highly practical for industrial use.

2. Experimental

2.1. Materials

BA-a type benzoxazine resin based on bisphenol-A, formaldehyde, and aniline was synthesized according to the patented solventless technology [4]. The BA-a resin is a yellow clear solid at room temperature. Bisphenol-A and paraformaldehyde were obtained from Thai Polycarbonate Co., Ltd. (TPCC) and Merck Co., respectively. An aromatic amine, i.e. aniline (99%), and the 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), including 1-methyl-2-pyrrolidone (NMP) solvent were purchased from Fluka Chemical Co. All chemicals were used as-received.

2.2. Processing method

Each resin component was first measured at the desirable mol ratios. The monomer mixture to be investigated was BA-a:BTDA ranging from 4:1, 3:1, 2:1, 1.5:1 and 1:1 mol ratios. The mixture was dissolved in NMP solvent and stirred at 80 °C until a homogeneous mixture was obtained. Then the obtained solution was cast on Teflon sheet. The NMP solvent was then removed by drying the sample in a vacuum oven at 80 °C for 24 h before undergoing a step cure in an air-circulating oven. The sample was then cured sequentially at 170 °C for 1 h, at 190, 210, 230 °C for 2 h each and 240 °C for 1 h to ensure a fully cure stage of the mixture.

2.3. Sample characterizations

FTIR measurement was conducted at room temperature on a Spectrum GX FTIR spectrometer from Perkin Elmer. The samples were sufficiently thin to be within a range where the Beer–Lambert law is obeyed. All spectra were taken with 64 scans at a resolution of 4 cm^{-1} and spectral range of 4000–400 cm^{-1}. Dynamic mechanical analysis (DMA) was conducted on NETZSCH, model DMA242 in the tensile geometry at 1 Hz with a strain value of 0.1% and at a heating rate of 2 °C min^{-1} from 30 to 350 °C using the sample size of 7.0 mm × 10 mm × 0.1 mm. Nanoindentation experiment was carried out on UMIS-2000 nanoindenter with a diamond Berkovich tip (a three-sided pyramidal diamond tip) from CRIRO, Australia. A maximum load of 50 mN with loading/unloading cycles and holding time of 60 s was used to evaluate the hardness from the penetration depth. The 3 × 3 arrays of indents were performed in the central region of a sample to eliminate edge effect. Thermogravimetric analysis (TGA), from Perkin Elmer (Diamond TG/DTA), was performed under nitrogen purging with a constant flow of 100 ml/min. Sample mass of 10 mg was heated at a linear heating rate of 20 °C min^{-1} from room temperature to 900 °C.

3. Results and discussion

3.1. FTIR study of the BA-a/BTDA systems

The IR spectra of bisphenol-A-aniline based benzoxazine (BA-a) resin, BTDA, bisphenol-A-aniline type polybenzoxazine (PBA-a), and PBA-a/BTDA copolymers are shown in Fig. 1. From the figure, the BA-a resin (Fig. 1(a)) was characterized by the band at 1232 cm^{-1} from the aromatic ether C–O–C stretching mode of an

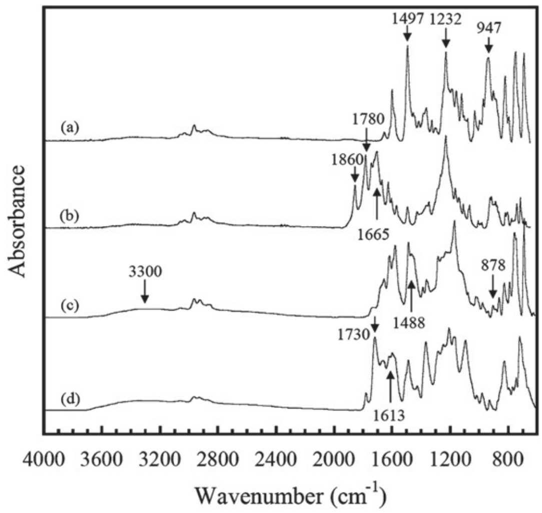


Fig. 1. IR spectra: (a) BA-a resin, (b) BTDA, (c) PBA-a, (d) BA-a:BTDA mol ratio = 1.5:1.

oxazine ring whereas the band around 947 cm^{-1}, and 1497 cm^{-1} were attributed to the tri-substituted benzene ring. After thermal cure, these bands completely disappeared indicating a complete loss of the oxazine ring in the BA-a resin. In addition, new absorption peaks at 878 cm^{-1} and 1488 cm^{-1} of the tetra-substituted aromatic ring were observed suggesting the ring-opening reaction to take place *ortho* to the phenolic moiety as displayed in Fig. 1(c) [5,11]. Furthermore, an indication of ring-opening reaction of the BA-a resin upon thermal treatment could also be observed from the appearance of a broad peak about 3300 cm^{-1} which was assigned to the phenolic hydroxyl group formation. For the BTDA material, the IR spectrum, in Fig. 1(b), revealed carbonyl characteristic absorption peaks in anhydride at 1780 and 1860 cm^{-1}, and the benzophenone carbonyl band near 1665 cm^{-1}. Furthermore, the band centered at 1232 cm^{-1} associated with the C–O–C stretching mode in the BTDA was also detected [29,30].

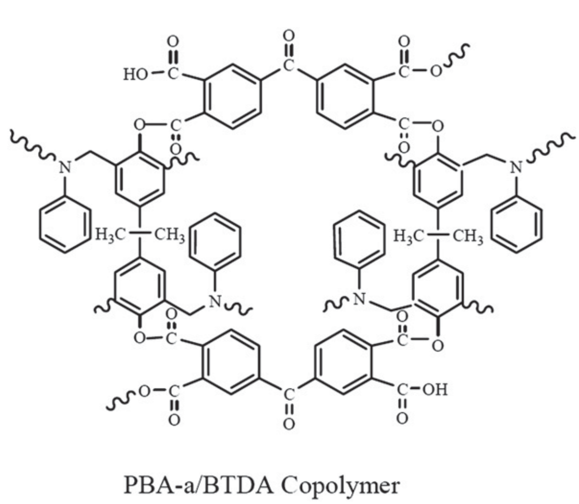
Polybenzoxazine obtained by thermal ring-opening polymerization of benzoxazine resin has phenolic hydroxyl groups in their structure [11]. We expect that these phenolic hydroxyl groups have a strong potential for interaction with carbonyl groups in BTDA to form ester linkage as similarly demonstrated by the covalent reaction between free hydroxyl groups of epoxy resin and carbonyl groups in dianhydride [28]. This characteristic provides a potential copolymer formation from the two monomers. As exemplification in Fig. 1(d) of the BA-a:BTDA = 1.5:1 mol ratio, we can see that the carbonyl stretching bands of BTDA at 1860 and 1780 cm^{-1} completely disappeared, indicating the reaction was completed. It was postulated therefore that the reaction between the phenolic OH of the PBA-a and the carbonyl group of the BTDA could occur to form ester linkage as evidenced by the observed peak in the spectrum at 1730 cm^{-1}. Generally, IR spectra for esters feature an intense band in the range 1730–1750 cm^{-1} of its C=O stretching band. This peak varies slightly depending on the functional groups attached to the carbonyl. For example, a benzene ring or double bond in conjugation with the carbonyl will bring the wavenumber down about 30 cm^{-1}. In addition, the characteristic absorption band of ester linkage C–O band at 1250–1310 cm^{-1} was observed. However, there was no frequency shift in the benzophenone carbonyl band near 1665 cm^{-1} indicating that the carbonyl group between the two phenyl rings in the BTDA did not participate in any chemical reaction [31]. Furthermore, the carboxylic acid occurred after thermal curing of the BA-a:BTDA mixture can be followed by monitoring the appearance band at 1613 cm^{-1} due to C=O stretching of the free acid [32]. In addition, carboxylic acid shows characteristic C–O stretching, in-plane and out-of-plane, and O–H bending bands at, 1283 cm^{-1}, 1425 cm^{-1} and 928 cm^{-1}, respectively [31,33]. Thus, the PBA-a/BTDA copolymer was formed from the combination of BA-a resin and BTDA via ester linkage formation as shown in Scheme 1 which was expected to enhance crosslink density in the resulting hybrid polymer network. Previously studied in anhydride-cured epoxy resin systems [28,34,35], the ester linkage formation has also been reported. FT-Raman analysis revealed that curing propagation mainly occurs by poly-esterification between epoxide and anhydride groups. The decrease of epoxide ring breathing vibration at 1260 cm^{-1} and anhydride ring followed by means of 1860 cm^{-1} result in the relative increase of new band observed at 1734 cm^{-1} due to ester group formation upon cure [34].

3.2. Network formation by thermal cure of PBA-a/BTDA copolymers

After thermal cure stages, a transparent brown PBA-a and red brown PBA-a/BTDA copolymer samples were obtained. The appearances of the cured PBA-a/BTDA copolymer samples are shown in Fig. 2. We can see that a PBA-a sample of about 100 μm thick is rather brittle, and can not be bent further than as shown in Fig. 2(a). Whereas the homogeneous samples of all the PBA-a/BTDA copolymers of the same thickness as illustrated Fig. 2(b)–(d) showed a remarkable improvement in their flexibility as recently reported in our patent [36]. The flexibility enhancement of the PBA-a/BTDA copolymer samples may be due to additional ester linkages, structurally flexible functional group, formed in the polybenzoxazine network as a result described in benzoxazine containing polyester by Tuzun et al. [32]. In addition, the great flexibility showed a similar trend for the PBA-a/BTDA copolymers in Fig. 2(b)–(d) with that of the commercial polyimide films such as Kapton films [37] and UPILEX-s film [38].

3.3. Dynamic mechanical properties

The storage modulus that provides the material stiffness of the PBA-a/BTDA copolymer samples at a glassy state region reflecting their molecular rigidity is depicted in Fig. 3. From this figure, we can clearly see that the storage modulus of the PBA-a/BTDA copolymers was higher than that of the neat PBA-a and the values increased with the BTDA contents. The room temperature modulus at 25 °C of the copolymers exhibited the values in the ranges of 2.63–2.94 GPa



Scheme 1. A possible copolymerization between PBA-a and BTDA.

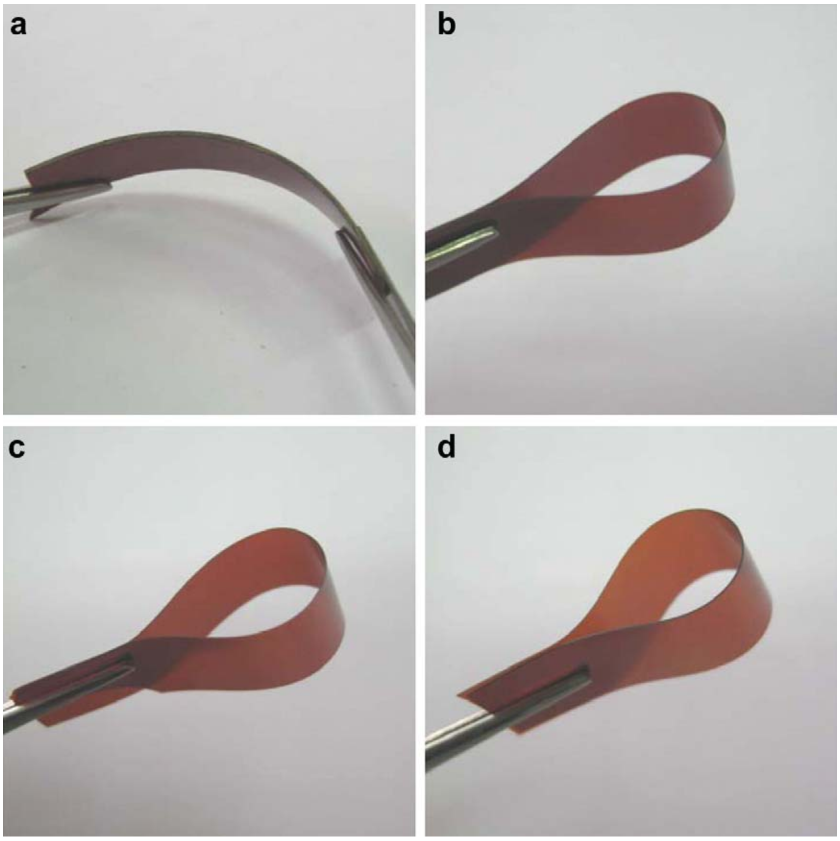


Fig. 2. Appearance of the fully cured PBA-a/BTDA copolymers at various BTDA mol ratio: (a) PBA-a, (b) BA-a/BTDA 4:1, (c) BA-a/BTDA 3:1, (d) BA-a/BTDA 1.5:1.

whereas that of the neat PBA-a was about 2.57 GPa. We can see that the storage modulus of the PBA-a/BTDA copolymers is approximately the same as that of the polyimide film systems (i.e. in the range 2.3–3.0 GPa) such as *s*-BPDA/ODA, ODPA/ODA, PMDA/ODA [39,40], or fluorinated polyimide [41]. However, some of polyimide films, i.e. UPILEX-s, show tensile modulus as high as 9.1 GPa at 25 °C and 42% for ultimate elongation [38]. From the same figure, it was obvious that the modulus in the rubbery plateau of the PBA-a/BTDA copolymer samples also increased with the content of the BTDA.

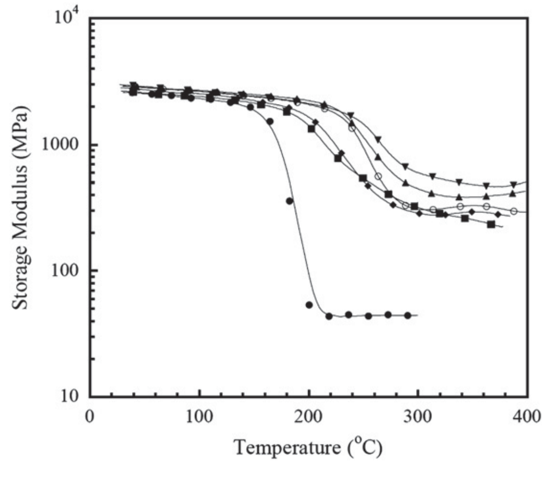


Fig. 3. Storage and loss modulus of PBA-a/BTDA copolymers as a function of temperature at different BTDA mol ratio: (●) PBA-a, (■) BA-a/BTDA 4:1, (◆) BA-a/BTDA 3:1, (▲) BA-a/BTDA 2:1, (▼) BA-a/BTDA 1.5:1, (○) BA-a/BTDA 1:1.

This result suggested that an addition of the BTDA resulted in a substantial enhancement in crosslink density of the PBA-a/BTDA copolymers from additional ester linkage as explained in the previous section. For a tight network structure i.e. rubbery plateau modulus greater than 10^7 Pa such as in our case, the non-Gaussian character of the polymer network becomes more and more pronounced and the equation from theory of rubbery elasticity is no longer applicable. The approximate relation expressed in the equation below proposed by Nielsen [42,43] is thus preferred and is reported to better describe the elastic properties of dense network e.g. in epoxy systems [44–46]. As a consequence, a crosslink density of these copolymer networks, ρ_x, can be estimated from a value of the equilibrium shear storage modulus in the rubbery region (G'_e) which equals to $E'_e/3$ as followed

$$\log\left[\frac{E'_e}{3}\right] = 7.0 + 293(\rho_x) \quad (1)$$

Where E'_e (dyne/cm^2) is an equilibrium tensile storage modulus in rubbery plateau, ρ_x (mol/cm^3) is crosslink density which is the mol number of network chains per unit volume of the polymers.

The calculated crosslink density clearly increased with an increase in BTDA in the copolymers as shown in Fig. 4. In theory, higher crosslink density of the polymer network can lead to higher storage modulus and glass transition temperature (Tg). In addition, the increase in modulus may be due to various kinds of possible hydrogen bonds between hydroxyl or amine groups in polybenzoxazine and the carbonyl group or hydroxyl group in carboxylic acid. Moreover, in Fig. 4, as the BTDA contents in the PBA-a/BTDA copolymers increased, the obtained slope of the storage modulus in the glassy state against temperature was less steep. This is due to the lower degree of molecular mobility of the more rigid

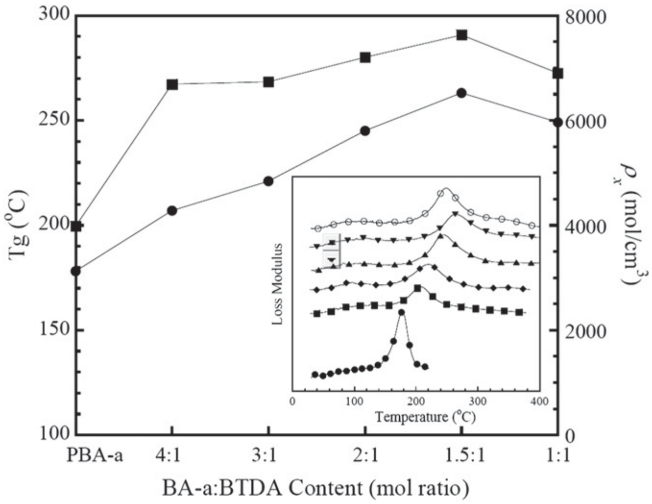


Fig. 4. Crosslink density (ρ_x) and glass transition temperature (Tg) at various BTDA mol ratio: (●) Tg, (■) ρ_x.

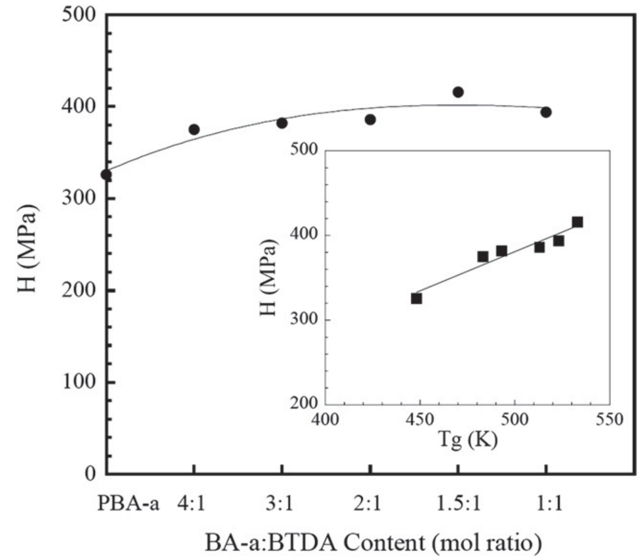


Fig. 5. Room temperature-measured microhardness (H) of PBA-a/BTDA copolymers at different BTDA mol ratio (●), and relationship between the room temperature-measured microhardness (H) and Tg (■).

PBA-a/BTDA copolymers compared to the PBA-a at the corresponding temperature. In other words, enhancement in thermal stability of PBA-a/BTDA systems was observed comparing with the neat PBA-a.

All PBA-a/BTDA copolymer samples are homogeneous and transparent, implying that no phase separation domain formed at the scale exceeding the wavelength of visible light. To verify the miscibility or co-cross-linking of the copolymers, the PBA-a/BTDA copolymer samples were subjected to thermal analysis by examining Tg characteristic. From an inset of Fig. 4, the Tg of PBA-a determined from the maximum of loss modulus curve in DMA experiment was about 178 °C and the value was found to be substantially enhanced by blending with the BTDA. All of the fully cured PBA-a/BTDA copolymer samples showed only single Tg ranging from 207 °C to 263 °C. This characteristic confirmed a presence of a single phase material in these copolymers. Additionally the copolymer of BA-a:BTDA at a mol ratio of 1.5:1 exhibited a maximum value in Tg. From the results, the optimal network formation reaction of the copolymer clearly required greater moles of benzoxazine monomers than those of the BTDA i.e. not a 1:1 mol ratio. This is likely due to an ability of the benzoxazine monomers to react among themselves (self-polymerizability) besides their ability to react with the dianhydrides. As a consequence, the consumption of the benzoxazine monomers tended to be greater than that of the dianhydrides in order to form a perfect network.

3.4. Nanoindentation behavior

Local hardness on surface, which is generally investigated as one of the most important factor that relates to wear resistance of a material, can be characterized using nanoindentation. The measurement is a powerful tool for probing mechanical property of a material in small volume. Fig. 5 depicts surface hardness (H) at room temperature (25 °C) of PBA-a/BTDA copolymer samples as a function of BTDA content. From the results, we can see that the hardness of the PBA-a/BTDA copolymer samples initially increased with the BTDA contents in a range of 4:1–1.5:1 mol ratios (BA-a:BTDA) and then decreased gradually with further addition of the BTDA. The ultimate hardness (465 ± 7.7 MPa) for the copolymer sample of BA-a:BTDA at a mol ratio of 1.5:1 exhibits 43% increment compared to the neat PBA-a (326 ± 11.5 MPa). This significant improvement in hardness of the PBA-a/BTDA copolymers was attributed to a greater molecular rigidity from the presence of the BTDA in the PBA-a. The result was consistent with the enhancement in the glass transition temperature and the glassy state modulus of the copolymer with the amount of the BTDA discussed previously. Furthermore, a relationship between the hardness and the Tg values for the copolymers was illustrated as an inset in Fig. 5. A fairly good linear relationship between the hardness value at room temperature and the Tg between 178 °C and 263 °C was observed in the form of the following equation,

$$H = kTg + C \tag{2}$$

where C = −82.27 MPa and k = 0.92 MPa/K, the regression coefficient being 0.9249. This type of correlation was also found and reported by Fakirov et al. [47] in the system of amorphous polymers, i.e. polyester.

However, in regard to the limitations of the relationship between hardness and Tg in Eq. (2), it seems worth recalling that it is derived from data obtained from measurements carried out at room temperature (25 °C). It is to be expected that the constant C will count on the temperature of relative measurement to Tg of the samples. This implies that to obtain a more fundamental relationship, one has to perform measurements at various temperatures and produce a Tg-scaled law of wider applications as suggested by Fakirov et al. [47].

3.5. Thermal stability investigation

The TGA curves of the neat PBA-a and PBA-a/BTDA copolymers are depicted in Fig. 6 and the degradation temperatures (Td) at 5% weight loss under nitrogen atmosphere of the copolymers with different BTDA contents are displayed in Fig. 7. As seen in the Fig. 7, the Td of the copolymer was shifted to a higher value than that of the neat PBA-a. The presence of the BTDA, therefore, helps enhance the Td of the neat PBA-a. The maximum Td of 364 °C belonged to the copolymer sample of BA-a:BTDA at mol ratio 1.5:1 while the Td of the BTDA and the neat PBA-a was measured to be about 317 °C and 339 °C, respectively. The formation of an additional ester linkage between the carbonyl group in the BTDA and

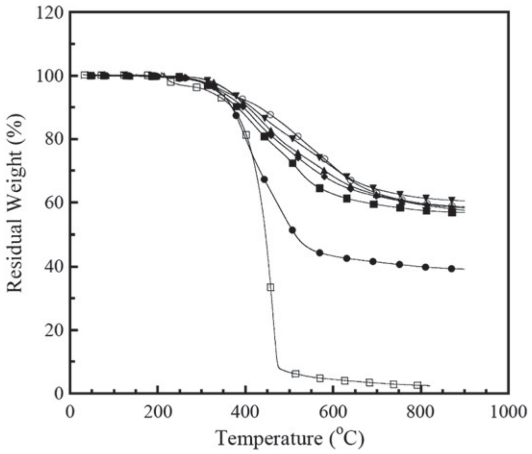


Fig. 6. TGA experiments of PBA-a/BTDA copolymers as a function of temperature at different BTDA mol ratio: (●) PBA-a, (■) BA-a/BTDA 4:1, (◆) BA-a/BTDA 3:1, (▲) BA-a/BTDA 2:1, (▼) BA-a/BTDA 1.5:1, (○) BA-a/BTDA 1:1, (□) BTDA.

hydroxyl group of the neat PBA-a was found to effectively improve the degradation temperature of the resulting PBA-a/BTDA copolymers. In addition, the higher crosslink density and the presence of an aromatic structure of the BTDA in the PBA-a could possibly suppress segmental decomposition via gaseous fragments thus providing an observed enhancement in Td of the samples.

The char yield values, the percent residue at 800 °C, of the PBA-a/BTDA copolymer samples are also determined from the TGA thermograms in Fig. 6. A remarkable improvement of char yield was clearly observed in the copolymers i.e. the char yields of all copolymers showed the values significantly greater than that of the neat PBA-a. In particular, the cured copolymer sample of BA-a:BTDA at the optimal mol ratio of 1.5:1 was found to render an ultimate char value compared to other compositions i.e. as high as 61% which was disclosed in our patent [36], while those of the neat PBA-a and the BTDA were 38% and 2.5%, respectively. Similar substantial enhancement in char yield formation was also reported in the PI/PBA-a hybrid systems [21] PBA-a/SPI systems [48]. However, the char yield at 800 °C under nitrogen atmosphere of some of benzoxazine containing polyester systems [32], i.e. poly(benzoxazine-carboxyterephthalate), was reported with less than 48% compared to that of the copolymer sample of BA-a:BTDA = 1.5:1 mol ratio sample. In principle, the higher char residue of the copolymer of BA-a:BTDA at the mol ratio of 1.5:1 should provide a sample with enhanced flammability. Char yield of a material can be used to estimate limiting oxygen index (LOI) according to Van Krevelen and Hoftyzer equation [49,50]. Thus polybenzoxazine and the PBA-a/BTDA copolymers can be classified in the self-extinguishing category.

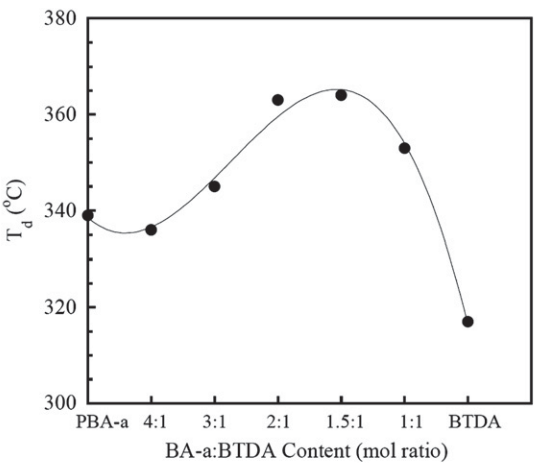


Fig. 7. Degradation temperature at 5% weight loss under nitrogen atmosphere of PBA-a/BTDA copolymers as a function of BTDA content.

4. Conclusions

The copolymers of bisphenol-A-aniline based polybenzoxazine (PBA-a) modified with dianhydride showed significant enhancement in their mechanical and thermal properties compared to those of the neat PBA-a. FTIR spectroscopy revealed that the ester linkage occurred from a reaction of hydroxyl group of PBA-a and carbonyl group of BTDA. DMA experiment showed an enhancement in crosslink density of the obtained copolymers resulting in an increase in the corresponding glass transition temperature. Moreover, an incorporation of BTDA into PBA-a resulted in higher surface hardness compared to the neat PBA-a. The thermal decomposition temperature and weight residue at 800 °C also remarkably increased with an incorporation of the BTDA. Therefore, the presence of BTDA into PBA-a to form PBA-a/BTDA copolymers was found to improve the reliability of the polymer hybrids thus suitable for applications at elevated temperature with enhanced mechanical integrity. Further studies in this pathway such as development of advanced composite materials are in progress.

Acknowledgments

This research receives financial supports from the Thailand Research Fund, the National Research University Project of the Ministry of Education (AM006B and AM1076A), Thailand, and 100th Anniversary of Chulalongkorn University Academic Funding. Additional fund is also provided by the University income, SWU, Government budget 2009. The authors also would like to acknowledge the Center of Excellence in Catalyst and Catalytic Reaction Engineering, Chulalongkorn University for DMA measurement. Bisphenol A is kindly donated by Thai Polycarbonate Co., Ltd. (TPCC).

References

[1] Wong CP. Advances of polymer science, vol. 84. Berlin: Springer-Verlag; 1988. pp. 63–83.
[2] Kinjo N, Ogata M, Nishi K, Kaneda A. Advances in polymer science, vol. 88. Berlin: Springer-Verlag; 1989. pp. 1–48.
[3] Ishida H. Process for preparation of benzoxazine compounds in solventless systems. US Patent 5,543,516, 1996.
[4] Ghosh NN, Kiskan B, Yagci Y. Polybenzoxazines-new high performance thermosetting resins: synthesis and properties. Prog Polym Sci 2007;32:1344–91.
[5] Takeichi T, Guo Y, Agag T. Synthesis and characterization of poly (urethane-benzoxazine) films as novel type of polyurethane/phenolic resin composites. J Polym Sci Polym Chem 2000;38:4165–76.
[6] Ning X, Ishida H. Phenolic materials via ring-opening polymerization synthesis and characterization of bisphenol-A based benzoxazines and their polymers. J Polym Sci Polym Chem 1994;32:1121–9.
[7] Ishida H, Allen DJ. Physical and mechanical characterization of near-zero shrinkage polybenzoxazines. J Polym Sci Polym Phys 1996;34:1019–30.
[8] Nair CPR. Advances in addition-cure phenolic resins. Prog Polym Sci 2004;29: 401–98.
[9] Ishida H, Sanders DP. Improved thermal and mechanical properties of polybenzoxazines based on alkyl-substituted aromatic amines. J Polym Sci Polym Phys 2000;38:3289–301.
[10] Ishida H, Sanders DP. Activated arylamine-based polybenzoxazines. US Patent 6,160,079, 2000.
[11] Ishida H, Sanders DP. Regioselectivity and network structure of difunctional alkyl-substituted aromatic amine-based polybenzoxazines. Macromolecules 2000;33:8149–57.
[12] Ishida H, Sanders DP. Regioselectivity of the ring-opening polymerization of monofunctional alkyl-substituted aromatic amine-based benzoxazines. Polymer 2001;42:3115–25.

[13] Cao GP, Chen WJ, Liu XB. Synthesis and thermal properties of the thermosetting resin based on cyano functionalized benzoxazine. Polym Degrad Stab 2008;93:739–44.
[14] Sponton M, Lligadas G, Ronda JC, Galia M, Cadiz V. Development of a DOPO-containing benzoxazine and its high-performance flame retardant copolybenzoxazines. Polym Degrad Stab 2009;94:1693–9.
[15] Uyar T, Koyuncu Z, Ishida H, Hacaloglu J. Polymerisation and degradation of an aromatic amine-based naphthoxazine. Polym Degrad Stab 2008;93:2096–103.
[16] Sponton M, Ronda JC, Galia M, Cadiz V. Studies on thermal and flame retardant behaviour of mixtures of bis(*m*-aminophenyl)methylphosphine oxide based benzoxazine and glycidylether or benzoxazine of Bisphenol A. Polym Degrad Stab 2008;93:2158–65.
[17] Rimdusit S, Pirstpindvong S, Tanthapanichakoon W, Damrongsakkul S. Toughening of polybenzoxazine by alloying with urethane prepolymer and flexible epoxy: a comparative study. Polym Eng Sci 2005;45:288–96.
[18] Kimura H, Murata Y, Matsumoto A, Hasegawa K, Ohtsuka K, Fukuda A. New thermosetting resin from terpenediphenol-based benzoxazine and epoxy resin. J Appl Polym Sci 1999;74:2266–73.
[19] Kimura H, Matsumoto A, Sugito H, Hasfgawa K, Ohtsuka K, Fukuda A. New thermosetting resin from poly(p-vinylphenol) based benzoxazine and epoly resin. J Appl Polym Sci 2001;79:555–65.
[20] Ishida H, Ohba S. Thermal analysis and mechanical characterization of maleimide-functionalized benzoxazine/epoxy copolymers. J Appl Polym Sci 2006;101:1670–7.
[21] Takeichi T, Guo Y, Rimdusit S. Performance improvement of polybenzoxazine by alloying with polyimide: effect of preparation method on the properties. Polymer 2005;46:4909–16.
[22] Santhosh Kumar KS, Reghunadhan Nair CP, Ninan KN. Investigation on the cure chemistry and polymer properties of benzoxazine-cyanate ester blend. Eur Polym J 2009;45:494–502.
[23] Takeichi T, Saito Y, Agag T, Muto H, Kawauchi T. High performance polymer alloys of polybenzoxazine and bismaleimide. Polymer 2008;49:1173–9.
[24] Serafini TT, Delvigs P, Lightsey GR. Thermally stable polyimides from solutions of monomeric reactants. J Appl Polym Sci 1972;16:905–15.
[25] Serafini TT, Vannucci RD, Alston WB. Second generation PMR polyimides. NASA TMX-71894; 1976.
[26] Meador MA. Recent advances in the development of processable high temperature polymers. Annu Rev Mater Sci 1998;28:599–630.
[27] Jain R, Choudhary V, Narula K. Curing and thermal behavior of DGEBA in presence of dianhydrides and aromatic diamine. J Appl Polym Sci 2007;105: 3804–8.
[28] Trappe V, Burchard W, Steinmann B. Anhydride-cured epoxies via chain reaction. 1. The phenyl glycidyl ether/phthalic acid anhydride system. Macromolecules 1991;24:4738–44.
[29] Chiang WY, Chan SC. Preparation and properties of UV-autocurable BTDA-based epoxy-multiacrylate resins. J Appl Polym Sci 1991;43:1827–36.
[30] Ahn TK, Kim M, Choe S. Hydrogen-bonding strength in the blends of polybenzimidazole with BTDA- and DSDA-based polyimides. Macromolecules 1997;30:3369–74.
[31] Stuart BH. Infrared spectroscopy: fundamentals and applications. Chichester: John Wiley & Son, Inc.; 2004. pp. 71–79.
[32] Tuzun A, Kiskan B, Alemdar N, Erciyes AT, Yagci Y. Benzoxazine containing polyester thermosets with improved adhesion and flexibility. J Polym Sci Polym Chem 2010;48:4279–84.
[33] Colthup NB, Daly LH, Wiberley SE. Introduction to infrared and Raman spectroscopy. London: Academic Press, Inc.; 1990. pp. 310–315.
[34] Rocksa J, Rintoula L, Vohwinkelc F, Georgea G. The kinetics and mechanism of cure of and amino-glycidyl epoxy by a co-anhydride as studied by FT-Raman spectroscopy. Polymer 2004;45:6799–811.
[35] Jain R, Choudhary V, Narula AK. Curing and thermal behavior of DGEBA in presence of dianhydrides and aromatic diamine. J Appl Polym Sci 2007;105: 3802–8.
[36] Rimdusit S, Jubsilp C. Polymer from anhydride modified polybenzoxazine. Thailand Patent pending. Issue number 0701003695, 2007.
[37] Hergenrother PM. In: Kroschwitz JI, editor. High performance polymers and composites: heat-resistant polymers. New York: John Wiley & Sons; 1991. p. 374.
[38] http://www.ube.com/content.php?pageid=81 [accessed 29.12.10].
[39] Rimdusit S, Benjapan W, Assabumrungrat S, Takeichi T, Yokota R. Surface segregation of siloxane containing component in polysiloxane-block-polyimide and s-BPDA/ODA polyimide blends. Polym Eng Sci 2007;47:489–98.
[40] Tiptipakorn S, Lorjai P, Ando S, Rimdusit S. Surface segregation-typed polyimide blends between silicon-containing polyimide and polyimide of varied chain flexibility. Synth React Inorg Met-Org Chem 2008;38:248–55.
[41] Wang C, Zhao X, Li G, Jiang J. Novel fluorinated polyimides derived from 9,9-bis(4-amino-3, 5-difluorophenyl)fluorene and aromatic dianhydrides. Polym Degrad Stab 2009;94:1746–53.
[42] Nielsen LE. Crosslinking-effect on physical properties of polymers. J Macromol Sci Rev Macromol Chem 1969;3:69–103.
[43] Neilsen LE, Landel RF. Mechanical properties of polymer and composites. New York: Marcel Dekker; 1994.
[44] Ishida H, Lee YH. Synergism observed in polybenzoxazine and poly(ε-caprolactone) blends by dynamic mechanical and thermogravimetric analysis. Polymer 2001;42:6971–9.
[45] Levita G, De Petris S, Marchetti A, Lazzeri A. J Mater Sci 1991;26:2348.
[46] Lam DCC, Chong ACM. Effect of cross-link density on strain gradient plasticity in epoxy. Mater Sci Eng A - Struct 2000;281:156–61.
[47] Fakirov S, Balta Calleja FJ, Krumova M. On the relationship between microhardness and glass transition temperature of some amorphous polymers. J Polym Sci Polym Phys 1999;37:1413–9.
[48] Tiptipakorn S, Damrongsakkul S, Ando S, Hemvichian K, Sarawut R. Thermal degradation behaviors of polybenzoxazine and silicon-containing polyimide blends. Polym Degrad Stab 2007;92:1265–78.
[49] Vankrevelen DW, Hoftyzer PJ. Properties of polymers. New York: Elsevier; 1976. p. 529.
[50] Jain R, Narula AK, Choudhary V. Studies on curing and thermal behavior of diglycidyl ether of bisphenol-A and benzoxazine mixtures. J Appl Polym Sci 2007;106:3327–34.

SPE: Polymer Engineering & Science Journal

Copy of e-mail Notification

SPE: Polymer Engineering & Science Published by John Wiley & Sons, Inc.

Dear Author,

Your article page proofs for SPE: Polymer Engineering & Science are ready for review.
John Wiley & Sons has made this article available to you online for faster, more efficient editing. Please follow the instructions below and you will be able to access a PDF version of your article as well as relevant accompanying paperwork.

First, make sure you have a copy of Adobe Acrobat Reader software to read these files. This is free software and is available for user downloading at http://www.adobe.com/products/acrobat/readstep.html.

Open your web browser, and enter the following web address:
http://115.111.50.156/jw/retrieval.aspx?pwd=83f9c6ef8fc7

You will be prompted to log in, and asked for a password. Your login name will be your email address, and your password will be 83f9c6ef8fc7

Example:

Login: your e-mail address
Password: 83f9c6ef8fc7

The site contains one file, containing:

- Author Instructions Checklist
- Adobe Acrobat Users - NOTES tool sheet
- Color Reproduction Form
- A copy of your page proofs for your article

Print out this file, and fill out the forms by hand. Read your page proofs carefully and:

- indicate changes or corrections in the margin of the page proofs
- answer all queries (footnotes A,B,C, etc.) on the last page of the PDF proof
- proofread any tables and equations carefully
- check your figure legends for accuracy

Within 48 hours, please return all materials via e-mail or fax to the address given below. This will include:

Page proofs with corrections

SPE: Polymer Engineering & Science Journal

Copy of e-mail Notification

Return to:

Production Editor, PEN
Cadmus Professional Communications
300 West Chestnut St., Suite A
Ephrata, PA 175□□-1987
TEL: (717) 738-93□4
FA□: 717-738-9478 or 717-738-9479
E-mail: jrnlprodpen□ cadmus.com

Technical problems? If you experience technical problems downloading your file or any other problem with the website listed above, please please contact Balaji/Ramesh/SA□ (e-mail: wileysupport□ kwglobal.com, phone: □91 (44) 4□05-8888 (ext.□17)). Be sure to include your article number.
□uestions regarding your article? Please don□t hesitate to contact me with any questions about the article itself, or if you have trouble interpreting any of the questions listed at the end of your file.
RE□E□BER TO INCLUDE YOUR ARTICLE NO. (11-0386.R□) WIT□ ALL CORRESPONDENCE. This will help both of us address your query most efficiently.

As this e-proofing system was designed to make the publishing process easier for everyone, we welcome any and all feedback. Thanks for participating in our e-proofing system□

This e-proof is to be used only for the purpose of returning corrections to the publisher.

Sincerely,

Production Editor, PEN
Cadmus Professional Communications
300 West Chestnut St., Suite A
Ephrata, PA 175□□-1987

TEL: (717) 738-93□4
FA□: 717-738-9478 or 717-738-9479
E-mail: jrnlprodpen□ cadmus.com

Publishers Since 1807

111 RIVER STREET, HOBOKEN, NJ 07030-5774

POLYMER ENGINEERING AND SCIENCE PRODUCTION

IMMEDIATE RESPONSE REQUIRED

Please follow these instructions to avoid delay of publication.

☐ **READ PROOFS CAREFULLY**

- This will be your only chance to review these proofs. **Please note that once your corrected article is posted online, it is considered legally published, and cannot be removed from the Web site for further corrections.**
- Please note that the volume and page numbers shown on the proofs are for position only.

☐ **INDICATE ALL CHANGES AND ANSWER ANY QUERIES ON PROOFS**

- Mark all corrections directly on the proofs. Note that excessive author alterations may ultimately result in delay of publication and extra costs may be charged to you.

☐ **CHECK FIGURES AND TABLES CAREFULLY**

- Check size, numbering, and orientation of figures.
- All images in the PDF are downsampled (reduced to lower resolution and file size) to facilitate Internet delivery. These images will appear at higher resolution and sharpness in the printed article.
- Review figure legends to ensure that they are complete.
- Check all tables. Review layout, title, and footnotes.

RETURN ☐**PROOFS**

PLEASE RETURN PROOFS (VIA FAX, E-MAIL, OR EXPRESS MAIL) WITHIN 48 HOURS OF RECEIPT TO:

QUESTIONS?

Production Editor, PEN
Cadmus Professional Communications
300 West Chestnut St., Suite A
Ephrata, PA 17522-1987
Phone: (717) 738-9324
FAX: 717-738-9478 or 717-738-9479
E-mail:jrnlprodpen@cadmus.com

Softproofing for advanced Adobe Acrobat Users - NOTES tool

NOTE: ACROBAT READER FROM THE INTERNET DOES NOT CONTAIN THE NOTES TOOL USED IN THIS PROCEDURE.

Acrobat annotation tools can be very useful for indicating changes to the PDF proof of your article. By using Acrobat annotation tools, a full digital pathway can be maintained for your page proofs.

The NOTES annotation tool can be used with either Adobe Acrobat 6.0 or Adobe Acrobat 7.0. Other annotation tools are also available in Acrobat 6.0, but this instruction sheet will concentrate on how to use the NOTES tool. Acrobat Reader, the free Internet download software from Adobe, DOES NOT contain the NOTES tool. In order to softproof using the NOTES tool you must have the full software suite Adobe Acrobat Exchange 6.0 or Adobe Acrobat 7.0 installed on your computer.

Steps for Softproofing using Adobe Acrobat NOTES tool:

1. Open the PDF page proof of your article using either Adobe Acrobat Exchange 6.0 or Adobe Acrobat 7.0. Proof your article on-screen or print a copy for markup of changes.

2. Go to Edit/Preferences/Commenting (in Acrobat 6.0) or Edit/Preferences/Commenting (in Acrobat 7.0) check “Always use login name for author name” option. Also, set the font size at 9 or 10 point.

3. When you have decided on the corrections to your article, select the NOTES tool from the Acrobat toolbox (Acrobat 6.0) and click to display note text to be changed, or Comments/Add Note (in Acrobat 7.0).

4. Enter your corrections into the NOTES text box window. Be sure to clearly indicate where the correction is to be placed and what text it will effect. If necessary to avoid confusion, you can use your TEXT SELECTION tool to copy the text to be corrected and paste it into the NOTES text box window. At this point, you can type the corrections directly into the NOTES text box window. **DO NOT correct the text by typing directly on the PDF page.**

5. Go through your entire article using the NOTES tool as described in Step 4.

6. When you have completed the corrections to your article, go to Document/Export Comments (in Acrobat 6.0) or Comments/Export Comments (in Acrobat 7.0). Save your NOTES file to a place on your harddrive where you can easily locate it. **Name your NOTES file with the article number assigned to your article in the original softproofing e-mail message.**

7. **When closing your article PDF be sure NOT to save changes to original file.**

8. To make changes to a NOTES file you have exported, simply re-open the original PDF proof file, go to Document/Import Comments and import the NOTES file you saved. Make changes and reexport NOTES file keeping the same file name.

9. When complete, attach your NOTES file to a reply e-mail message. Be sure to include your name, the date, and the title of the journal your article will be printed in.

WILEY
Publishers Since 1807

COLOR REPRODUCTION IN YOUR ARTICLE

Color figures were included with the final manuscript files that we received for your article. Because of the high cost of color printing, we can only print figures in color if authors cover the expense.

Please indicate if you would like your figures to be printed in color or black and white. Color images will be reproduced online in *Wiley Online Library* at no charge, whether or not you opt for color printing.

Failure to return this form will result in the publication of your figures in black and white.

JOURNAL Polymer Engineering & Science ______ VOLUME ______ ISSUE ______

TITLE OF MANUSCRIPT ______

MS. NO. ______ NO. OF COLOR PAGES ______ AUTHOR(S) ______

No. Color Pages	Color Charges	No. Color Pages	Color Charges	No. Color Pages	Color Charges
1	950	5	3400	9	5850
2	1450	6	3900	10	6350
3	1950	7	4400	11	6850
4	2450	8	4900	12	7350

Please contact the Production Editor for a quote if you have more than 12 pages of color

☐ Please print my figures in black and white

☐ Please print my figures in color $ ______

***International orders must be paid in currency and drawn on a U.S. bank*

Please check one: ☐ Check enclosed ☐ Bill me ☐ Credit Card

If credit card order, charge to: ☐ American Express ☐ Visa ☐ MasterCard

Credit Card No ______ Signature ______ Exp. Date ______

BILL TO:

Name ______ **Purchase Order No.** ______

Institution ______ Phone ______

Address ______

______ Fax ______

______ E-mail ______

Effects of Aromatic Carboxylic Dianhydrides on Thermomechanical Properties of Polybenzoxazine-Dianhydride Copolymers

Chanchira Jubsilp,[1] Boonthariga Ramsiri,[2] Sarawut Rimdusit[2]

[1] *Department of Chemical Engineering, Faculty of Engineering, Srinakharinwirot University, Nakhonnayok 26120, Thailand*

[2] *Polymer Engineering Laboratory, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand*

Enhanced thermomechanical properties of polybenzoxazine (PBA) copolymers obtained by reacting bisphenol-A-aniline-type benzoxazine (BA-a) resin with three different aromatic carboxylic dianhydrides, i.e., pyromellitic dianhydride (PMDA), 3,3′,4,4′ biphenyltetracarboxylic dianhydride (s-BPDA), or 3,3′,4,4′ benzophenonetetracarboxylic dianhydride (BTDA) were reported. Glass transition temperature (T_g), of the copolymers was found to be in the order of PBA-a:PMDA>PBA-a:s-BPDA>PBA-a:i-BTDA. The difference in the T_g of the copolymers is related to the rigidity of the dianhydride components. Furthermore, the T_g of PBA-a:PMDA, PBA-a:s-BPDA, and PBA-a:i-BTDA films was observed to be significantly higher than that of the neat PBA-a owing to the enhanced crosslink density by the dianhydride addition. This greater crosslink density results from additional ester linkage formation between the hydroxyl group of PBA-a and the anhydride group of dianhydrides formed by thermal curing. Moreover, the copolymers exhibit enhanced thermal stability with thermal degradation temperature (T_d) ranging from 410°C to 426°C under nitrogen atmosphere. The char yield at 800°C of the copolymers was found to be remarkably greater than that of the neat PBA-a with a value up to 60% vs. that of about 38% of the PBA-a. Toughness of the copolymer films was greatly improved compared to that of the neat PBA-a. POLYM. ENG. SCI., 00:000–000, 2012. © 2012 Society of Plastics Engineers

Correspondence to: Sarawut Rimdusit; e-mail: sarawut.r@chula.ac.th
Contract grant sponsor: New Researcher's Grant; Contract grant sponsor: Thailand Research Fund-Commission on Higher Education; contract grant numbers: TRF-CHE; MRG5380077; Contract grant sponsors: Matching Fund of Srinakharinwirot University, Higher Education Research Promotion and National Research University Project of Thailand; Contract grant sponsor: Office of the Higher Education Commission; contract grant number: AM1076A; Contract grant sponsors: Ratchadapiseksomphot Endowment Fund, Thai Polycarbonate Co., Ltd. (TPCC).
AQ2
DOI 10.1002/pen.23107
Published online in Wiley Online Library (wileyonlinelibrary.com).

INTRODUCTION

Recently, there has been an increasing high temperature requirement from the aerospace industry and other industrial applications such as composite matrices, protecting coatings, and microelectronic materials using a thermosetting polymer. An improvement of polymeric material properties particularly by modification of the existing polymers through forming alloy, blend, or composite to achieve high thermal stability, high char yield, and high glass transition temperature becomes increasingly important [1–3]. Polymer blends between polybenzoxazines (PBAs) and other polymers have been subjected to many current investigations, which intend to utilize some outstanding properties of PBAs. Nowadays, there are various companies in the world which have produced benzoxazine resin for trading including multiplicity requirements of individual applications, e.g., Shikoku Chemicals Corporation, Huntsman Corporation, and Henkel Co., Ltd. PBAs are particularly applied to enhance the processability, mechanical, and thermal properties of the resulting polymer blends. They can be synthesized via a simple and cost-competitive solvent-less method [4]. Moreover, the molecular design flexibility of the resins, comparable to that of epoxy or polyimide (PI), provides wide range of properties that can be tailor-made. Importantly, the polymers have been reported to possess many intriguing properties to overcome several shortcomings of conventional novolac- and resole-type phenolic resins such as low viscosity, near-zero volumetric shrinkage upon curing, the glass transition temperature (T_g) much higher than cure temperature, fast mechanical property build-up as a function of degree of polymerization, high char-yield, low coefficient of thermal expansion, (CTE), low moisture absorption, and excellent electrical properties [4, 5]. As mentioned above, the ability of benzoxazine resins to form alloys or blends with other polymers or resins [5–10] provides the resins with even broader range of applications. In recent years, the investigation of PBA hybrid systems have been reported such as PBA-a/PU [6–8], PBA-a/phenolic novolac [10, 11], PBA-a/epoxy resin [6, 11, 12], PBA-a/PI [13], and PBA-a/dianhydride [14, 15].

Interestingly, organic acid dianhydrides which contain aromatic structure and have high functionality have been found to impart improved heat resistance, as well as increased chemical and solvent resistance to the polymeric materials such as epoxy resin [16, 17] and PBA-a [18, 19]. The success of pyromellitic dianhydride (PMDA) and 3,3′,4,4′ benzophenonetetracarboxylic dianhydride (BTDA) as epoxy hardening agents is attributed to their tetrafunctionality, which leads to higher density of crosslinks, thus higher heat distortion temperature (HDT) and increased chemical and solvent resistance [17]. Furthermore, muti-component polymeric materials of PBA and aromatic carboxylic dianhydride-based PI have been investigated. Takeichi et al. [18] studied the thermal property of the polymer alloys between bisphenol-A-aniline-type polybenzoxazine (PBA-a) and BPADA/ODA PI. The authors reported that the T_g of the PBA-a were improved significantly by blending with PI due to higher thermal stability of PI (T_g of PI = 222°C) than that of the PBA-a, i.e., 152°C.

AQ1

Silicon-containing polyimide (SPI) has also been reported to provide significant enhancement on the decomposition temperature of PBA-a [13]. The decomposition temperatures (T_ds) of the blends increase from about 360°C to 430°C with the SPI content in range of 0–75 wt%. Interestingly, the char yields of the blends were substantially higher than that of the neat PBA-a and SPI. The highest char yield value at 800°C of about 45% was found at 75 wt% of the SPI content. This synergy in the char formation was also observed in the systems of PBA blended with other types of PIs [18]. Recently, a novel PBA modified with dianhydride was successfully prepared by reacting bisphenol-A-aniline-based bifunctional benzoxazine resin (BA-a) with BTDA [14, 15]. The PBA-a:BTDA copolymer samples showed only one T_g with the value as high as 263°C at BA-a:BTDA = 1.5:1 mole ratio. The value is remarkably higher than that of the unmodified PBA-a, i.e., 178°C. In addition, the resulting PBA-a:BTDA copolymer displays relatively high thermal stability with T_d up to 364°C and substantial enhancement in char yield of up to 61% vs. that of 38% of the PBA-a.

In this study, we prepared a series of the high performance copolymers of PBA-a and aromatic carboxylic dianhydrides, i.e., PMDA, 3,3′,4,4′ biphenyltetracarboxylic dianhydride (s-BPDA), and BTDA. The effect of these aromatic carboxylic dianhydrides on thermomechanical properties of the obtained PBA-a:aromatic carboxylic dianhydride copolymers is investigated. As aforementioned, blending of the PBA with the PI or an aromatic carboxylic dianhydride is an excellent method to modify the properties of the PBA suitable for such applications as microelectronics or prepreg fabrication.

EXPERIMENTAL

Materials

Materials used in this study are bisphenol-A-aniline-based bifunctional benzoxazine resin (BA-a), dianhydrides, and 1-methyl-2-pyrrolidone (NMP) as solvent. The BA-a based on bisphenol-A, paraformaldehyde, and aniline was synthesized according to the patented solventless technology [4]. Bisphenol-A (polycarbonate grade) was provided by Thai Polycarbonate Co., Ltd. (TPCC). Paraformaldehyde (AR grade) and aniline (AR grade) were purchased from Merck Co. and Panreac Quimica SA, respectively. Aromatic carboxylic dianhydrides used in this work were PMDA purchased from Acros organics, 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) obtained from Japan Aerospace Exploration Agency, JAXA, (Prof. R. Yokota), and BTDA supplied by Sigma Aldrich Co. NMP solvent was purchased from Fluka Chemical Co. All chemicals were used as-received.

Preparation of Benzoxazine-Dianhydride Copolymer Films

BA-a resin was blended with various types of dianhydrides (DA) at BA-a:DA = 1.5:1 mole ratio which is an optimal composition with good thermomechanical properties as reported in our previous work [14, 15]. The mixtures, i.e., BA-a:PMDA = 15:1 mole ratio, BA-a:s-BPDA = 1.5:1 mole ratio, and BA-a:BTDA = 1.5:1 mole ratio, were dissolved in NMP and stirred at 80°C until a clear homogeneous mixture was obtained. The solution was cast on Teflon sheet and dried at room temperature for 24 h. Additional drying was carried out at 80°C for 24 h in a vacuum oven followed by thermal curing at 150°C for 1 h, 170°C for 1 h, at 190°C, 210°C, 230°C for 2 h each, and 240°C for 1 h to guarantee complete curing of the mixtures.

Characterizations of the Samples

Fourier transform infrared spectra of fully cured samples were acquired at room temperature using a Spectrum GX FTIR spectometer from Perkin Elmer with an ATR accessory. In the case of a BA-a resin and a pure aromatic carboxylic dianhydride, a small amount of aromatic carboxylic dianhydride powder was cast as thin film on a potassium bromide (KBr) window. All spectra were taken with 64 scans at a resolution of 4 cm^{-1} and in a spectral range of 4000–400 cm^{-1}.

The glass transition temperature (T_g) of all samples were examined using a differential scanning calorimeter (DSC) model 2910 from TA Instruments. The thermogram was obtained at a heating rate of 10 °C/min from 30°C to 300°C under nitrogen purging with a constant flowrate of 50 ml/min. A sample with a mass in a range of 8–10 mg was sealed in an aluminum pan with lid. The $T_{g,\ DSC}$ was obtained from the temperature at half extrapolated tangents of the step transition midpoint.

The dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH was used to investigate the viscoelastic properties of all samples. The dimension of the samples was 7.0 mm × 10 mm × 0.1 mm. The test was performed in a tension mode at a frequency of 1 Hz with strain amplitude of 0.1% and at a heating rate of 2 °C/min from 30°C to 400°C under constant nitrogen flow of 80 ml/min. The storage modulus (E'), loss modulus (E''), and loss tangent or damping curve (tan δ) were then obtained. The $T_{g,DMA}$ was taken as the maximum point on the loss modulus curve in a DMA thermogram.

Degradation temperature (T_d) and char yield of all samples were acquired using a Diamond TG/DTA from Perkin Elmer. The testing temperature program was ramped at a heating rate of 20 °C/min from 30°C to 1000°C under nitrogen purging with a constant flow of 50 ml/min. The sample mass used was measured to be approximately 8–15 mg. The T_ds and char yields of the samples were reported at their 10% weight loss and at 800°C, respectively.

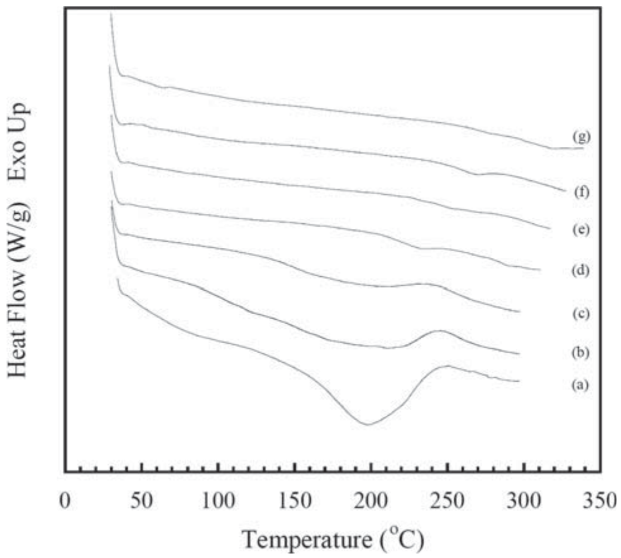


FIG. 1. DSC thermograms of the benzoxazine blending with BTDA at 1.5:1 mole ratio at various curing conditions: (a) 60°C, 80 °C/24 h, (b) 60°C, 80 °C/24 h + 150 °C/1 h, (c) 60°C, 80 °C/24 h + 150°C, 170 °C/1 h, (d) 60°C, 80 °C/24 h + 150°C, 170 °C/1 h + 190°C, 210 °C/2 h, (e) 60°C, 80 °C/24 h + 150°C, 170 °C/1 h + 190°C, 210°C, 230 °C/2 h + 240 °C/1 h, (f) 60°C, 80 °C/24 h + 150°C, 170 °C/1 h +190°C, 210 °C, 230 °C/2 h + 240 °C/1 h (BA-a:s-BPDA = 1.5:1 mole ratio), (g) 60°C, 80 °C/24 h + 150°C, 170 °C/1 h + 190°C, 210°C, 230 °C/2 h + 240 °C/1 h (BA-a:PMDA = 1.5:1 mole ratio).

RESULTS AND DISCUSSION

Network Formation by Thermal Cure of PBA-a:Dianhydride Copolymers

BA-a containing BTDA-type aromatic carboxylic dianhydride at BA-a:BTDA = 1.5:1 mole ratio was selected to examine the curing reaction by DSC as displayed in F1 Fig. 1. From the DSC thermograms as line (a) in Fig. 1, after vacuum drying at 80°C, BA-a:BTDA mixture showed endothermic peak at 200°C which corresponded to boiling point of NMP solvent (b.p. = 202°C). This endothermic peak decreased with an increase of heat treatment temperature, and completely disappeared after heat treatment at 150°C as line (b) in Fig. 1. This implied that the NMP solvent was completely removed from the BA-a:BTDA mixture at this heat-treatment stage. Furthermore, the BA-a:BTDA mixture possessed an exothermic peak at 245°C as line (e) in Fig. 1. The area under the exothermic peak was observed to decrease as the cure temperature increased, and completely disappeared after curing at 240°C. This suggested that the fully cured stage of BA-a:BTDA = 1.5:1 mole ratio was achieved at up to 240°C heat treatment. Additionally, we obtained similar fully cured samples of BA-a:PMDA = 1.5:1 mole ratio as line (f) in Fig. 1 and BA-a:s-BPDA = 1.5:1 mole ratio as line (g) in Fig. 1 after the same heat treatment up to 240°C.

After thermal curing at elevated temperature up to 240°C, the obtained thickness of the transparent PBA-a:PMDA, PBA-a:s-BPDA, and PBA-a:BTDA films was F2 about 100 μm as shown in Fig. 2b–d. It is well known that PBA-a film is very brittle and we could not bend the film more than as being shown in Fig. 2a. Interestingly, all of PBA-a:PMDA, BA-a:s-BPDA, and BA-a:BTDA copolymer films exhibited greatly improved toughness compared to the neat PBA-a as can be seen in Fig. 2b–d. The flexibility enhancement of all copolymer samples due to additional ester linkages, structurally flexible functional group, formed in the PBA-a network as a result quoted in previous publications [15, 19]. Furthermore, the tensile properties, e.g., tensile modulus, tensile strength, and elongation at break, are displayed in Table 1. From the table, T1 we can see that the tensile modulus of all copolymer films were slightly higher than that of the neat PBA-a. Interestingly, tensile strength and elongation at break of the neat PBA-a were found to increase with an addition of PMDA or s-BPDA or BTDA dianhydrides. Especially, the tensile strength of PBA-a:aromatic carboxylic dianhydride copolymer films were observed to be about three times greater than that of the neat PBA-a. This behavior was attributed to ester linkage formation in copolymer structures. In addition, the great toughness showed a similar trend for all copolymer samples with that of the commercial PI films such as Kapton film [20] and UPILEX-s film.

Fourier Transform Infrared Spectroscopy Investigation

Chemical structures of BA-a, PBA-a, dianhydride modifiers, and their network formation reactions between

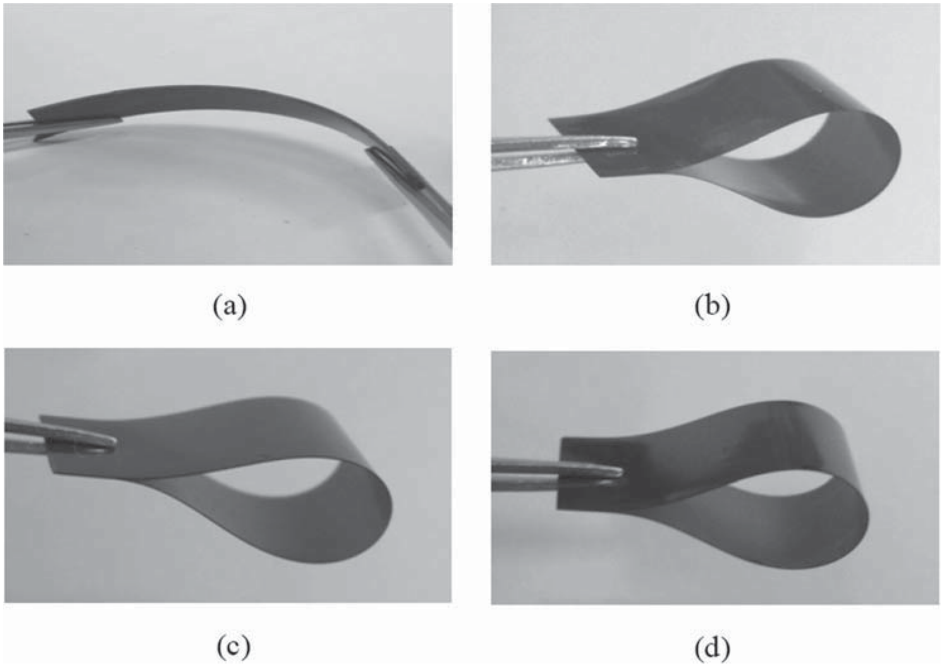


FIG. 2. Photographs of aromatic carboxylic dianhydride-modified PBA-a films: (a) PBA-a, (b) PBA-a:PMDA, (c) PBA-a:s-BPDA, (d) PBA-a:BTDA.

the PBA-a and dianhydride modifiers were studied by FTIR spectroscopic technique. The FTIR spectra of BA-a resin and the PBA-a are previously reported in detail [18, 21, 22]. Characteristic absorption bands of the BA-a resin were found at 1232 cm^{-1} assigned to C—O—C stretching mode of oxazine ring whereas the band around 1497 cm^{-1} and 947 cm^{-1} were attributed to the tri-substituted benzene ring. Following the curing phenomenon, an infinite three dimensional network was formed from benzoxazine ring opening by the breakage of C—O bond and then the benzoxazine molecule transformed from a ring structure to a network structure. During this process, the backbone of benzoxazine ring, the tri-substituted benzene ring around 1497 cm^{-1}, became tetra-substituted benzene ring centered at 1488 cm^{-1} and 878 cm^{-1} which led to the formation of a phenolic hydroxyl group-based polybenzoxazine (PBA-a) structure. In addition, an indication of ring opening reaction of the BA-a resin upon thermal treatment could also be observed from the appearance of a broad peak about 3300 cm^{-1} which was assigned to the hydrogen bonding of the phenolic hydroxyl group formation. The chemical transformation of BA-a:PMDA, BA-a:s-BPDA, and BA-a:BTDA at 1.5:1 mole ratio upon thermal curing was investigated and the resulting spectra
F3 are shown in Fig. 3a–c. The important characteristic infrared absorptions of the neat PBA-a structure were clearly observed as aforementioned. On the other hand, the aromatic carboxylic dianhydride, i.e., PMDA, s-BPDA, and BTDA, may be identified by a distinctive carbonyl band region. From the Fig. 3a–c, the spectra of all aromatic carboxylic dianhydrides provided the strong carbonyl characteristic absorption peaks with component in the 1860 cm^{-1} and 1780 cm^{-1} region. Moreover, all dianhydrides also showed a strong C—O stretching band in range of 1300–1100 cm^{-1} [15, 23]. After fully cured stage, the new absorption bands of PBA-a:PMDA, PBA-a:s-BPDA, and PBA-a:BTDA copolymers at 1.5:1 mole ratio was observed. The phenomenon was ascribed to the appearance of carbonyl stretching bands of ester linkage [24]. From the PBA-a:aromatic carboxylic dianhydride spectra in Fig. 3a–c, we can see that the carbonyl stretching bands of aromatic carboxylic dianhydride at 1860 cm^{-1} and 1780 cm^{-1} completely disappeared. It was suggested that the reaction between the phenolic hydroxyl group of the PBA-a and the anhydride group of the aromatic carboxylic dianhydrides could occur to form ester linkage as evidenced by the observed peak in the spectrum at 1730 cm^{-1}. In general, IR spectra for esters exhibit an intense band in the range 1750–1730 cm^{-1} of its C═O stretching band. This peak varies slightly depending on the functional groups attached to the carbonyl with exemplification of a benzene ring or double bond in conjugation with the carbonyl which will bring the wavenumber down to 30 cm^{-1}. Furthermore, the car-

TABLE 1. Tensile properties of PBA-a and aromatic carboxylic dianhydride-modified PBA-a copolymers.

Samples (mole ratio)	Modulus (GPa)	Strength (MPa)	Elongation (%)
PBA-a	2.10	25	1.9
PBA-a:PMDA (1.5:1)	2.60	78	5.4
PBA-a:s-BPDA (1.5:1)	2.68	95	6.6
PBA-a:BTDA (1.5:1)	2.50	88	6.0

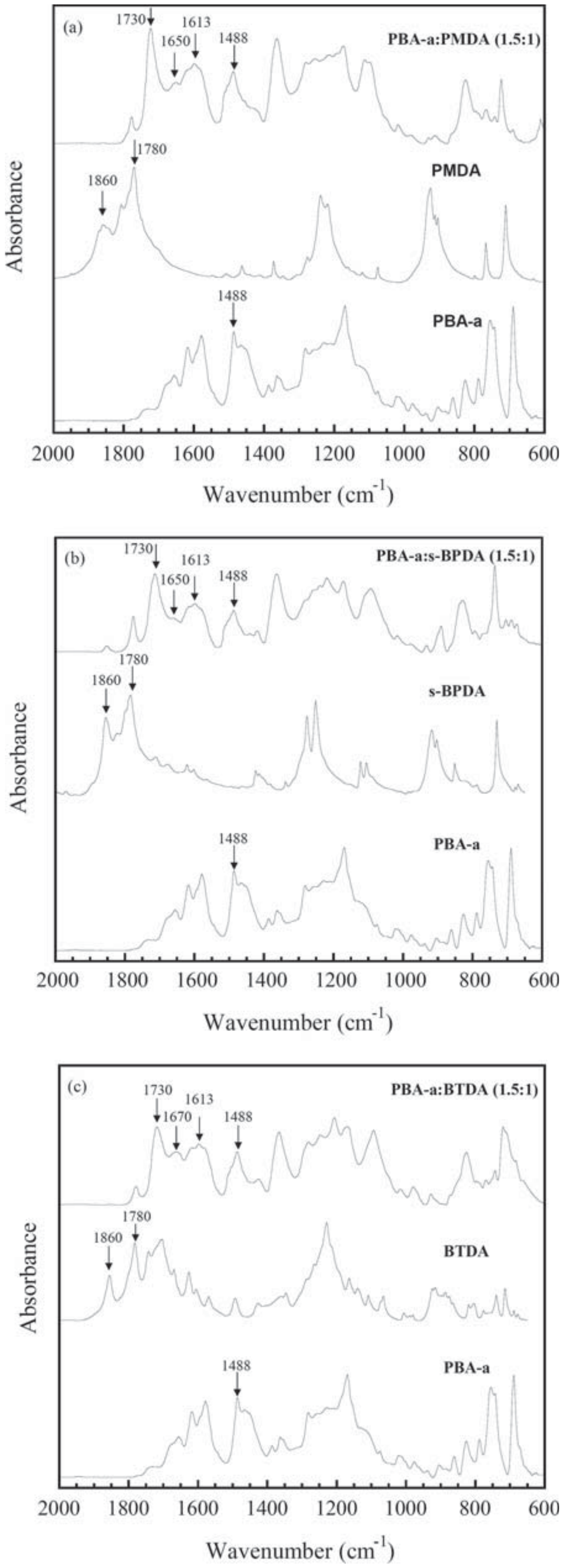
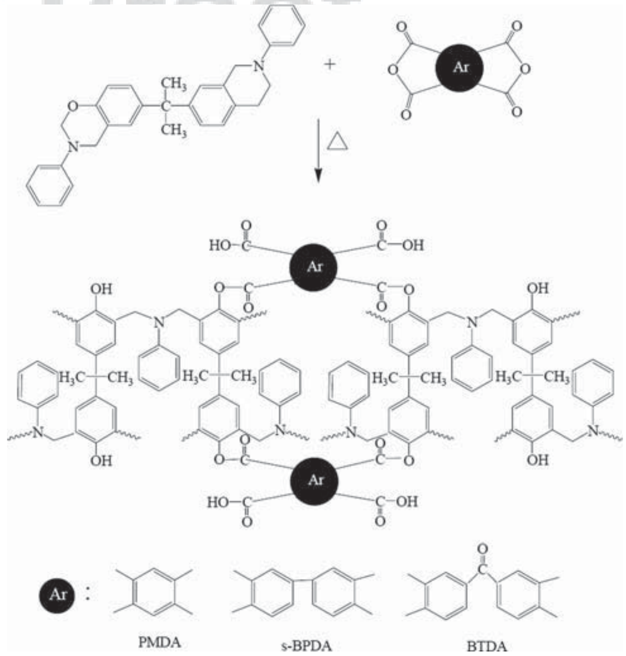


FIG. 3. FTIR spectra of PBA:PMDA (a), PBA-a:s-BPDA (b), PBA-a:BTDA (c).

boxylic acid occurred after thermal curing of the PBA-a:aromatic carboxylic dianhydride mixture can also be followed by monitoring a band at 1650–1670 cm^{-1} [25] and 1613 cm^{-1} [19] due to C=O stretching. In addition, carboxylic acid shows characteristic C—O stretching, in-plane and out-of-plane, and O—H bending bands at 1320–1210 cm^{-1}, 1440–1395 cm^{-1}, and 960–900 cm^{-1}, respectively [23, 26]. As a consequence, we proposed a reaction model of these PBA-a:aromatic carboxylic dianhydride copolymers as shown in Scheme 1. The reaction S1
mechanism was similar to the esterification of di-(2-ethylhexyl) phthalate and hydroxyl group of allyl alcohol [27] as well as the reaction between BTDA dianhydride and hydroxyl group of 2-hydroxyethyl acrylate [28]. Moreover, the ester linkage formation in anhydride-cured epoxy resin systems has also been reported [29, 30]. FT-Raman analysis revealed that curing propagation of the epoxy-anhydride system mainly occurs by polyesterification between hydroxyl group of the ring-opened epoxide and anhydride groups. The decrease of epoxide ring at 1260 cm^{-1} and anhydride ring at 1860 cm^{-1} resulted in a relative increase of a new band observed at 1734 cm^{-1} due to ester group formation on curing [31].

Dynamic Mechanical Properties of PBA-a:Diandydride Copolymers

Viscoelastic properties of PBA-a:PMDA, PBA-a:s-BPDA, and PBA-a:BTDA copolymer films at a mole ratio of 1.5:1 were evaluated and storage modulus (E'), loss modulus (E''), and tan δ are illustrated in Figs. 4–6. Generally, the storage modulus demonstrates the deformation



SCHEME 1. Model reaction of dianhydride-modified polybenzoxazine copolymers.

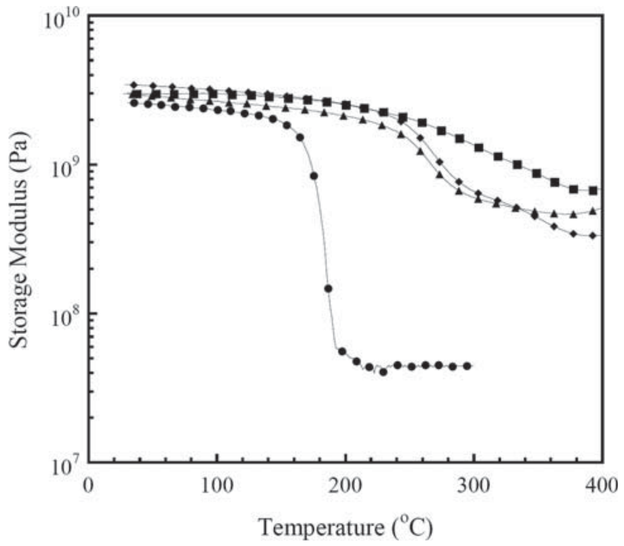


FIG. 4. Storage modulus of aromatic carboxylic dianhydride-modified PBA-a films: (●) PBA-a, (■) PBA-a:PMDA, (◆) PBA-a:s-BPDA, (▲) PBA-a:BTDA.

resistances of the material when external force is applied sinusoidally. The E' at room temperature (25°C) of the PBA-a:aromatic carboxylic dianhydride copolymer systems shown in Fig. 4 exhibited values of 3.02 GPa for PBA-a:PMDA, 3.42 GPa for PBA-a:s-BPDA, and 2.94 GPa for PBA-a:BTDA, which are higher than that of the neat PBA-a, i.e., 2.57 GPa. We can see that the storage modulus of all PBA-a:aromatic carboxylic dianhydride copolymers is approximately equal to that of typical PI films with a reported value in the range of 2.3–3.0 GPa such as in s-BPDA/ODA, ODPA/ODA, PMDA/ODA PIs [32, 33], and fluorinated PI [34].

F4

F5

Figure 5 displays T_g which shows the dimension stability, from the maximum point of a loss modulus curve, of the PBA-a:aromatic carboxylic dianhydride copolymers, i.e., PBA-a:PMDA, PBA-a:s-BPDA, and PBA-a:BTDA at a fixed mole ratio of 1.5:1. From the figure, PBA-a and its copolymers showed only single T_g which suggested that all the PBAa:aromatic carboxylic dianhydride copolymer films were a homogeneous network and no phase separation occurred. The ultimate T_g value of the neat PBA-a was determined to be about 178°C and that of the copolymers, i.e. PBA-a:PMDA, PBA-a:s-BPDA, and PBAa:BTDA was found to be 300°C, 270°C, and 263°C, respectively. That is the T_g value of PBA-a was significantly enhanced by an incorporation of all aromatic carboxylic dianhydrides. In addition, we can clearly see that the T_g of the copolymers is in the order of PBA-a:PMDA > PBA-a:s-BPDA > PBA-a:BTDA which is a similar trend as that found in aromatic carboxylic dianhydride-based PI films derived from those dianhydrides, i.e., PMDA, s-BPDA, BTDA mixed with DADE [35], and with ODA [36]. This observed behavior is attributed to the nature of the stiffness/bulkiness of the dianhydride moieties and the bridging group in the dianhydrides which strongly affects T_g of the copolymers. From our result, it is found that T_g values of aromatic carboxylic dianhydride modified with PBA were decreased according to the increase of structural flexibility of selected dianhydrides. As expected, the PBA-a:PMDA film showed the highest T_g due to the rigid pyromellitimide unit while the PBA-a:s-BPDA and the PBA-a:BTDA exhibited the lower T_g than that of the PBAa:PMDA due to the presence of a more flexibility bridging group, i.e., biphenyl and benzophenone units in a dianhydride structure [37, 38]. Moreover, an enhanced crosslink density via ester linkage between phenolic hydroxyl group of PBA-a and anhydride group of dianhydride as depicted in FTIR spectra results in further T_g improvement of the copolymers. In a tight network structure, in which rubbery plateau modulus is greater than 10^7 Pa such as in our case, the non-Gaussian character of the polymer network becomes increasingly more pronounced and the equation from theory of rubbery elasticity is no longer applicable. The approximate relation expressed in the equation below proposed by Nielsen and Landel [39] is thus preferred and is reported to better describe the elastic properties of dense network, e.g., in epoxy systems [40, 41]. As a consequence, a crosslink density of these copolymer networks, ρ_x, can be estimated from a value of the equilibrium storage shear modulus in the rubbery region (G_e') which equals to $\frac{E_e'}{3}$ as follow:

$$\log\left[\frac{E_e'}{3}\right] = 7.0 + 293(\rho_x) \tag{1}$$

where E_e'(dyne/cm^2) is an equilibrium tensile storage modulus in rubbery plateau, ρ_x (mol/cm^3) is crosslink density which is the mole number of network chains per unit volume of the polymers.

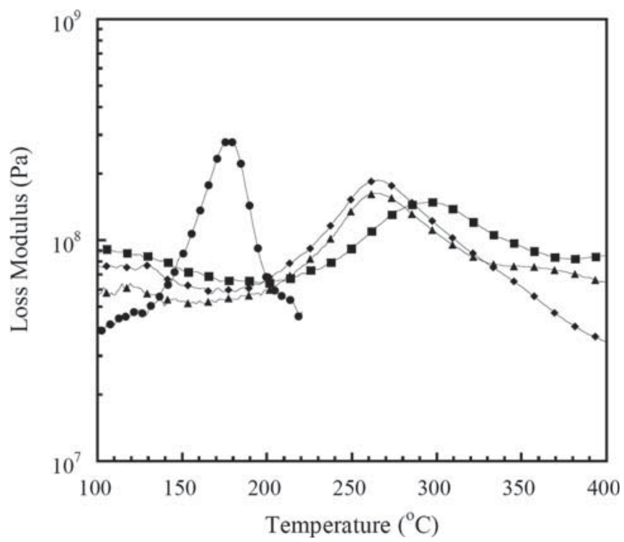


FIG. 5. Loss modulus of aromatic carboxylic dianhydride-modified PBA-a films: (●) PBA-a, (■) PBA-a:PMDA, (◆) PBA-a:s-BPDA, (▲) PBA-a:BTDA.

DOI 10.1002/pen

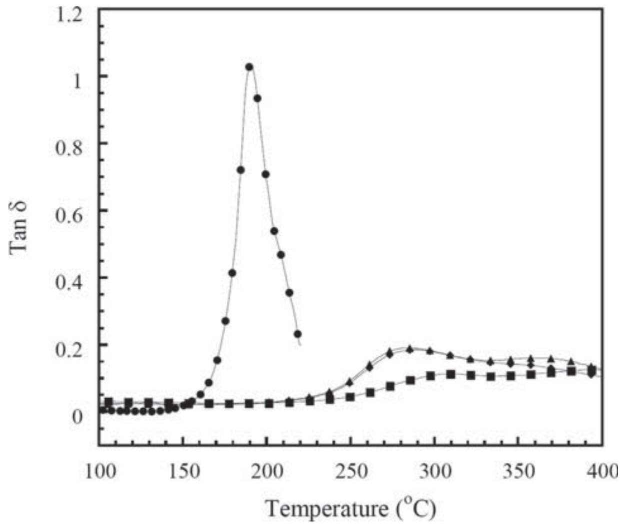


FIG. 6. Loss tangent of aromatic carboxylic dianhydride-modified PBA-a films: (●) PBA-a, (■) PBA-a:PMDA, (◆) PBA-a:s-BPDA, (▲) PBA-a:BTDA.

Crosslink density values of the PBA-a and its copolymers, i.e., PBA-a:PMDA, PBA-a:s-BPDA, and PBA-a:BTDA at an equal mole ratio of 1.5:1, calculated from *Eq. 1* are 3981 mol/cm^3, 8656 mol/cm^3, 7664 mol/cm^3, and 7630 mol/m^3, respectively. It is evident that the crosslink density of the neat PBA-a was greatly enhanced by an addition of PMDA, s-BPDA, or BTDA, corresponding to an enhancement in their T_g values discussed previously. An effect of crosslink density which is one key parameter on T_g of aromatic carboxylic diandydride-modified PBA-a network can be accounted for using Fox–Loshaek equation [42].

$$T_g = T_g(\infty) - \frac{k}{M_n} + k_x \rho_x \qquad (2)$$

where $T_g(\infty)$ is glass transition temperature of infinite molecular weight linear polymer, k and k_x are numerical constants, M_n is number average molecular weight which equals infinity in a crosslinking system (therefore, this term, $\frac{k}{M_n}$, can be neglected), (x is the crosslink density. From the equation, the higher the crosslink density, the greater the T_g of the copolymers, which was in excellent agreement with our DMA results.

F6 Loss tangent (tan δ) of the PBA-a and their copolymers of various aromatic carboxylic dianhydride types is illustrated in Fig. 6. A peak height of tan δ of PBA-a:PMDA, PBA-a:s-BPDA, and PBA-a:BTDA at an equal mole ratio of 1.5:1 tended to decrease while the peak position of their copolymers clearly shifted to higher temperature. The results suggested that an increase in the crosslink density caused a restriction of the chain's segmental mobility in aromatic carboxylic dianhydride-modified PBA copolymers thus a more elastic nature of the copolymer films compared to the PBA-a. In addition, the width-at-half-height of tan δ curves was found to be broader in their PBA-a copolymers, which indicated a more heterogeneous network in the resulting copolymers due to a hybrid polymer network formation. Moreover, the obtained transparent copolymer films and the single tan δ peak observed in each copolymer suggested no macroscopic phase separation in these copolymer films.

Thermal Stability of PBA-a:Dianhydride Copolymers

Thermal stability of the PBA-a and their copolymers including PBA-a:PMDA, PBA-a:s-BPDA, and PBA-a:BTDA was investigated by thermogravimetric analysis (TGA). Figure 7 compares TGA thermograms of the F7
PBA-a and its copolymers in nitrogen atmosphere. From the figure, we can see that the degradation temperature (T_d) reported at 10% weight loss of the neat PBA-a was 361°C while the T_d of the copolymers increased in the order of PBAa:PMDA (426°C) > PBA-a:s-BPDA (422°C) > PBA-a:BTDA (410°C). In other words, the order of thermal stability (T_d) with respect to aromatic skeleton of acid dianhydride component is phenylene unit > biphenyl unit > benzophenone unit [40]. Furthermore, the T_d value of the neat PBA-a film was observed to significantly increase with an incorporation of aromatic carboxylic dianhydrides. This is due to the formation of poly(aromatic ester) in the copolymers, i.e., reported T_d of polyester ~ 320–400°C [43, 44], which clearly had higher T_d than the neat PBA-a. As previously reported in FTIR spectra, the formation of additional crosslinking sites via ester linkage between the anhydride group in the aromatic carboxylic dianhydride and hydroxyl group of the neat PBA-a thus clearly contributed this T_d enhancement. In summary, the higher crosslink density and the presence of an aromatic structure of these aromatic carboxylic dianhy-

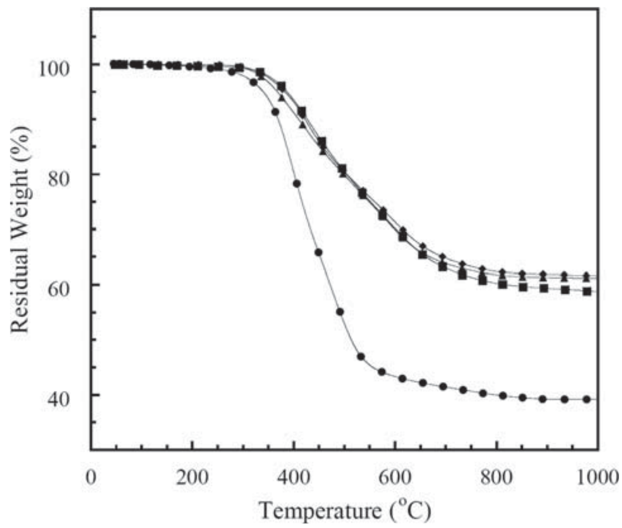


FIG. 7. Thermal degradation of aromatic carboxylic dianhydride-modified PBA-a films: (●) PBA-a, (■) PBA-a:PMDA, (◆) PBA-a:s-BPDA, (▲) PBA-a:BTDA.

drides could suppress segmental decomposition via gaseous fragments of the neat PBA-a thus providing an observed improvement in T_d of the samples.

Another interesting feature in the TGA thermograms is an amount of carbonized residue or char yield at 800°C of all samples shown in Fig. 7. The char yields of those copolymer films provided a value as high as 60% which is much greater than that of the neat PBA-a, i.e. 38%, implying that these copolymers possess excellent thermal stability. The high char yield value of these aromatic carboxylic dianhydride-modified PBAs in nitrogen could also be attributed to their greater aromatic content unit in the molecular structure [35, 45] and enhanced crosslink density of the resulting copolymers. In principle, the greater the char yield, the higher the flame retardancy of the polymer. Therefore, these copolymers tended to provide a sample with potentially substantial improvement in their flame retardancy which was highly useful in some applications such as aviation, automotive, and electronic industries. Recently, PI derived from 1,4-bis(4-amino-2-trifluoromethylphenoxy) benzene systems studied by Li et al. [46] exhibited a char yield at 10% weight loss of 49% at 800°C under nitrogen atmosphere which was attributed to the presence of high fluorine contents in the polymer backbone. In our research, the high char yields of aromatic carboxylic dianhydride-modified PBA-a films did not require any presence of fluorine moieties in these copolymers. In addition, char yield's copolymers were also higher than that of the commercial PI films such as Kapton®H film (53%) and UPILEX®S film (48%) [47]. However, it is found that the improved char yield of aromatic carboxylic dianhydride-modified PBA copolymer films is as high as that of PIs derived from similar dianhydrides such as PMDA, s-BPDA/MCDEA and PMDA, s-BPDA/DAM [45].

CONCLUSIONS

A series of PBA-a containing aromatic carboxylic dianhydride copolymers as transparent films was prepared. Networks of aromatic carboxylic dianhydride-modified PBA-a copolymer films were formed by reaction between hydroxyl groups of the PBA-a and the anhydride group of dianhydride as revealed by FTIR spectroscopy. The obtained copolymers exhibited excellent toughness, excellent thermal stability, and good mechanical properties. Glass transition temperature of the neat PBA-a was substantially enhanced by blending with the aromatic carboxylic dianhydrides. The effect of types of dianhydrides on T_g was found to be as follows: PBA-a:PMDA > PBA-a:s-BPDA > PBA-a:BTDA. Furthermore, degradation temperature and char yield at 800°C of the copolymer films were also improved with an incorporation of the aromatic carboxylic dianhydrides. The copolymers may be considered as potential candidates for high temperature materials with enhanced mechanical integrity.

REFERENCES

1. H.Y. Xu, H.X. Yang, L.M. Tao, L. Fan, and S.Y. Yang, *J. Appl. Polym. Sci.*, **117**, 1173 (2010).
2. R. Sengupta, M. Bhattacharya, S. Bandyopadhyay, and A.K. Bhowmick, *Prog. Polym. Sci.*, **36**, 638 (2011).
3. H. Ishida and S. Rimdusit, *Thermochim. Acta*, **320**, 177 (1998).
4. H. Ishida, U.S. Patent 5,543,516 (1996).
5. C.P.R. Nair, *Prog. Polym. Sci.*, **29**, 401 (2004).
6. S. Rimdusit, S. Pirstpindvong, W. Tanthapanichakoon, and S. Damrongsakkul, *Polym. Eng. Sci.*, **45**, 288 (2005).
7. C. Jubsilp, T. Takeichi, S. Hiziroglu, and S. Rimdusit, *Polym. Eng. Sci.*, **49**, 1022 (2009).
8. H. Yeganeh, M. Razavi-Nouri, and M. Ghaffari, *Polym. Eng. Sci.*, **48**, 1329 (2008).
9. S. Rimdusit, P. Kunopast, and I. Dueramae, *Polym. Eng. Sci.*, **47**, 140 (2011).
10. H. Qi, G. Pan, Y. Zhuang, F. Huang, and L. Du, *Polym. Eng. Sci.*, **50**, 1751 (2010).
11. S.W. Kuo and W.C. Liu, *J. Appl. Polym. Sci.*, **117**, 3121 (2010).
12. H. Zhong, Y. Lu, J. Chen, W. Xu, and X. Liu, *J. Appl. Polym. Sci.*, **118**, 705 (2010).
13. S. Tiptipakorn, S. Damrongsakkul, S. Ando, K. Hemvichain, and S. Rimdusit, *Polym. Degrad. Stab.*, **92**, 1265 (2007).
14. S. Rimdusit and C. Jubsilp, Thailand Patent pending. Issue number 0,701,003,695 (2007).
15. C. Jubsilp, T. Takeichi, and S. Rimdusit, *Polym. Degrad. Stab.*, **96**, 1047 (2011).
16. H. Dodiuk, U.S. Patent 4,841,010 (1989).
17. W. P. Barie Jr. and N.W. Franke, *Ind. Eng. Chem. Prod. Res. Dev.*, **8**, 72 (1969).
18. T. Takeichi, Y. Guo, and S. Rimdusit, *Polymer*, **46**, 4909 (2005).
19. A. Tuzun, B. Kiskan, N. Alemdar, A.T. Erciyes, and Y. Yagci, *J. Polym. Sci. Part A: Polym. Chem.*, **48**, 4279 (2010).
20. P.M. Hergenrother, in *High Performance Polymers and Composites*, J.I. Kroschwitz, Ed., Wiley, New York, 374 (1991).
21. H. Ishida and H.Y. Low, *Macromolecules*, **30**, 1099 (1997).
22. H. Ishida and Y. Rodriguez, *J. Appl. Polym. Sci.*, **58**, 1751 (1995).
23. B.H. Stuart, *Infrared Spectroscopy: Fundamentals and Applications*, Wiley, Chichester, 77 (2004).
24. M. Konieczny, H. Xu, R. Battaglia, S.L. Wunder, and W. Volksen, *Polymer*, **38**, 2969 (1997).
25. F.A. Settle, *Handbook of Instrumental Techniques for Analytical Chemistry*, Prentice Hall, Inc., New Jersey (1997).
26. N.B. Colthup, L.H. Daly, and S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, Inc., London, 310 (1990).
27. H.A. Wittcoff, B.G. Reuben, and J.S. Plotkin, *Industrial Organic Chemicals*, 2nd ed., Wiley-interscience, Hobogen, NJ (2004).
28. W.Y. Chiang and S.C. Chan, *J. Appl. Polym. Sci.*, **43**, 1827 (1991).

29. V. Trappe, W. Burchard, and B. Steinmann, *Macromolecules*, **24**, 4738 (1991).
30. R. Jain, V. Choudhary, and A.K. Narula, *J. Appl. Polym. Sci*., **105**, 3802 (2007).
31. J. Rocksa, L. Rintoula, F. Vohwinkelc, and G. Georgea, *Polymer*, **45**, 6799 (2004).
32. S. Rimdusit, W. Benjapan, S. Assbumrungrat, T. Takeichi, and R. Yokjota, *Polym. Eng. Sci*., **47**, 489 (2007).
33. S. Tiptipakorn, P. Lorjai, S. Ando, and S. Rimdusit, *Synth. React. Inorg. Met.Org. Chem*., **38**, 248 (2008).
34. C. Wang, X. Zhao, G. Li, and J. Jiang, *Polym. Degrad. Stab*., **94**, 1746 (2009).
35. H. Inoue, H. Okamoto, and Y. Hiraoka, *Radiat. Phys. Chem*., **29**, 283 (1987).
36. S. Tamai, A. Yamaguchi, and M. Ohta, *Polymer*, **37**, 3683 (1996).
37. C.P. Yang, S.H. Hsiao, and K.L. Wu, *Polymer*, **44**, 7067 (2003).
38. K.L. Wang, W.T. Liou, D.J. Liaw, and S.T. Huang, *Polymer*, **49**, 1538 (2008).
39. L.E. Neilsen, R.F. Landel, *Mechanical Properties of Polymer and Composites*, Marcel Dekker, New York (1994).
40. H. Ishida and Y.H. Lee, *Polymer*, **42**, 6971 (2001).
41. D.C.C. Lam and A.C.M. Chong, *Mater. Sci. Eng. A Struct*., **281**, 156 (2000).
42. J.E. Mark, Ed., *Physical Properties of Polymer Handbook*, Springer, New York (1996).
43. A.I. Balabanovich, D. Pospiech, A. Korwitz, L. Häuβler, and C. Harnisch, *Polym. Degrad. Stab*., **94**, 355 (2009).
44. S.Y. Tawfik, J.N Asaad, and M.W. Sabaa, *Polym. Degrad. Stab*., **91**, 385 (2006).
45. T.L. Grubb, V.L. Ulery, T.J. Smith, G.L. Tullos, H. Yagci, L.J. Mathias, and M. Langsam, *Polymer*, **40**, 4279 (1999).
46. H. Li, J. Liu, K. Wang, L. Fan, and S. Yang, *Polymer*, **47**, 1443 (2006).
47. R.H. Vora, *Mater. Sci. Eng. B*, **168**, 71 (2010).

AQ1: Please spell out 'BPADA, ODA, ATR.'

AQ2: Please check whether the grant information is OK as set.

eXPRESS Polymer Letters Vol.6, No.x (2012) x–x
Available online at www.expresspolymlett.com
DOI: 10.3144/expresspolymlett.2012.?

Characterizations of polybenzoxazine modified with isomeric biphenyltetracarboxylic dianhydrides

S. Rimdusit[1*], *B. Ramsiri*[1], *C. Jubsilp*[2], *I. Dueramae*[1]

[1]Polymer Engineering Laboratory, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, 10330 Bangkok, Thailand
[2]Department of Chemical Engineering, Faculty of Engineering, Srinakharinwirot University, 26120 Nakhonnayok, Thailand

Received 25 February 2012; accepted in revised form 22 April 2012

Abstract. A series of polymeric alloying films were prepared from bisphenol A/aniline-based bifunctional benzoxazine resin (BA-a) with three isomeric biphenyltetracarboxylic dianhydrides, i.e., 2,3′,3,4′-biphenyltetra carboxylic dianhydride (a-BPDA), 2,2′,3,3′-biphenyltetracarboxylic dianhydride (i-BPDA), and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) through fully thermal curing. Chemical structure, thermomechanical property and thermal stability of bisphenol A/aniline type polybenzoxazine (PBA-a) copolymers were evaluated. Their chemical structures analyzed via Fourier transform infrared spectroscopy reveal ester carbonyl linkage formation between hydroxyl group of the PBA-a and anhydride group in the isomeric dianhydride. Glass transition temperatures (T_gs) of the dianhydride-modified PBA-a increased with PBA-a<<i-BPDA<a-BPDA<s-BPDA. Degradation temperatures (T_d) of the PBA-a copolymers recorded to be in the range of 365–402°C were significantly higher than that of the neat PBA-a i.e. 334°C. Finally, char yield of the PBA-a copolymers was found to be about 54–57% which is about twofold increase from that of the parent PBA-a.

Keywords: *polymer blends and alloys, polybenzoxazine, isomeric dianhydride, thermal properties, mechanical properties*

1. Introduction

Polybenzoxazine, synthesized by the ring-opening polymerization reaction of cyclic benzoxazine resin only by thermal treatment without the need of catalyst and without producing any harmful by-products during the polymerization process, is recognized as an interesting new class of phenolic resin [1–5]. Moreover, polybenzoxazine provides some characteristics such as excellent dimension stability, high heat resistance, flame retardance and low moisture absorption as well as good dielectric properties in which cannot be found in traditional phenolic resins [6, 7]. Alloying of polybenzoxazine with various other resins or polymers has been reported to economically provide a novel class of resin systems with superior performance [1, 4, 8–15]. However, the major shortcoming of polybenzoxazine is its relatively high rigidity. Therefore, various efforts have been done to toughen polybenzoxazine such as by easily blending with more flexible monomers or polymers e.g. flexible epoxy resins [9, 12], urethane elastomers [8, 13], polyimides [14, 15] or dianhydrides [16, 17].

In recent reports, thermal and thermo-oxidative stabilities of polybenzoxazines have been substantially improved by alloying techniques [8, 15–18]. Alloying between benzoxazine resin and epoxy resin is considered to be a potentially effective measure to enhance thermal, mechanical properties, and flammability as well as processability of the polymers. Rimdusit *et al.* [12] investigated effects of epoxy resin on various arylamine-based benzoxazine resins,

*Corresponding author, e-mail: sarawut.r@chula.ac.th

i.e. aniline (BA-a), m-toluidine (BA-mt), and 3,5-xylidine (BA-35x) on processability, thermal, and mechanical properties of the polybenzoxazine copolymers. The authors reported that processing windows of the polybenzoxazine copolymers were found to be widened with epoxy resin content. Glass transition temperature (T_g) of the polybenzoxazine copolymers, i.e., PBA-a/epoxy resin and PBA-mt/epoxy resin, exhibited a synergistic behavior with the maximum T_g value, i.e. 183 and 215°C, respectively, at the polybenzoxazine blended with epoxy content of 20 wt%. Moreover, flexural strength and elongation at break of the polybenzoxazine alloys increased with increasing amount of the epoxy resin. Spontón *et al.* [19] developed a mixture of bis(m-aminophenyl)methylphosphine oxide-based benzoxazine (Bz-BAMPO) and glycidylether (DGEBA). The authors reported that the Bz-BAMPO: DGEBA at 2:1 mole ratio showed degradation temperature (T_d) at 5% weight loss of about 347°C compared to 333°C of Bz-BAMPO. Moreover, thermomechanical properties of bisphenol A and aniline-based polybenzoxazine (PBA-a) modified with highly flexible urethane elastomer (PU) [13] were reported. The obtained T_g of the PBA-a: PU copolymers was in a range of 177 to 245°C which was substantially greater than those of the parent polymers, i.e. T_g = 166°C for PBA-a, and T_g = –70°C for PU. Coefficient of thermal expansion of the copolymers showed a minimum value at PBA-a:PU (90:10) mass ratio. In addition, flexural strength of the alloys also exhibited a synergistic characteristic at the PBA-a:PU mass ratio of 90:10 with an ultimate value of 142 MPa. Takeichi *et al.* [15] disclosed a performance improvement of bisphenol A and aniline type polybenzoxazine (PBA-a) by blending with polyimide (PI). The authors reported that T_g values, degradation temperature and char yield of the copolymers were enhanced as the PI component increased. T_g of the PBA-a:PI copolymers was in a range of 186–205°C which was greater than that of the neat polybenzoxazine.

In more recent reports, organic acid dianhydrides have been shown to easily copolymerize with benzoxazine resin leading to substantially higher crosslink density of the copolymer network, thus greatly enhancing thermal stability of the polybenzoxazine [15, 16]. Jubsilp *et al.* [16] reported property enhancement of a novel bisphenol A and aniline-based polybenzoxazine (PBA-a) modified with 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA). Fourier-transform infrared spectroscopy (FTIR) reveals ester linkage formation between hydroxyl group of the PBA-a and anhydride group of the BTDA. The PBA-a:BTDA copolymer films showed single T_g with the value as high as 263°C at BA-a:BTDA = 1.5:1 mole ratio. The value is remarkably higher than that of the unmodified PBA-a. In addition, the resulting PBA-a:BTDA copolymers display relatively high thermal stability with T_d at 5% weight loss up to 364°C and substantial enhancement in char yield at 800°C with a value up to 61% vs. that of 38% of the PBA-a.

In this work, a series of aromatic biphenyltetracarboxylic dianhydride isomers including a-BPDA, i-BPDA, and s-BPDA are investigated for their ability to form copolymer with bisphenol A-based benzoxazine resin (BA-a). The three isomers are originally synthesized to provide polyimides with improved solubility [20–22]. Curing behaviors, dynamic mechanical properties and thermal stability of the obtained polybenzoxazine copolymers are also reported.

2. Experimental

2.1. Materials

Materials used in this study are bisphenol A/aniline-based bifunctional benzoxazine resin (BA-a), dianhydrides, 1-methyl-2-pyrrolidone (NMP) as solvent. Benzoxazine resin based on bisphenol A, paraformaldehyde and aniline was synthesized according to the patented solventless technology [7]. Bisphenol A (polycarbonate grade) was provided by Thai Polycarbonate Co., Ltd., TPCC, (Rayong, Thailand). Paraformaldehyde (AR grade) and aniline (AR grade) were purchased from Merck Co., Ltd. (Darmstadt, Germany) and Panreac Quimica SA (Barcelona, Spain), respectively. Biphenyltetracarboxylic dianhydride isomers which are 2,3′,3,4′-biphenyltetracarboxylic dianhydride (a-BPDA), 2,2′,3,3′-biphenyltetracarboxylic dianhydride (i-BPDA), and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) are obtained from Japan Aerospace Exploration Agency, JAXA, (Prof. R. Yokota) (Ibaraki, Japan) and Akron Polymer Systems, Inc. (Ohio, United States). 1-methyl-2-pyrrolidone (NMP) solvent was purchased from Fluka Chemical Co. (Bushs, Switzerland). All chemicals were used as-received.

BA-a resin was blended with various types of biphenyltetracarboxylic dianhydride isomers (DA) at BA-a:DA = 4:1, 3:1, 2:1, 1.5:1, and 1:1 mole ratios. The mixtures were dissolved in NMP and stirred at 80°C until a clear homogeneous mixture was obtained. The solution was cast on Teflon sheet and dried at room temperature for 24 h. Additional drying was carried out at 80°C for 24 h in a vacuum oven followed by thermal curing at 170°C for 1 h, at 190, 210, 230°C for 2 h each and 240°C for 1 h to guarantee complete curing of the mixtures.

2.2. Characterization methods

Glass transition temperatures (T_g) of all specimens were determined using a differential scanning calorimeter (DSC) model 2910 from TA Instruments (New Castle, DE, United States). The thermogram was obtained using a heating rate of 10°C/min from 30 to 300°C under nitrogen purging with a constant flow 50 mL/min. The specimen with a mass of 8–10 mg was sealed in an aluminum pan with lid. The $T_{g,\,DSC}$ was obtained from the temperature at half extrapolated tangents of the step transition midpoint.

Fourier transform infrared spectra of fully cured specimens were acquired at room temperature using a Spectrum GX FT-IR spectometer with an ATR accessory from PerkinElmer, Inc. (Waltham, Massachusette, United States). In the case of a BA-a and a pure biphenyltetracarboxylic isomers, a small amount of biphenyltetracarboxylic isomer powder was cast as thin film on a potassium bromide (KBr) window. All spectra were taken with 64 scans at a resolution of 4 cm^{-1} and in a spectral range of 4000–400 cm^{-1}.

A dynamic mechanical analyzer (DMA) model DMA242 from Netzsch, Inc. (Bavaria, Germany) was used to investigate viscoelastic properties of all specimens. The dimension of specimens has a width of 7.0 mm, a long 10 mm, and a 0.1 mm thick. The test was performed in a tension mode at a frequency of 1 Hz with a strain value of 0.1% and at a heating rate of 2°C/min from 30 to 400°C under nitrogen atmosphere with a constant flow 80 mL/min. The storage modulus (E'), loss modulus (E''), and loss tangent or damping curve ($\tan\delta$) were then obtained. The $T_{g,\,DMA}$ was taken as the maximum point on the loss modulus curve in the DMA thermograms.

Degradation temperature (T_d) at 5% weight loss and char yield at 800°C of all specimens were acquired using a Diamond TG/DTA from PerkinElmer, Inc. (Waltham, Massachusetts, United States). The testing temperature program was ramped at a heating rate of 20°C/min from 30 to 1000°C under nitrogen purging with a constant flow of 50 mL/min. The sample mass used was approximately 15 mg. T_ds and char yields of the specimens were reported at their 5% weight loss and at 800°C, respectively.

3. Results and discussion

3.1. Optimal composition of BA-a:dianhydride isomer mixtures

DSC thermograms of the fully cured PBA-a copolymers of BA-a:s-BPDA at various mole ratios ranging from 4:1, 3:1, 2:1, 1.5:1 and 1:1 are depicted in Figure 1. From this figure, we can see that the glass transition temperature ($T_{g,\,DSC}$) determined from a mid-point in initial slope change of DSC thermograms of the PBA-a copolymers increases with increasing amount of s-BPDA content until BA-a:s-BPDA = 1.5:1 mole ratio and then the $T_{g,\,DSC}$ value of the copolymer at 1:1 mole ratio tends to decrease. In other words, the ultimate value of $T_{g,\,DSC}$ of the copolymer was obtained at the BA-a:s-BPDA composition of 1.5:1 mole. All of the fully cured PBA-a:s-BPDA copolymers showed only single $T_{g,\,DSC}$ ranging from 170 to 257°C suggesting a single phase

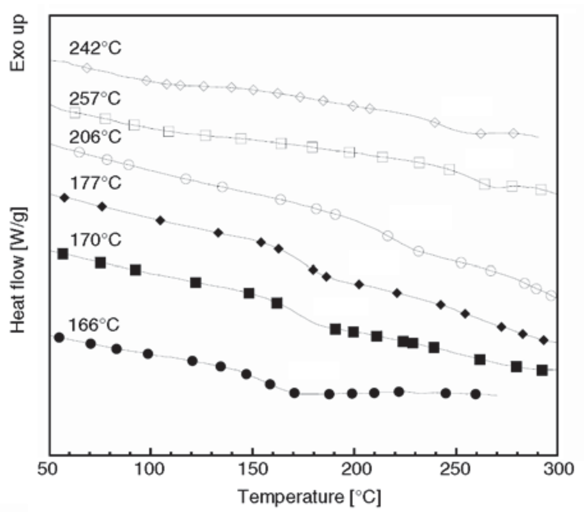


Figure 1. DSC thermograms of PBA-a:s-BPDA copolymer films at various mole ratios: (●) PBA-a, (■) BA-a:s-BPDA = 4:1, (◆) BA-a:s-BPDA = 3:1, (○) BA-a:s-BPDA = 2:1, (□) BA-a:s-BPDA = 1.5:1, and (◇) BA-a:s-BPDA = 1:1

material in these PBA-a-dianhydride copolymers. Those values are substantially greater than the $T_{g,\,DSC}$ of the neat PBA-a i.e. 166°C. From the $T_{g,\,DSC}$ results, the optimal network formation reaction of the PBA-a copolymers clearly required greater moles of benzoxazine monomers than those of the s-BPDA or did not follow the stoichiometric ratio of the two monomers. This is because an ability of the benzoxazine monomers to undergo self-polymerizability upon heating besides their ability to react with the dianhydrides. As a consequence, the consumption of the benzoxazine monomers tended to be greater than that of the dianhydrides in order to form a perfect network which may be related to the phenoxy-phenolic rearrangement that occurs during the formation for PBA-a [23]. This result is also in good agreement with the reaction of BA-a with BTDA [16]. In addition, DSC thermograms of the fully cured BA-a:a-BPDA and BA-a:i-BPDA copolymers at various dianhydride contents (not shown here) also provided similar trend on the T_g values. The maximum $T_{g,\,DSC}$ value of the copolymers prepared from BA-a:a-BPDA = 1.5:1 mole and BA-a:i-BPDA = 1.5:1 mole indicated about 245 and 237°C, respectively. The results show that each isomeric BPDA significantly affected the glass transition temperature of the copolymers as previously observed in polyimides based on isomeric BPDA [24].

3.2. Network formation by thermal cure of PBA-a:dianhydride isomer copolymers

Chemical structures of BA-a, PBA-a, isomeric dianhydride modifiers and their network formation reactions between the PBA-a and those isomeric dianhydride modifiers were studied using Fourier transform infrared spectroscopy (FT-IR) technique. The FT-IR absorption bands of the BA-a resin are previously reported in details [1, 15, 18]. In Figure 2, the important characteristics of infrared absorptions of BA-a resin were obviously observed at 947 and 1497 cm^{-1} attributed to the tri-substituted benzene ring and at 1232 cm^{-1} assigned to the asymmetric stretching of C–O–C group of oxazine ring. On the other hand, the biphenyltetracarboxylic dianhydride isomers, i.e., a-BPDA, i-BPDA, and s-BPDA, were identified by a distinctive carbonyl band region. From Figure 2, the spectrum of biphenyltetracarboxylic dianhydride isomer, e.g. a-BPDA, provided

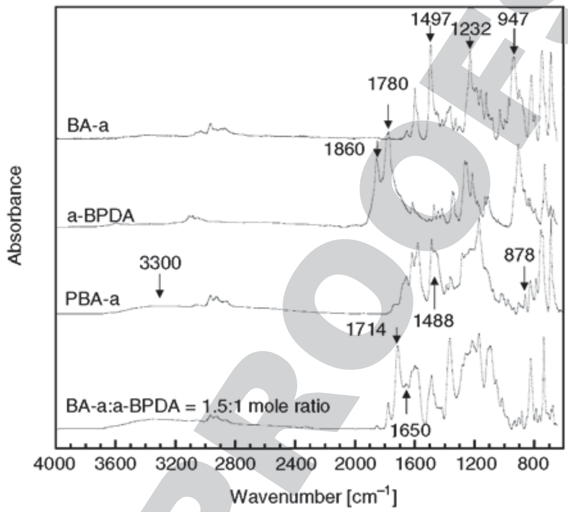


Figure 2. FTIR spectra of isomeric biphenyltetracarboxylic dianhydrides-modified PBA-a films of BA-a: a-BPDA = 1.5:1 mole

the characteristic absorption peaks with component in the 1780–1740 cm^{-1} region assigned to symmetric and 1860–1800 cm^{-1} region assigned to asymmetric starching of strong anhydride carbonyl groups [16, 25]. After thermal curing, an infinite three dimensional network was formed from benzoxazine ring opening by the breakage of C–O bond and then the benzoxazine molecule transformed from a ring structure to a network structure [6, 26]. During this curing process via ring opening reaction of the BA-a resin upon thermal treatment, the tri-substituted benzene ring around 1497 cm^{-1} which is the backbone of benzoxazine ring, became tetra-substituted benzene ring centered at 1488 and 878 cm^{-1} which led to the formation of a phenolic hydroxyl group-based polybenzoxazine structure. The phenolic hydroxyl group is also confirmed by the appearance of new absorption peak about 3300 cm^{-1}.

The chemical transformations of BA-a:a-BPDA at 1.5:1 mole ratio upon thermal curing were investigated and the resulting spectra are shown in Figure 2. The new absorption bands of PBA-a:a-BPDA copolymer were observed. The phenomenon was ascribed to the appearance of carbonyl stretching bands of ester linkages. From the PBA-a:biphenyltetracarboxylic dianhydride isomer spectrum in Figure 2, we can see that the anhydride carbonyl stretching bands of biphenyltetracarboxylic dianhydride at 1860 and 1780 cm^{-1} completely disappeared. It was suggested that the reaction between the phenolic hydroxyl group of the PBA-a and the anhydride group of the biphenyl tetracarboxylic dianhydride isomer could occur to form ester carbonyl linkage as evidenced by the observed peak in the spectrum at 1730–1700 cm^{-1} of its C=O stretching of ester carbonyl group bonded phenolic hydroxyl group of the PBA-a modified with biphenyltetracarboxylic dianhydride [18]. Furthermore, the carboxylic acid occurred after thermal curing of the PBA-a:dianhydride isomer mixture can also be followed by monitoring a band at 1650–1670 cm^{-1} due to C=O stretching [27]. In addition, carboxylic acid shows characteristic C–O–H in-plane bending band at 1440–1395 cm^{-1}, C–O stretching band at 1320–1210 cm^{-1}, and C–O–H out-of-plane bending band at 960–900 cm^{-1}, respectively [25, 28]. Furthermore, the FTIR results for the i-BTDA and s-BTDA-modified PBA-a (not shown here) are relatively similar to a-BTDA-modified PBA-a.

As a consequence, the proposed reaction model of these mixtures was shown in Figure 3 which was similar to the cure reaction between anhydride group and hydroxyl group of the ring-opened epoxide group to form the ester carbonyl linkage [29–31] and a diglycidyl ether of bisphenol A-based epoxide resin (DGEBA) with dodecyl succinic anhydride (DDSA) [32] as well as reaction between BTDA dianhydride and hydroxyl group of 2-hydroxyethyl acrylate (HEA) [33].

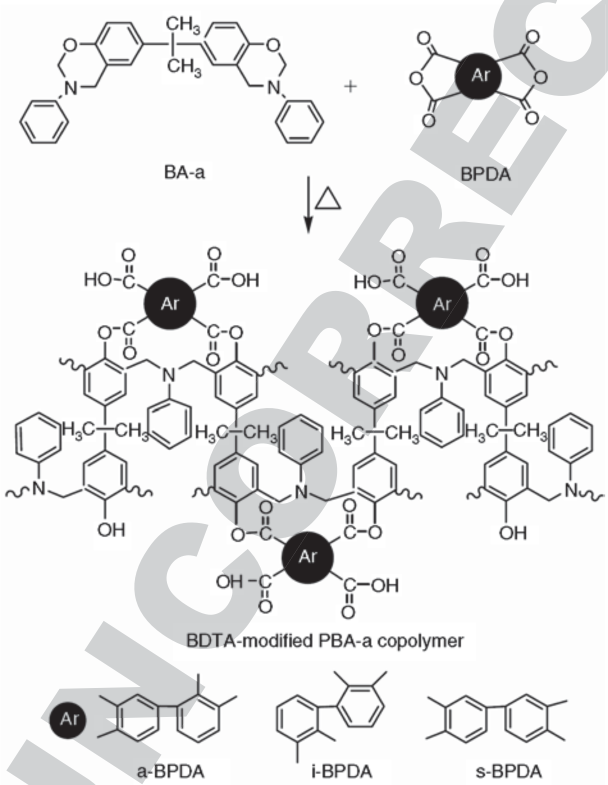


Figure 3. Model compound of isomeric BPDA-modified polybenzoxazine copolymers

3.3. Thermomechanical properties of PBA-a:dianhydride isomer copolymers

The mechanical properties of the PBA-a modified with isomeric biphenyltetracarboxylic dianhydrides, i.e. BA-a:a-BPDA, BA-a:i-BPDA, and BA-a:s-BPDA at 1.5:1 mole ratio were measured as a function of temperature. In this study dynamic tensile property was applied as dynamic mechanical analysis (DMA). The DMA thermograms were displayed in Figure 4, 5, and 6, respectively. Generally, the storage modulus of the materials demonstrates the deformation resistances of material when external force were applied sinusoidally. The storage moduli at room temperature (25°C) of PBA-a:a-BPDA, PBA-a:i-BPDA, and PBA-a: s-BPDA copolymers exhibited the values of 2.91, 2.89 and 3.42 GPa, respectively, which were higher than that of the neat PBA-a of 2.57 GPa as shown in Figure 4. This is due to higher crosslink density and greater aromatic content of the PBA-a copolymers with a greater amount of the isomeric biphenyltetracarboxylic dianhydride.

The effects of isomeric biphenyltetracarboxylic dianhydride on the crosslink density, ρ_x, of their polymer alloy network can be calculated from a value of the equilibrium storage shear modulus in the rubbery region, G_e', which equals to $E_e'/3$ as follow in Equation (1) derived from the statistical theory of rubber elasticity by Nielsen [34]:

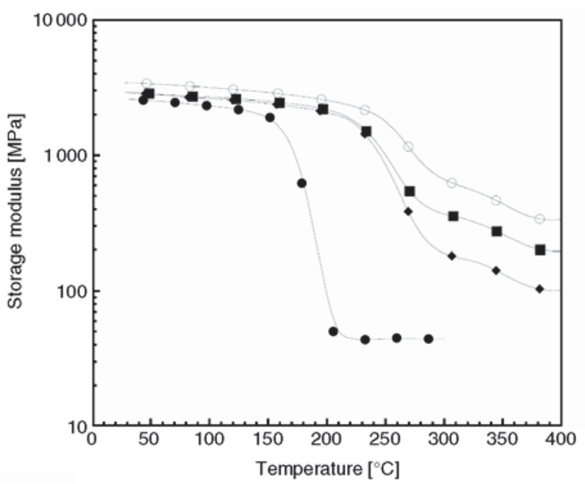


Figure 4. Storage modulus of isomeric biphenyltetracarboxylic dianhydrides-modified PBA-a films of BA-a:BPDA = 1.5:1 mole: (●) PBA-a, (■) PBA-a:a-BPDA, (◆) PBA-a:i-BPDA, (○) PBA-a:s-BPDA

$$\log(E'_e/3) = 7.0 + 293(\rho_x) \qquad (1)$$

where E'_e is an equilibrium storage modulus in rubbery plateau [dyne/cm^2] and ρ_x is crosslink density [mol/cm^3] which is the mole number of network chains per unit volume of the polymers.

As expected, crosslink density values of the PBA-a and its copolymers i.e. PBA-a:a-BPDA, PBA-a:i-BPDA, and PBA-a:s-BPDA, calculated from Equation (1) are 3981, 7157, 6353 and 7664 mol/m^3, respectively. It is evident that the crosslink density of the neat PBA-a was greatly enhanced by an addition of isomeric biphenyltetracarboxylic dianhydrides, corresponding to an enhancement in their storage modulus values discussed previously. Moreover, we can see that the storage modulus at room temperature of the isomeric BPDA-modified PBA-a copolymer films increases with i-BPDA < a-BPDA < s-BPDA as similarly reported in polyimide film derived from isomeric BPDA/*p,p'*-ODA and isomeric BPDA/1,4,4-APB [35]. This behavior results from the greater interaction of the macromolecules and denser packing of s-BPDA than those of a-BPDA and i-BPDA. In case of i-BPDA based polyimides, the polyimides tend to form internal cyclization which may be lead to obtain lower interaction of the macromolecules and rather low molecular weights than s-BPDA based polyimides [36].

Figure 5 displays glass transition temperature, the maximum point on the loss modulus curve ($T_{g,\,DMA}$), related to molecular motion at structural level determimed from of the PBA-a:a-BPDA, PBA-a:i-BPDA, and PBA-a:s-BPDA copolymer films. From the figure, the neat PBA-a and its copolymers showed only single $T_{g,\,DMA}$ as reported in DSC thermogram in Figure 1. This result suggested that all kinds of PBA-a:isomeric biphenyltetracarboxylic dianhydride copolymer films were homogeneous and no phase separation occurred in these copolymers. From Figure 5, the $T_{g,\,DMA}$ value of the neat PBA-a was determined to be about 178°C and those of the PBA-a modified with isomeric biphenyltetracarboxylic dianhydrides films were found to be in the range of 239–266°C. The $T_{g,\,DMA}$ value of the neat PBA-a was clearly enhanced by blending with the a-BPDA or i-BPDA or s-BPDA dianhydrides. The obtained high $T_{g,\,DMA}$ value of PBA-a:isomeric biphenyltetracarboxylic dianhydride copolymers can be attributed to the improved crosslink structure

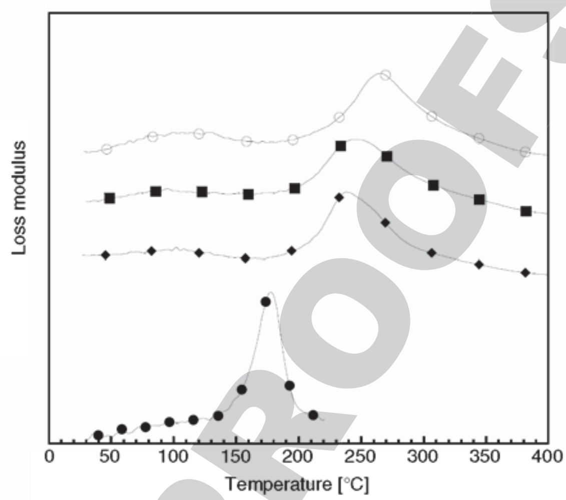


Figure 5. Loss modulus of isomeric biphenyltetracarboxylic dianhydrides-modified PBA-a films of BA-a:BPDA = 1.5:1 mole: (●) PBA-a, (■) PBA-a:a-BPDA, (◆) PBA-a:i-BPDA, (○) PBA-a:s-BPDA

via ester carbonyl linkage between phenolic hydroxyl group of PBA-a and anhydride group of isomeric biphenyltetracarboxylic dianhydride as seen in FT-IR spectra and their high aromatic content from the presence of the dianhydrides in the copolymers network as well as hydrogen bonding between ester carbonyl group (C=O) or OH groups in a carboxylic acid and phenolic hydroxyl group (–OH) of the PBA-a. Moreover, the T_g values of PBA-a copolymers measured by DMA displayed descending order on basis of both molecular packing and chain conformation such as semirigid s-BPDA and bent chain a-BPDA structures of isomeric biphenyltetracarboxylic dianhydrides [37, 38]. In our experiments, the order of T_g's PBA-a: s-BPDA (266°C) > PBA-a:a-BPDA (247°C) > PBA-a: i-BPDA (239°C) was observed as similarly investigated in [23]. This observation implied that the T_g values were also dependent on stiff/linear chain of these isomeric biphenyltetracarboxylic dianhydride moieties that a decrease in the chain linearity as follow s-BPDA > a-BPDA > i-BPDA caused an increase of energy to motivate motions in PBA-a:s-BPDA copolymer as compared with that of PBA-a:a-BPDA and PBA-a:i-BPDA copolymers and thus results in higher T_g for the PBA-a:s-BPDA copolymer as compared to latter copolymers.

The loss tangent (tan δ) of the neat PBA-a and their copolymers with various types of isomeric biphenyltetracarboxylic dianhydrides was illustrated in Figure 6. The peak height of the tan δ of the PBA-a:

EPL_0003486

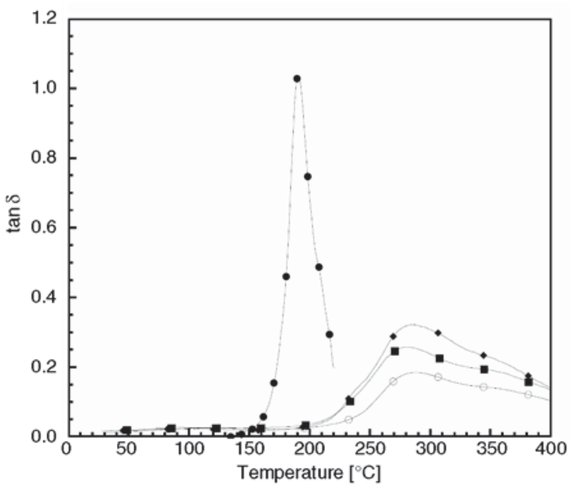


Figure 6. Loss tangent of isomeric biphenyltetracarboxylic dianhydrides-modified PBA-a films of BA-a:BPDA = 1.5:1 mole: (●) PBA-a, (■) PBA-a:a-BPDA, (◆) PBA-a:i-BPDA, (○) PBA-a:s-BPDA

a-BPDA, PBA-a:i-BPDA, and PBA-a:s-BPDA tended to decrease while the peak position of their PBA-a copolymers shifted to a higher temperature. The results indicated that the increase in the crosslink density with decreasing the chain's segmental mobility in the PBA-a modified with biphenyltetracarboxylic dianhydride isomers. This characteristic of the copolymers conformed to increasing of T_g's copolymer as follow s-BPDA > a-BPDA > i-BPDA. Furthermore, the width-at-half-height of tan δ curves was broader in their PBA-a copolymers, which confirmed the more heterogeneous network in the resulting copolymers due to a hybrid polymer network formation. Moreover, the obtained transparent copolymer films and the single tan δ peak observed in each copolymer suggested no macroscopic phase separation in their PBA-a copolymer films.

3.4. Visual appearance of PBA-a:dianhydride isomer copolymers

Because of the ester carbonyl linkage, structurally flexible functional group, formed after thermal curing stages, the enhancement of the PBA-a:dianhydride isomer copolymer bending was expected. A transparent brown neat PBA-a film and red brown PBA-a blended with isomeric biphenyltetracarboxylic dianhydrides at the neat BA-a equal to 1.5 mole and dianhydride isomer equal to 1 mole which showed the highest $T_{g,\,DMA}$ value of the PBA-a copolymers were obtained. The visual appearances of the cured PBA-a copolymer specimens are presented in Figure 7. We can see that the PBA-a specimen of about 100 μm thick is rather brittle, and it can not be bent further than as shown in Figure 7a due to the internal hydrogen bonding among hydroxyl and amino groups of the PBA-a. Whereas the homogeneous specimens of all the PBA-a copolymers of the same thickness as illustrated in Figures 7b–7d showed a remarkable improvement in their tough-

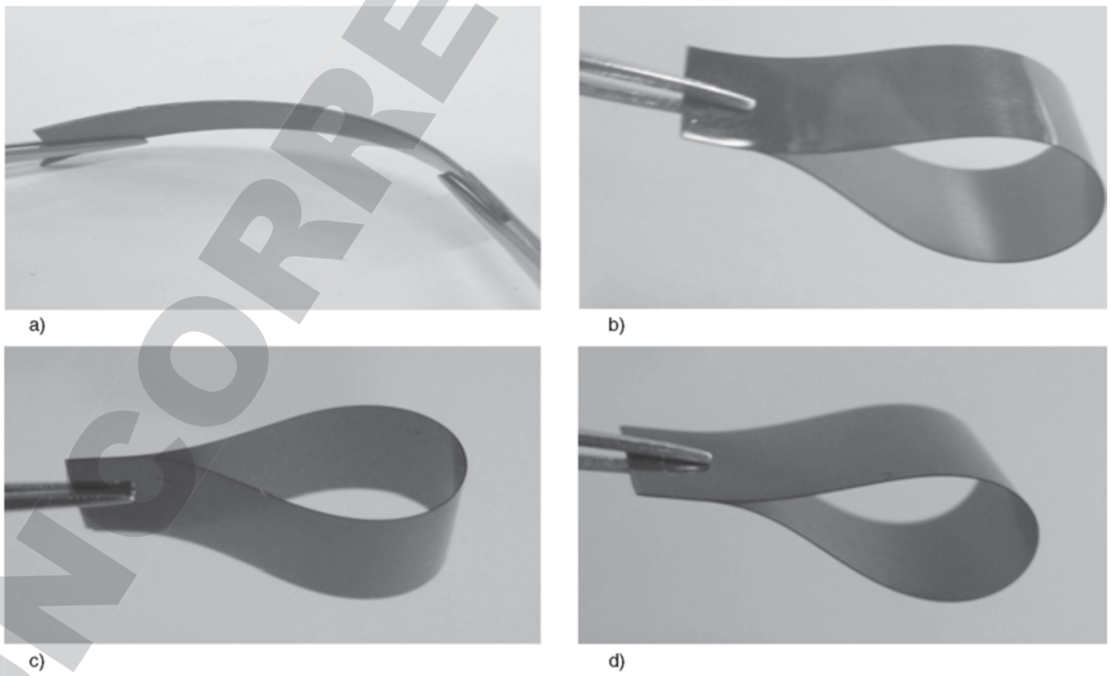


Figure 7. Visual appearances of isomeric biphenyltetracarboxylic dianhydrides-modified PBA-a films of BA-a:BPDA = 1.5:1 mole: (a) PBA-a, (b) PBA-a:a-BPDA, (c) PBA-a:i-BPDA, (d) PBA-a:s-BPDA

ness. The toughness enhancement of the PBA-a copolymer specimens, actually, due to ester carbonyl linkages (C=O) formed in the PBA-a copolymer network. Moreover, the formation of the esters might result in the breaking of the internal hydrogen bonding of the PBA-a. The new hydrogen-bonding tends to be random; therefore, the total polymer network structure could be more flexible. In addition, the great toughness of the PBA-a copolymers in Figures 7b–7d is similar to that of the commercial polyimide films such as UPILEX®S film presented by Ube Industries, Ltd. and Kapton®H films [39].

3.5. Thermal stability of PBA-a:dianhydride isomer copolymers

Figure 8 depicted the TGA thermogram results of three kinds of representative isomeric biphenyltetracarboxylic dianhydride-modified PBA-a, i.e., PBA-a:a-BPDA, PBA-a:i-BPDA, and PBA-a:s-BPDA copolymer films consisted of BA-a equal to 1.5 mole and dianhydride isomer equal to 1 mole. The degradation temperature (T_d), expressed as the 5% weight loss under nitrogen atmosphere in TGA of the neat PBA-a, was determined to be 334°C. The T_d values at 5% weight loss of the all sort of PBA-a:isomeric biphenyltetracarboxylic dianhydrides copolymer films were higher than that of the neat PBA-a films, i.e., 379°C for PBA-a:a-BPDA, 365°C for PBA-a:i-BPDA, and 402°C for PBA-a:s-BPDA. This is due to the effect of the ester carbonyl linkage formation in the PBA-a copolymer network as the T_d of polyester reported ~353–550°C

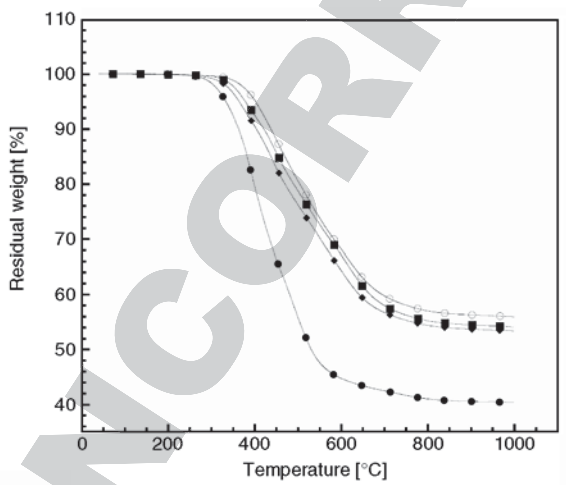


Figure 8. TGA thermograms of isomeric biphenyltetracarboxylic dianhydrides-modified PBA-a films of BA-a:BPDA = 1.5:1 mole: (●) PBA-a, (■) PBA-a:a-BPDA, (◆) PBA-a:i-BPDA, (○) PBA-a:s-BPDA

[40, 41] which had higher thermal stability than that of the neat PBA-a. In addition, the improved crosslink density of the PBA-a with an addition of the isomeric biphenyltetracarboxylic dianhydrides via esterification reaction between the hydroxyl group of the polybenzoxazine and the anhydride group of the isomeric dianhydrides as mentioned previously as well as additional hydrogen bonding between –OH group and C=O group in the copolymers. Moreover, we can see that T_d at 5% weight loss in TGA falls in the same order as T_g: i.e., T_d at 5% weight loss of the PBA-a copolymers with respect to the structure of isomeric biphenyltetracarboxylic dianhydride component increases in the order of i-BPDA < a-BPDA < s-BPDA which shows the similar trend in polyimides based on isomeric biphenyltetracarboxylic dianhydrides [42]. Interestingly, T_g-thermal energy absorption relationship shows that the molecular chain with greater mobility or lower T_g may absorb more thermal energy and less thermal stability than a chain with less mobility.

Additionally, the amount of carbonized residue (char yield) at 800°C under nitrogen for the PBA-a and all kind of the PBA-a:isomeric biphenyltetracarboxylic dianhydride copolymer films also showed in Figure 8. Their PBA-a:isomeric biphenyltetracarboxylic dianhydride copolymer films were 54, 55 and 60% for i-BPDA, a-BPDA, and s-BPDA-modified PBA-a, respectively, which was much great than that of the neat PBA-a (i.e. 38% at 800°C). The high char yield of these PBA-a copolymers due to their higher aromatic content in the molecular structure and enhanced crosslink density through inter hydrogen bonding in the copolymers of the resulting PBA-a copolymers as previously reported in [16].

4. Conclusions

High temperature bisphenol-A-aniline type polybenzoxazine (PBA-a) copolymer films were prepared from mixtures of BA-a resin and a-BPDA, i-BPDA, or s-BPDA isomeric biphenyltetracarboxylic dianhydrides. The obtained network structures were due to reaction between the hydroxyl group of polybenzoxazine and the anhydride group of isomeric biphenyltetracarboxylic dianhydrides. The T_g value, crosslink density, and T_d value of PBA-a was enhanced by blending with the isomeric biphenyltetracarboxylic dianhydrides. Moreover, T_g and T_d values of polybenzoxazine copolymers with respect to the structure of isomeric aromatic carboxylic dianhydride were as follow: PBA-a:s-BPDA > PBA-a:a-BPDA > PBA-a:i-BPDA. The char yield of their copolymer films at 800°C under nitrogen is much higher than that of the neat polybenzoxazine. Therefore, the polybenzoxazine modified with the isomeric biphenyltetracarboxylic dianhydrides should be considered as good potential candidates for high-temperature resistant materials with outstanding mechanical integrity at high temperatures.

Acknowledgements

This research is supported by the Rachadaphiseksomphot Endowment Fund Part of the "Strengthen CU's Researcher's Project," and the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission (AM1076A). Additional fund was also provided by Research Grants of Faculty of Engineering and Research Grants of Graduate School, Srinakharinwirot University 2011 (C. Jubsilp). The authors would like to acknowledge Prof. Rikio Yokota of JAXA, Japan for the research fellowship of S.R. Bisphenol A is kindly provided by Thai Polycarbonate Co., Ltd. (TPCC).

References

[1] Ishida H.: Handbook of benzoxazine resins. Elsevier, New York (2011).

[2] Ghosh N. N., Kiskan B., Yagci Y.: Polybenzoxazines – New high performance thermosetting resins: Synthesis and properties. Progress in Polymer Science, **32**, 1344–1391 (2007).
DOI: 10.1016/j.progpolymsci.2007.07.002

[3] Santhosh Kumar K. S., Reghunadhan Nair C. P.: Polybenzoxazines: Chemistry and properties. Rapra, Shawbury (2010).

[4] Reghunadhan Nair C. P.: Advances in addition-cure phenolic resins. Progress in Polymer Science, **29**, 401–498 (2004).
DOI: 10.1016/j.progpolymsci.2004.01.004

[5] Cao G. P., Chen W. J., Wei J. J., Li W. T., Liu X. B.: Synthesis and characterization of a novel bisphthalonitrile containing benzoxazine. Express Polymer Letters, **8**, 512–518 (2007).
DOI: 10.3144/expresspolymlett.2007.73

[6] Ishida H., Low H. Y.: A study on the volumetric expansion of benzoxazine-based phenolic resin. Macromolecules, **30**, 1099–1106 (1997).
DOI: 10.1021/ma960539a

[7] Ishida H.: Process for preparation of benzoxazine compounds in solventless systems. U.S. Patent 5543516, USA (1996).

[8] Rimdusit S., Pirstpindvong S., Tanthapanichakoon W., Damrongsakkul S.: Toughening of polybenzoxazine by alloying with urethane prepolymer and flexible epoxy: A comparative study. Polymer Engineering and Science, **45**, 288–296 (2005).
DOI: 10.1002/pen.20273

[9] Jubsilp C., Takeichi T., Hiziroglu S., Rimdusit S.: Effect of resin compositions on microwave processing and thermophysical properties of benzoxazine-epoxy-phenolic ternary systems filled with silicon carbide (SiC) whisker. Polymer Engineering and Science, **49**, 1022–1029 (2009).
DOI: 10.1002/pen.21358

[10] Grishchuk S., Mbhele Z., Schmitt S., Karger-Kocsis J.: Structure, thermal and fracture mechanical properties of benzoxazine-modified amine-cured DGEBA epoxy resins. Express Polymer Letters, **3**, 273–282 (2011).
DOI: 10.3144/expresspolymlett.2011.27

[11] Kimura H., Ohtsuka K., Matsumoto A.: Curing reaction of bisphenol-A based benzoxazine with cyanate ester resin and the properties of the cured thermosetting resin. Express Polymer Letters, **5**, 1113–1122 (2011).
DOI: 10.3144/expresspolymlett.2011.108

[12] Rimdusit S., Kunopast P., Dueramae I.: Thermomechanical properties of arylamine-based benzoxazine resins alloyed with epoxy resin. Polymer Engineering and Science, **51**, 1797–1807 (2011).
DOI: 10.1002/pen.21969

[13] Rimdutsit S., Bangsen W., Kasemsiri P.: Chemorheology and thermomechanical characteristics of benzoxazine-urethane copolymers. Journal of Applied Polymer Science, **121**, 3669–3678 (2011).
DOI: 10.1002/app.34170

[14] Tiptipakorn S., Damrongsakkul S., Ando S., Hemvichain K., Rimdusit S.: Thermal degradation behaviors of polybenzoxazine and silicon-containing polyimide blends. Polymer Degradation and Stability, **92**, 1265–1278 (2007).
DOI: 10.1016/j.polymdegradstab.2007.03.021

[15] Takeichi T., Guo Y., Rimdusit S.: Performance improvement of polybenzoxazine by alloying with polyimide: Effect of preparation method on the properties. Polymer, **46**, 4909–4916 (2005).
DOI: 10.1016/j.polymer.2005.03.096

[16] Jubsilp C., Takeichi T., Rimdusit S.: Property enhancement of polybenzoxazine modified with dianhydride. Polymer Degradation and Stability, **96**, 1047–1053 (2011).
DOI: 10.1016/j.polymdegradstab.2011.03.021

[17] Rimdusit S., Jubsilp C.: Polymer from modification of polybenzoxazine with anhydride. Thailand Patent 0701003695, Thailand (2007).

[18] Rajput A. B., Ghosh N. N.: Preparation and characterization of novel polybenzoxazine–polyester resin blends. International Journal of Polymeric Materials, **60**, 27–39 (2010).
DOI: 10.1080/00914037.2010.504153

[19] Spontón M., Ronda J. C., Galià M., Cádiz V.: Studies on thermal and flame retardant behaviour of mixtures of bis(m-aminophenyl)methylphosphine oxide based benzoxazine and glycidylether or benzoxazine of bisphenol A. Polymer Degradation and Stability, **93**, 2158–2165 (2008).
DOI: 10.1016/j.polymdegradstab.2008.08.004

[20] Zhou H., Chen C., Kanbara R., Sasaki T., Yokota R.: Synthesis and properties of copolyimides derived from isometric biphenyltetracarboxylic dianhydrides (a-BPDA and i-BPDA) and oxydiphthalic dianhydride (ODPA) with 4,4′-oxydianiline (4,4′-ODA). High Performance Polymer, **17**, 213–224 (2005).
DOI: 10.1177/0954008305044856

[21] Tong Y., Huang W., Luo J., Ding M.: Synthesis and properties of aromatic polyimides derived from 2,2′,3,3′-biphenyltetracarboxylic dianhydride. Journal of Polymer Science Part A: Polymer Chemistry, **37**, 1425–1433 (1999).
DOI: 10.1002/(SICI)1099-0518(19990515)37:10<1425::AID-POLA4>3.0.CO;2-G

[22] Hergenrother P. M., Watson K. A., Smith Jr J. G., Connell J. W., Yokota R.: Polyimides from 2,3,3′,4′-biphenyltetracarboxylic dianhydride and aromatic diamines. Polymer, **43**, 5077–5093 (2002).
DOI: 10.1016/S0032-3861(02)00362-2

[23] Liu C., Shen D., Sebastián R. M., Marquet J., Schönfeld R.: Mechanistic studies on ring-opening polymerization of benzoxazines: A mechanistically based catalyst design. Macromolecules, **44**, 4616–4622 (2011).
DOI: 10.1021/ma2007893

[24] Gerber M. K., Pratt J. R., St Clair T. L.: Materials, chemistry, and characterization. in 'Polyimide' (eds.: Feger C., Khojasteh M. M., MacGrath J. M.) Elsevier, Amsterdam, 487–??? (1989).

[25] Stuart B. H.: Infrared spectroscopy: Fundamentals and applications. Wiley, Chichester (2004).

[26] Dunkers J., Zarate E. A., Ishida H.: Crystal structure and hydrogen-bonding characteristics of N,N-bis(3,5-dimethyl-2-hydroxybenzyl)methylamine, A benzoxazine dimer. The Journal of Physical Chemistry, **100**, 13514–13520 (1996).
DOI: 10.1021/jp961293e

[27] Settle F. A.: Handbook of instrumental techniques for analytical chemistry. Prentice Hall, New Jersey (1997).

[28] Colthup N. B., Daly L. H., Wiberley S. E.: Introduction to infrared and raman spectroscopy. Academic Press, London (1990).

[29] Trappe V., Burchard W., Steinmann B.: Anhydride-cured epoxies via chain reaction. 1. The phenyl glycidyl ether/phthalic acid anhydride system. Macromolecules, **24**, 4738–4744 (1991).
DOI: 10.1021/ma00017a002

[30] Jain R., Choudhary V., Narula A. K.: Curing and thermal behavior of DGEBA in presence of dianhydrides and aromatic diamine. Journal of Applied Polymer Science, **105**, 3804–3808 (2007).
DOI: 10.1002/app.26620

[31] Rocks J., Rintoul L., Vohwinkel F., George G.: The kinetics and mechanism of cure of an amino-glycidyl epoxy resin by a co-anhydride as studied by FT-Raman spectroscopy. Polymer, **45**, 6799–6711 (2004).
DOI: 10.1016/j.polymer.2004.07.066

[32] Ghaemy M., Riahy M. H.: Kinetics of anhydride and polyamide curing of bisphenol A-based diglycidyl ether using DSC. European Polymer Journal, **32**, 1207–1212 (1996).
DOI: 10.1016/S0014-3057(96)00066-3

[33] Chiang W-Y., Chan S-C.: Preparation and properties of UV-autocurable BTDA-based epoxy-multiacrylate resins. Effects of the degree of polymerization and the epoxy type. Journal of Applied Polymer Science, **43**, 1827–1836 (1991).
DOI: 10.1002/app.1991.070431006

[34] Nielsen L. E.: Cross-linking–effect on physical properties of polymers. Journal of Macromolecular Science Part C: Polymer Reviews, **3**, 69–103 (1969).
DOI: 10.1080/15583726908545897

[35] Fryd M.: Structure–Tg relationship in polyimides. in 'Polyimides: Synthesis, characterizations and properties' (ed.: Mittal K. L.) Plenum Press, New York, Vol 1, 377–383 (1984).

[36] Ding M.: Isomeric polyimides. Progress in Polymer Science, **32**, 623–668 (2007).
DOI: 10.1016/j.progpolymsci.2007.01.007

[37] Hasegawa M., Sensui N., Shindo Y., Yokota R.: Structure and properties of novel asymmetric biphenyl type polyimides. Homo- and copolymers and blends. Macromolecules, **32**, 387–396 (1999).
DOI: 10.1021/ma9808629

[38] Li F., Ge J. J., Honigfort P. S., Fang S., Chen J-C., Harris F. W., Cheng S. Z. D.: Dianhydride architectural effects on the relaxation behaviors and thermal and optical properties of organo-soluble aromatic polyimide films. Polymer, **40**, 4987–5002 (1999).
DOI: 10.1016/S0032-3861(98)00721-6

[39] Hergenrother P. M.: High performance polymers and composites. Wiley, New York (1991).

[40] Evans S. J., Haines P. J., Skinner G. A.: The thermal degradation of polyester resins II. The effects of cure and of fillers on degradation. Thermochimica Acta, **291**, 43–49 (1997).
DOI: 10.1016/S0040-6031(96)03102-4

[41] Sato H., Kikuchi T., Koide N., Furuya K.: Thermal degradation and combustion process of liquid crystalline polyesters studied by directly coupled thermal analysis-mass spectrometry. Journal of Analytical and Applied Pyrolysis, **37**, 173–183 (1996).
DOI: 10.1016/0165-2370(96)00944-8

[42] Inoue H., Okamoto H., Hiraoka Y.: Effect of the chemical structure of acid dianhydride in the skeleton on the thermal property and radiation resistance of polyimide. International Journal of Radiation Applications and Instrumentation Part C: Radiation Physics and Chemistry, **29**, 283–288 (1987).
DOI: 10.1016/1359-0197(87)90033-6

Author Query Form

(EPL_0003486)

Author please write responses to queries directly on the printed Galley proofs. Please scan the corrected pages and then upload them through the manuscript central. If you can not write your notice directly on the proof, please describe it here, indicating the page and row numbers. We would like to draw your attention that you may not request major corrections or inclusions in this final stage of the manuscript.

Please complete the reference [24] (missing page to page).
Please complete the Figure 2 and 5 (missing dimension at Y axis).

AUTHOR QUERY FORM

ELSEVIER	Journal: REACT Article Number: 3058	Please e-mail or fax your responses and any corrections to: E-mail: corrections.eseo@elsevier.sps.co.in Fax: +31 2048 52799

Dear Author,

Please check your proof carefully and mark all corrections at the appropriate place in the proof (e.g., by using on-screen annotation in the PDF file) or compile them in a separate list. Note: if you opt to annotate the file with software other than Adobe Reader then please also highlight the appropriate place in the PDF file. To ensure fast publication of your paper please return your corrections within 48 hours.

For correction or revision of any artwork, please consult http://www.elsevier.com/artworkinstructions.

Any queries or remarks that have arisen during the processing of your manuscript are listed below and highlighted by flags in the proof. Click on the 'Q' link to go to the location in the proof.

Location in article	Query / Remark: click on the Q link to go Please insert your reply or correction at the corresponding line in the proof
Q1	Please confirm that given names and surnames have been identified correctly.
Q2	Please note that reference 'Takeichi and Guo (2000)' is cited in text but not provided in the list. Kindly check.
Q3	Please note that 'Hatsuo and Tarek' in Ref. [27] does not match with list. Kindly check.
Q4	Please update Ref. [42].

Please check this box if you have no corrections to make to the PDF file ☐

Thank you for your assistance.

Reactive & Functional Polymers xxx (2012) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

Polybenzoxazine alloys and blends: Some unique properties and applications

Sarawut Rimdusit [a,*], Sunan Tiptipakorn [b], Chanchira Jubsilp [c], Tsutomu Takeichi [d]

[a] Polymer Engineering Laboratory, Department of Chemical Engineering, Chulalongkorn University, Patumwan, Bangkok 10330, Thailand
[b] Department of Chemistry, Faculty of Liberal Arts and Science, Kasetsart University, Kamphaeng Saen, Nakhon Pathom 73140, Thailand
[c] Department of Chemical Engineering, Srinakharinwirot University, Ongkharak, Nakhonnayok 26120, Thailand
[d] Department of Environmental and Life Sciences, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441-8580, Japan

ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Polybenzoxazine alloys and blends
High performance thermosetting
Synergy
Thermal properties

ABSTRACT

Polybenzoxazine (PBZ), a novel class of high performance thermosetting phenolic resin, has been developed in order to overcome many shortcomings of conventional phenolic materials from either novolac or resole type resins. The paper first provides the overview of this high temperature material including main types, chemical structure of each type, and properties of the polymer, especially the synergistic behavior in thermal properties. It then describes the manufacturing technique to produce the monomeric resin as well as some applications of the polymer.

1. Introduction

Phenolic resins have been well known as addition-cure thermosetting polymers widely used in various applications due to their several desirable properties such as good mechanical strength, electrical insulation, and dimensional stability, resistance against many types of solvents, flame retardation, and low smoke emission from burning. However, many shortcomings of these materials are from their brittleness, short shelf life, requirement of acid or base catalyst for the resin preparation, which potentially causes corrosion in the processing equipments. Furthermore, the by-products when curing of the resins are such as ammonium compounds, water, and so forth. These generated volatiles could have an effect on the properties of cured resins because of void formation in the final products. In order to overcome these problems, a novel class of high performance thermosetting phenolic resin, namely polybenzoxazine (PBZ), has been developed. The polybenzoxazines have been attracted great attention as versatile materials for structural and engineering applications because they possess good flame retardance, and thermal properties of phenolic resins including their high mechanical properties, with good sound and noise absorbance [1–8].

Typically, benzoxazine resins are synthesized from phenol (or substituted phenols), aldehyde (such as formaldehyde, acid aldehyde, or pyromucic aldehyde), and amine groups. Even though these resins were firstly produced by Holly and Cope [9], the capability of polybenzoxazine has become well known recently [10]. This novel kind of polymers can be synthesis via either solvent or solventless technology. In addition, the curing of the resins involves ring-opening polymerization with no need of any catalyst or curing agent and there is no by-product during curing, which leads to no void in the products. Interestingly, benzoxazine resins are also able to undergo hybrid network formation with various other resins or polymers, therefore rendering a novel class of resin systems with intriguing properties [11–17]. Additionally, polybenzoxazines have many reported outstanding characteristics such as high glass transition temperature (T_g), high thermal stability, fast mechanical property development, near-zero volumetric shrinkage or expansion upon cure, high processability due to low melt viscosity before polymerization, low water uptake, high char yield, and low coefficient of thermal expansion (CTE). Moreover, the polymers render low dielectric constant and dissipation loss, high mechanical performance and great molecular design flexibility [1,3,6,18–22]. Though, some researches about the synthesis and characteristics of benzoxazine resins and polybenzoxazines have been carried out, the reviews on their alloys and blends particularly on aspects of synergism in their thermal properties are still limited. Therefore, this review article is dedicated to the overviews of polybenzoxazine due to the high performance and great attraction of these novel materials, including the synergistic behaviors of the high temperature polybenzoxazine-based alloys or blends.

2. Structure of benzoxazine resins

2.1. Monofunctional benzoxazine resins

Holly and Cope [9] performed the two-step condensation reaction of primary amines, formaldehyde and substituted phenols in a solvent to yield the product of benzoxazine resins. Then several

* Corresponding author. Tel.: +66 2 2186862; fax: +66 2 2186877.
E-mail address: Sarawut.r@chula.ac.th (S. Rimdusit).

1381-5148/$ - see front matter © 2012 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.reactfunctpolym.2012.04.022

years later, Burke [23] reported that the benzoxazine ring reacts with the free *ortho* position of phenolic compound and the Mannich bridge (–CH_2–NR–CH_2–) forms. The appropriate steps to synthesize monofunctional benzoxazine resins are as follows: (i) adding amine to formaldehyde at low temperature to render the *N,N*-dihydroxymethylamine derivative, (ii) further reacting the obtained substance with the active hydrogen of the hydroxyl group at *ortho* position of the phenol at high temperature to generate oxazine ring as shown in Fig. 1 [24,25]. Liu and Ishida [10] reported that in the presence of some compounds with active hydrogen (HA), i.e. carbanzole, indoles, imides, naphthol, aliphatic nitro compound, and phenol, the ring opening of some monofunctional benzoxazine resins occurs, leading to the formation of Mannich bridge structure. And then, some oligomers occur as by-products in acidic medium (HA) as shown in Fig. 2.

The polymerization of monofunctional benzoxazine resins based on phenol leads to the formation of only oligomers with molecular weight of approximately 1000 Da. Therefore, this approach could not make any materials because the thermal dissociation of the resin competed with chain propagation reaction in order that high molecular weight structures could not be obtained; however, they might be useful as reactive diluent to facilitate the processing.

2.2. Bifunctional or multifunctional benzoxazine resins

Since 1990s, Ishida et al. [7,10,26] have developed a novel type of bifunctional or bifunctional benzoxazine resins. The initiating compounds for bifunctional or multifunctional benzoxazine resin were bisphenol-A, paraformaldehyde, and aniline. The structure of this resin abbreviated as BA-a is shown in Fig. 3. The major resulting products derived from bisphenol-A and aniline as the starting compounds were a resin comprising of bisphenol-A with functionalized oxazine ring structure at both ends. The minor products are composed of the mixture of dimers and oligomers. It was reported that the composition of the products depends on the solvent polarity. Generally, multifunctional phenolic or amine derivatives can also be used to synthesize multifunctional benzoxazine resins. Thus a wide difference in the performance of polybenzoxazine can be achieved as reported by Ning and Ishida [7] that only bifunctional or multifunctional benzoxazine resins can offer the crosslink structure that makes polybenzoxazines possess excellent mechanical properties and high glass transition temperatures. The chemical structures of other bifunctional benzoxazine resins based on various bisphenols are also presented in Fig. 4. Higher functionality benzoxazine resins can also provide high performance polybenzoxazines [27] but only the bifunctional benzoxazine resins are commercially available at present and their modification to broaden their properties will be discussed in the next section.

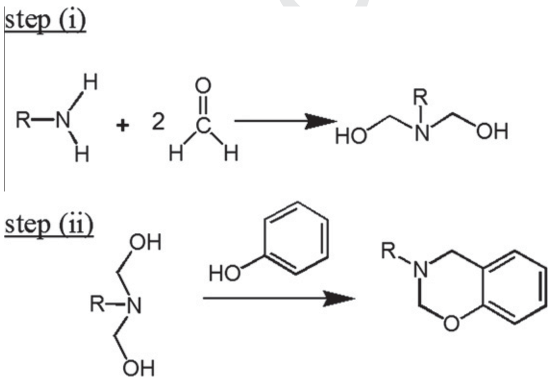


Fig. 1. Synthesis of monofunctional benzoxazine monomer.

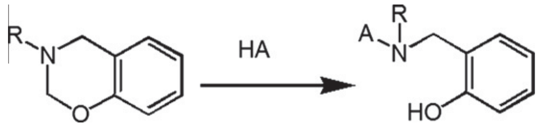


Fig. 2. Ring opening of benzoxazine resin in acidic compound.

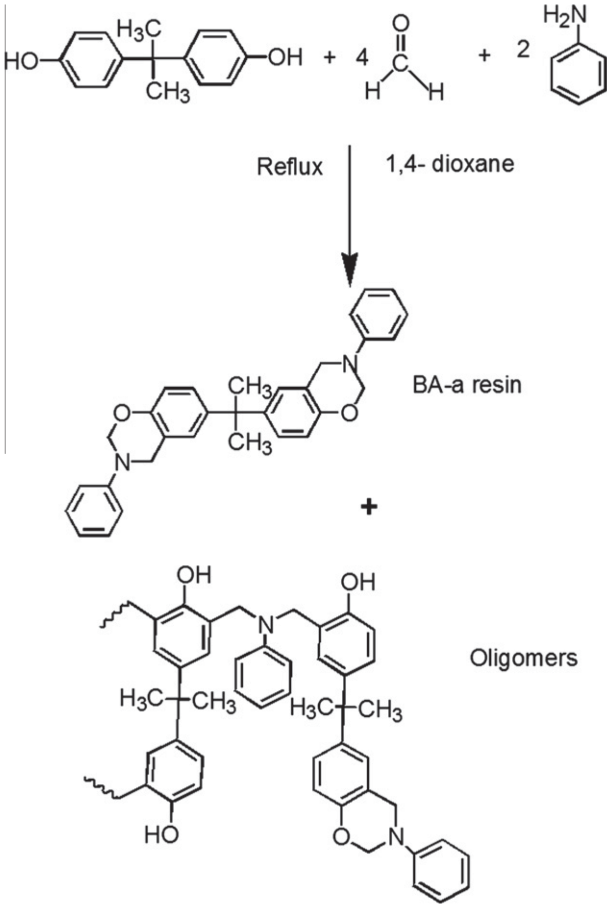


Fig. 3. Synthetic method to produce BA-a resin.

3. Bifunctional polybenzoxazines used for high temperature alloys and blends

Polybenzoxazine from bifunctional precursor show greatest interest for industrial applications of high performance thermoset polymers. The family of bifunctional polybenzoxazines can be categorized into two main types depending on the backbone structure of a crosslinked network. The first type is bisphenol-based bifunctional polybenzoxazine while another type of bifunctional polybenzoxazines is diamine-based bifunctional polybenzoxazines.

3.1. Bisphenol-based polybenzoxazines

For most of the published researches, polybenzoxazines have been mainly based on the phenolic compound, typically a bisphenol, which is able to provide multifunctionality to form an infinite network. If the benzoxazine resins were polymerized only at the *ortho* phenolic sites, a phenolic Mannich bridge network structure

Please cite this article in press as: S. Rimdusit et al., React. Funct. Polym. (2012), http://dx.doi.org/10.1016/j.reactfunctpolym.2012.04.022

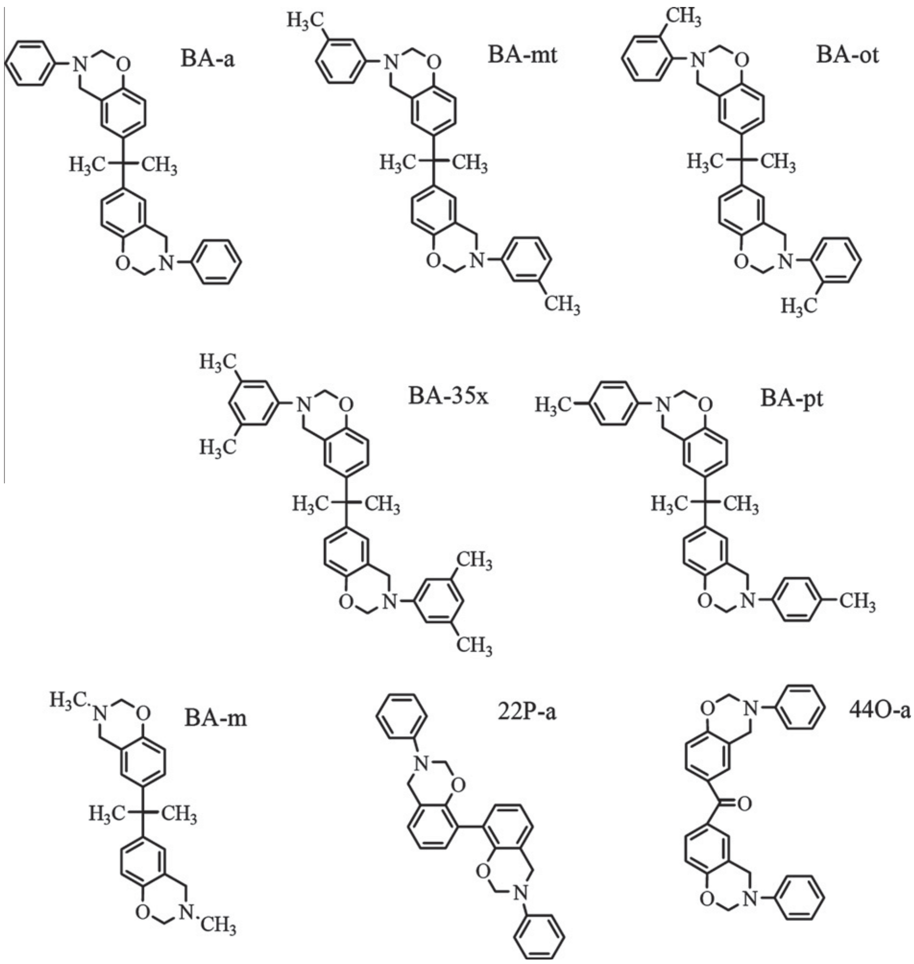


Fig. 4. Chemical structures of common bifunctional benzoxazine resins.

would develop. In comparison among all types of compounds, bisphenol-A is the most common chemicals often found in the backbone structure of polybenzoxazine and commonly used also in the backbone of polycarbonate and epoxy. The chemical structure of a bisphenol-A based polybenzoxazine as abbreviated poly(-BA-a) is shown in Fig. 5a. The poly(BA-a) displays high thermal properties, i.e. high glass transition temperature (T_g) and degradation temperature (T_d). By molecular design of phenol and amine, the T_g of bifunctional polybenzoxazines can range from subzero temperature to nearly 400 °C, and the char yield at 800 °C up to around 80% under nitrogen atmosphere [14,15,27]. However, It could be noticed that due to the aromatic ring in backbone structure of bisphenol-A-based polybenzoxazine the rigidity properties of the polymer would be expected [28].

3.2. Diamine-based polybenzoxazines

This type of bifunctional polybenzoxazines includes an amine portion in the backbone structure instead of bisphenol which lead to elimination of phenolic linkage and displays much more flexible than the bisphenol-based polybenzoxazine. The chemical structure of linear aliphatic diamine linkage is presented in Fig. 5b. From the study of Allen and Ishida [28], this kind of polybenzoxazine possesses less brittleness than typical bisphenol-based polybenzoxazine, which incorporates with a flexible bifunctional amine in centered portion. It was reported that the density of the polybenzoxazine synthesized from phenol and linear aliphatic diamine abbreviated as P-ad is systematically decreased with the length of linear aliphatic diamine chain from 1.22 g/cm^3 for P-ad2 ($n = 2$) to 1.08 g/cm^3 for P-ad12 ($n = 12$), while those of bisphenol-based polybenzoxazine ranges from 1.08 g/cm^3 for the polybenzoxazine based on bisphenol-A and n-butyl amine (BA-b) to 1.26 g/cm^3 for the polybenzoxazine based on bisphenol-A and 3,5 xylidene (BA-35x). Furthermore for the linear aliphatic diamine based polybenzoxazine, the storage modulus at room temperature was systematically decreased from 2.1 GPa for P-ad2 ($n = 2$) to 0.9 GPa for P-ad12 ($n = 12$). Interestingly, the glass transition temperature (T_g) of the short-chain diamine based polybenzoxazine (P-ad2) is ca. 184 °C, which is higher than that of bisphenol-A based polybenzoxazine, i.e. T_g of BA-*a* = 170 °C). However, the T_g was expectedly decreased when increasing the length of diamines, e.g. 169 °C for P-ad6, and 118 °C for for P-ad12. In aspects of the crosslink density of the linear diamine-based polybenzoxazine, the value was decreased with an increase of the chain length. The crosslink densities were ranged from 7.1×10^{-3} mol/cm^3 for P-ad6 to 5.4×10^{-3} mol/cm^3 for P-ad12. However, these values are still higher than 1.1×10^{-3} mol/cm^3 of bisphenol-A and aniline-based polybenzoxazine (poly(BA-a)) [26].

In addition to the linear aliphatic diamine-based polybenzoxazine, another type is aromatic diamine-based polybenzoxazines which have been reported in the literatures [29–31]. The aromatic diamine-based polybenzoxazine can provide higher glass transition temperature and thermal stability than the conventional bisphenol-A-based polybenzoxazine. Moreover, this kind of benzoxazine resin can be polymerized in the same manner as the bisphenol-based polybenzoxazine.

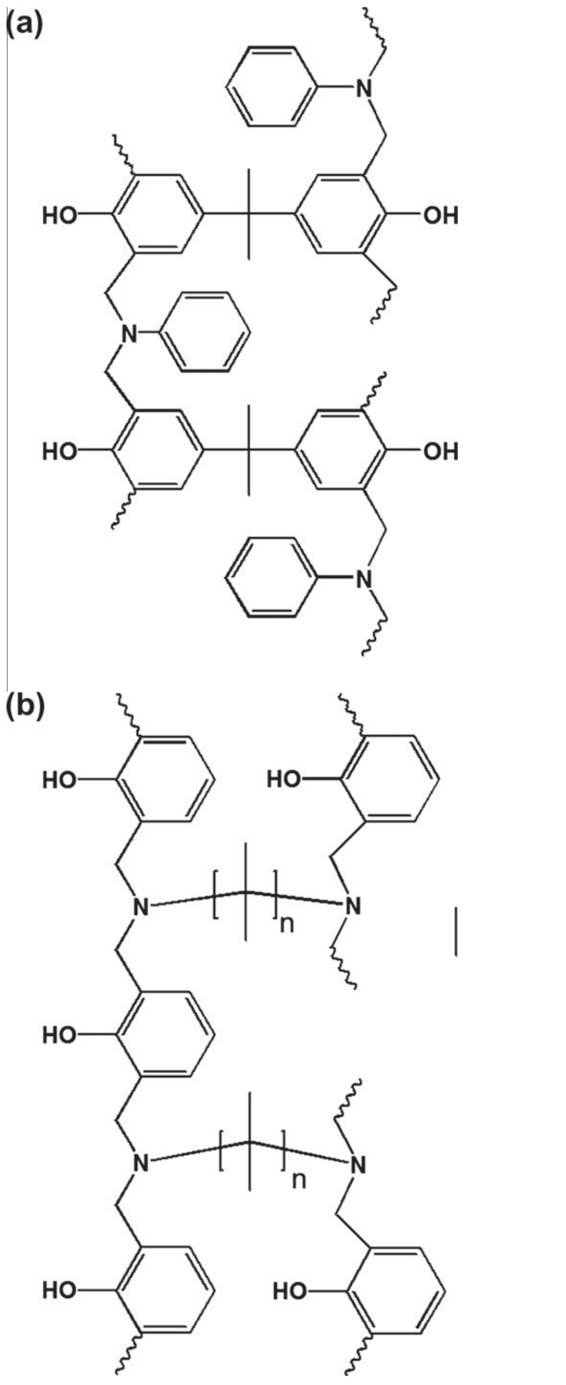


Fig. 5. Network structure in comparison between (a) bisphenol A-based polybenzoxazine, (b) linear aliphatic diamine-based polybenzoxazine.

4. Alloys and blends of polybenzoxazines

4.1. Major properties of polybenzoxazine homopolymers

Polybenzoxazine (PBZ) homopolymers possesses various interesting properties, that combine outstanding thermal properties and flame retardance of phenolic resins with excellent mechanical performance and molecular design flexibility of advanced epoxy resins [32]; the physical and mechanical characteristics of PBZ are presented in Table 1. In order to compare with epoxy phenolics and cyanate ester. It could be noticed that the PBZ provides many distinguish features, e.g. near-zero shrinkage and expansion upon curing, low water uptake, much higher glass transition temperature than curing temperature, high char yield, low viscosity. From the table, it is obviously noticed that the shrinkage of the PBZ is closed to zero. It could be attributed to the consequence of molecular packing affected by intermolecular and intramolecular hydrogen bonding [1]. Furthermore, the glass transition temperature of PBZ is in the range of 170–340 °C, which depends on the structure of PBZ. The degradation onset temperature of 4,4′-dihydroxy benzophenone and aniline based PBZ is as high as approximately 400 °C, which is due to highly strong intramolecular hydrogen bonding between phenolic hydroxide group and the Mannich bridge. In addition, some physical and thermal properties of commonly used benzoxazine resins are presented in Table 2.

4.2. Properties of polybenzoxazine alloys and blends: synergy in thermal properties

4.2.1. Benzoxazine–epoxy copolymers

Although PBZ homopolymers render high glass transition temperature and modulus, it is found that the crosslink density of PBZ is rather lower than that of other thermosetting polymers with the same properties. The reason is proposed that hydrogen-bonding of the homopolymers could be sufficient to hinder the chain mobility and induce the rigidity observed in the glassy state [19]. Ishida and Allen [20] studied the copolymer system between PBZ and diglycidyl ether of bisphenol-A (DGEBA), the most commonly used commercial epoxy resin. The results revealed that the presence of epoxy resin in the copolymer could lead to higher crosslink network and glass transition temperature (T_g) than the parent polymers as similarly reported by Rimdusit et al. [33,34]. The authors proposed that the reaction between benzoxazine and epoxy were expected to comprise of a least two reactions; the first reaction is the curing among the benzoxazine monomers, whereas the second one is likely to be the reaction between the epoxide group on the epoxy with the phenolic hydroxyl group on the polybenzoxazine. The reaction between the epoxide groups with phenolic hydroxyl group on polybenzoxazine was expected to proceed after phenolic hydroxyl group from the ring-opening of the benzoxazine monomer was produced [8,17,34]; the sequence of the reaction is presented in Fig. 6.

In addition, from dynamic mechanical analysis (DMA) results, the synergistic behavior of T_g is presented as shown in Fig. 7. However, it could be noticed that the copolymer at beyond 45 wt% of epoxy content exhibits the significant decrease in T_g with the system containing equal amount of both two components. This behavior is due to the fact that the stoichiometric ratio of components was approached. The unreacted or small molecular weight epoxy molecules might remain in the network formed and might interfere with network formation or acted as a plasticizer in the fully cured network as discussed by Rimdusit et al. [34].

4.2.2. Benzoxazine/epoxy/phenolic ternary system

Rimdusit and Ishida [35] developed the ternary system of bisphenol-A-aniline based benzoxazine, epoxy, and phenolic resins and revealed that the properties of the mixtures depend on the mass ratios of the starting materials. Interestingly, the synergistic behavior of glass transition temperature (T_g) was observed in these ternary mixtures with great variety of resin properties, particularly their processing ability and mechanical characteristics. The relationships between the epoxy content and T_g of the mixture with six blending mass ratios of biphenol-A-aniline based benzoxazine/epoxy/phenolic resin (3/6/1; 4/5/1; 5/4/1; 6/3/1, 7/2/1, and 8/1/1) from differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) are exhibited in Fig. 8. It could be noticed that the highest T_g observed from DMA is 180 °C, when the mass ratio of bisphenol-A-aniline based benzoxazine/epoxy/phe-

Table 1
Comparison of the properties of PBZ with other high temperature polymers.

Characteristic	Epoxy	Phenolics	Cyanate ester	Typical PBZ
Density (g/cm^3)	1.20–1.25	1.24–1.32	1.10–1.35	1.19
Maximum use temperature (°C)	180	200	150–200	130–280
Tensile strength (MPa)	90–120	24–45	70–130	100–125
Tensile modulus (GPa)	3.1–3.8	03/05	3.1–3.4	3.8–4.5
Elongation (%)	3.0–4.3	0.3	02/04	2.3–2.9
Curing temperature (°C)	RT to 180	150–190	180–250	160–220
Curing shrinkage (%)	>3	0.002	ca. 3	ca. 0
TGA onset temperature (°C)	260–340	300–360	400–420	380–400
Glass transition temperature (°C)	150–220	170	250–270	170–340

Table 2
Properties of commonly used polybenzoxazines.

Properties	BA-a [32]	BA-m [32]	BA-mt [26,34]	BA-35x [18,26]
Density of polymer (g/cm^3)	1.195	1.122	–	–
Flexural modulus (GPa)	4.5	3.8	5.4	4.7
Flexural strength (MPa)	126	103	129	112
Strain at break (%)	2.9	2.6	2.5	2.8
Glass transition temperature (°C)	150[a], 170[b]	180	209	238
Temperature at 5% weight loss (°C)	310	264	350	350
Char yield (%)	32	34	31	28

[a] Synthesis via a solventless method.
[b] Synthesis in 1,4-dioxane.

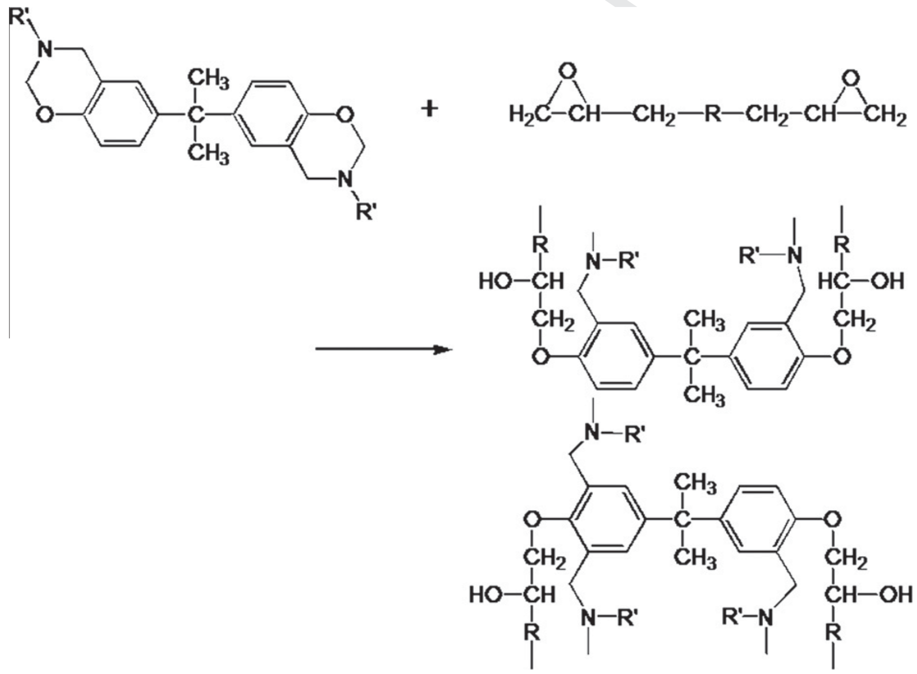


Fig. 6. Proposed reaction between benzoxazine resin and epoxy.

nolic resin is 5/4/1 [20,35,36]. The authors concluded that epoxy not only acted as a reactive diluent in the bisphenol-A-aniline based benzoxazine/epoxy/phenolic resin systems but also contributed to higher crosslinked density and flexibility compared with the neat polybenzoxazine based on bisphenol-A and aniline. In addition, the researchers reported that the addition of small amount of phenolic resin in the ternary system could enhance the crosslink density, and hence the T_g of the benzoxazine and epoxy copolymer. The phenolic resin in the range of 6–10 wt% was required to obtain the ultimate T_g. Furthermore, it was proposed that the T_g synergism was contributed to the rigidity from benzoxazine molecules and the enhanced crosslink density from epoxy. Moreover, the addition of small amount of phenolic resin into the bisphenol-A-aniline based benzoxazine/epoxy resin systems resulted in a mixture to be cured at lower temperature when compared with curing reaction of the bisphenol-A-aniline based benzoxazine/epoxy systems.

4.2.3. Poly(benzoxazine-urethane) alloys

The poly(benzoxazine-urethane) alloys were synthesized from urethane prepolymer and monofunctional or bifunctional benzoxazine resins. For example, the synthesis of the alloy using 3,4-dihydro-3.6-dimethyl-2H-1,3-benzoxazine (Cm as monofunctional benzoxazine resins synthesized from *p*-cresol, formaldehyde, and

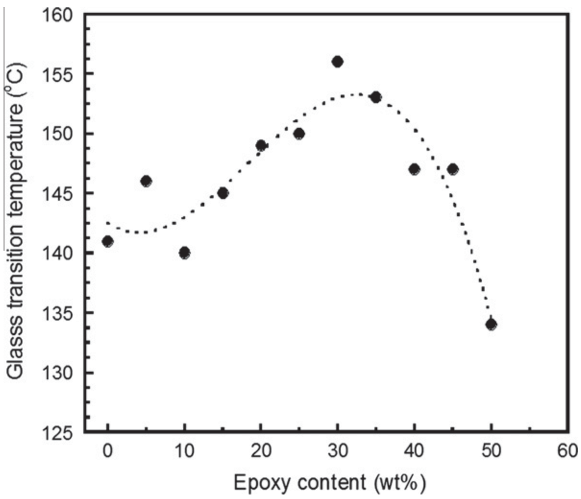


Fig. 7. Synergistic behavior of glass transition temperature in the systems benzoxazine resin and epoxy.

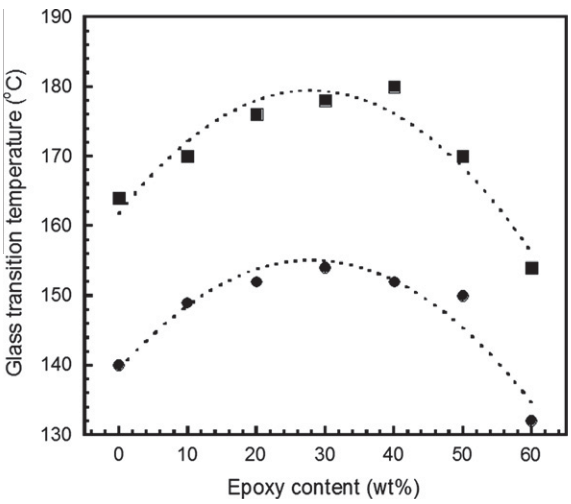


Fig. 8. Relationships between the epoxy content and glass transition temperature in the ternary system (■) DMA values, (●) DSC values.

methylamine) and urethane prepolymer (derived from polyethyleneadipate polyol with a molecular weight of 1000 and 2,4-tolylene diisocyanate at molar ratio of 1:2) are shown in Fig. 9 (Takeichi and Guo, 2000). It was reported that the ring-opening of benzoxazine monomer providing phenolic hydroxyl groups could react with isocyanate group (NCO) in urethane prepolymer during polymerization and the allophanate formation via the intermolecular reaction of the urethane prepolymer (PU). The cured PU/BA-a films were transparent, suggesting good compatibility between the PU and BA-a components. All of PU/BA-a films have only one T_g from their viscoelastic properties, indicating no phase separation in poly(benzoxazine-urethane) alloys due to the *in situ* polymerization. Moreover, the authors has also reported thermal stability of bifunctional benzoxazine resin (BA-a derived from bisphenol-A, formaldehyde, and aniline) alloyed with urethane prepolymer that initial decomposition temperatures at 5% weight loss of PU/BA-a films are higher than that of the PU itself and increasing the BA-a content led to a higher decomposition temperature, and that even a small amount of BA-a is effective to enhance thermal stability of PUs. Thus, incorporating polybenzoxazine into PU can open an effective way to an improvement on the thermal stability of PU.

Rimdusit et al. [12] studied the alloy between bifunctional benzoxazine resin based on bisphenol-A and aniline (BA-a) and urethane prepolymer (PU prepared from isophorone diisocyanate (IPDI) and polyether polyol with molecular weight of 2000 at the molar ratio of 2:1), the enhancement of the T_g of the alloys was observed. The T_g of the alloys are noticeably higher than those of the parent resins, e.g., the alloy at 30 wt% of PU renders the T_g of approximately 220 °C, while those of pure PU and neat poly(BA-a) are reported to be about −70 °C and 165 °C, respectively. In addition, effects of polyol molecular weight e.g. 1000, 2000, 3000 and 5000 on properties of benzoxazine-urethane polymer alloys have been investigated [37]. They reported that T_g increase from 160 °C of poly(BA-a) to 240 °C in BA-a:PU at mass ratio equal to 70:30 as shown in DSC thermograms of the poly(benzoxazine-urethane) alloys at various PU contents presented in Fig. 10. Furthermore, the polyol molecular weight shows no effect on the T_g of the BA-a:PU alloys. The synergistic behavior in T_g of polybenzoxazine has been reported in various alloy systems as the polymer itself possesses relatively low crosslink density comparing with e.g. epoxy of the same type of bisphenol as a starting material. The research in model benzoxazine dimer and trimer structures has indicated that intermolecular and intramolecular hydrogen bonding is prevalent in this polymer. It is likely that hydrogen bonds in this resin impede the network formation to achieve high crosslink density e.g. by formation of microgel or heterogeneous network. The apparent crosslink density obtained is thus relatively low [19]. The addition of second polymer to form polybenzoxazine alloy was often found to enhance crosslink density of the polybenzoxazine thus its T_g and crosslink density value of poly(BA-a) alloyed with PU elastomer (synthesized from polypropylene glycol polyol at a molecular weight of 2000 with toluene diisocyanate (TDI) was displayed in Fig. 11 and also described in our recent work [33]. Moreover, it was reported that one glass transition temperature is observed for the alloy synthesized from urethane prepolymer and either monofunctional or bifunctional benzoxazine

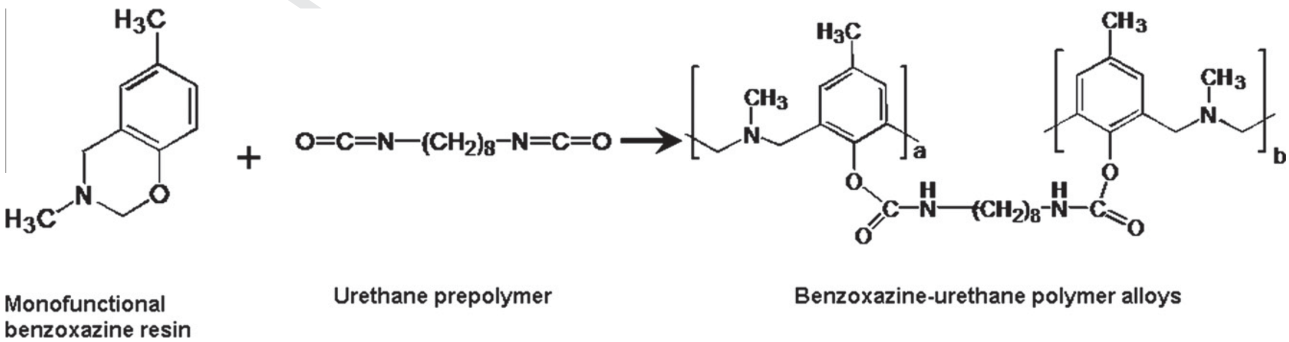


Fig. 9. Synthesis reactions of Ca benzoxazine resin and urethane prepolymer.

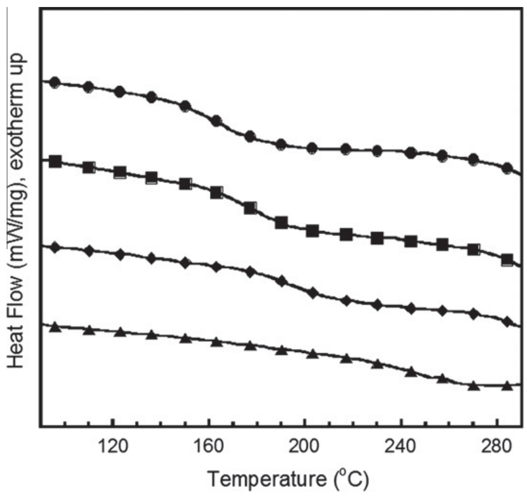


Fig. 10. DSC thermograms of the fully cured poly (benzoxazine-urethane) alloys at various compositions: (●) 100:0, (■) 90:10, (♦) 80:20, (▲) 70:30.

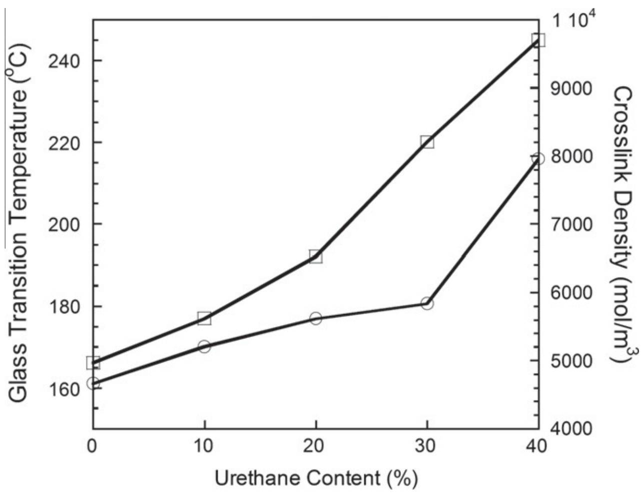


Fig. 11. Effect of urethane content on glass transition temperature and crosslink density of polybenzoxazine: (□) glass transition temperature, (○) crosslink density.

resins. That exhibits high miscibility between the starting polymeric components because of the copolymer reaction [12,38,35].

4.2.4. Polybenzoxazine/polyimide blends

Takeichi et al. [16] prepared polymeric blends using a bifunctional benzoxazine resin, 6,6′-(1-methylethylidene)bis(3,4-dihydro-3-2H-1,3-benzoxazine) (BA-a) and a soluble polyimide (PI) or polyamic acid (PAA, an intermediate compound to synthesize polyimide) derived from bisphenol A di(phthalic anhydride) ether (BPADA) and oxydianiline (ODA). The results revealed that only one glass transition temperature (T_g) from both loss modulus (E'') and loss tangent (tan δ) was observed in both poly(BA-a)/PI and poly(BA-a)/PAA alloy systems, indicating full miscibility in the blends. The T_gs shift to higher temperature with imide content incased and the T_gs of the polymer alloys from poly(BA-a):PAA was slightly higher than that of poly(BA-a):PI in the same ratio e.g. T_g = 205 °C for poly(BA-a):PI = 30:70 wt% and T_g > 215 °C for poly(BA-a):PAA = 30:70 wt% . This is also another evidence indicating the formation of AB cross-linked structure in the case of poly(BA-a):PAA.

In addition, the thermal stability of both poly(BA-a)/PI and poly(BA-a)/PAA alloy systems were significantly increased with imide content. The synergism of char yield was observed as presented in Fig. 12. It was reported that an interpenetrating polymer network (IPN) structure was formed in the systems, the imidization of PAA occurred *in situ* with the polymerization of BA-a, leading to aromatic ester formation (AR-COOR) that might form between carboxylic acid of PAA and phenolic hydroxyl group of polybenzoxazine as shown in Fig. 13. And it was suggested that the polymer alloys from the combination of poly(BA-a) and PAA contain crosslinked structure, which is different from those of poly(BA-a):PI that is supposed to be pure semi-IPN structures.

4.2.5. Polybenzoxazine-dianhydride copolymer

As previously reported by Takeichi et al. [16], the authors found that the phenolic OH of poly(BA-a) can react with the carboxylic acid of poly(amide) to form aromatic ester (Ar-COOR). Therefore, ester linkage formation was expected in poly(BA-a) modified with dianhydride, i.e. 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) which is a chemical used as co-monomer for high tensile strength polyimide fibers, films and foams to provide excellent mechanical and electrical performances as well as outstanding heat insulation and fire retardant properties of the materials. Recently, the copolymers prepared from bisphenol-A-aniline type benzoxazine resin (BA-a) and BTDA dissolved in 1-methyl-2-pyrrolidone (NMP) were discussed by Rimdusit and Jubsilp [39] and Jubsilp et al. [40]. FTIR results of their works revealed that the chemical bonding between hydroxyl groups of poly(BA-a) and anhydride groups of dianhydride which could occur to form ester linkages evidenced by the observed peak in the spectrum at 1730 cm^{-1} as a result described in benzoxazine containing polyester by Tuzun et al. [41].

From ester linkage formation, structurally flexible functional group, the bending of poly(BA-a), which is rigidity thermosetting polymer in nature, can be significantly improved by an addition of dianhydride. Interestingly, The transparent cured BTDA-modified poly(BA-a) copolymer films suggested the good compatibility between BTDA and BA-a components. The appearance of a single T_g in viscoelastic measurements indicated that no phase separation in the cured copolymer films and the synergism in glass transition temperature (T_g) of BTDA-modified poly(BA-a) copolymer was reported as high as 263 °C at the BA-a:BTDA weight ratio of 60:40 (1.5:1 mol ratio). This T_g value was remarkably higher than that of the unmodified poly(BA-a), i.e. 173 °C as seen in Fig. 14. The enhancement of poly(BA-a)'s T_g is due to increasing of crosslink density presented by dynamic mechanical analysis (DMA)

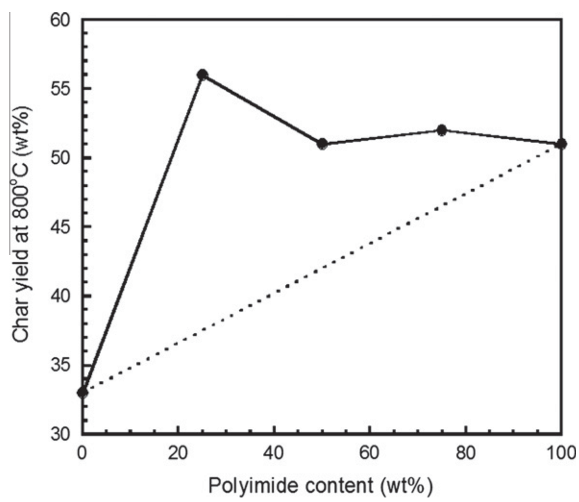


Fig. 12. Synergism of char yield in the system of polybenzoxazine/polyimide blends.

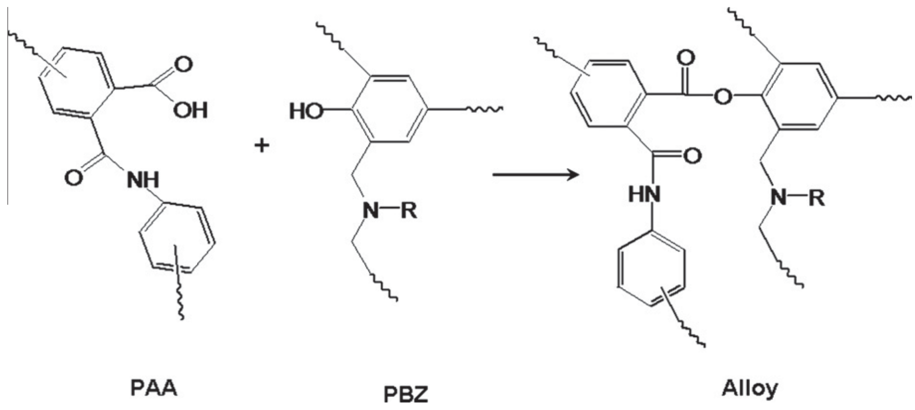


Fig. 13. Proposed reaction between PBZ and PAA.

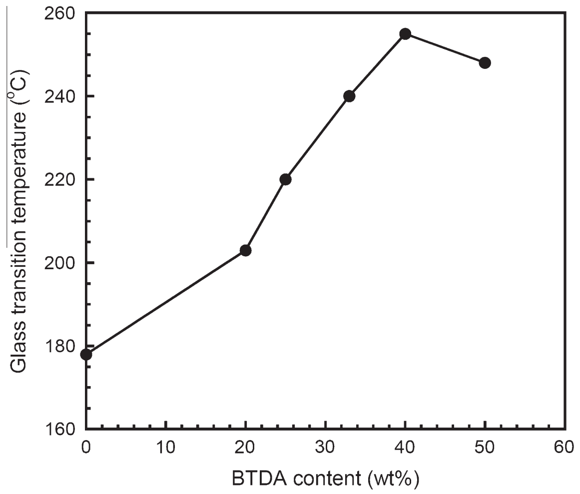


Fig. 14. Glass transition temperature of the polybenzoxazine-dianhydride copolymer at various BA-a:BTDA molar ratios.

experiment of the obtained copolymers. In addition, the degradation temperatures of the copolymers were significant higher than those of the parent compound as presented in Fig. 15. Moreover, the char yield of the copolymer was as high as 61% which was substantially higher than pure poly(BA-a). Therefore, the obtained copolymer provided high mechanical properties with fire retardance properties.

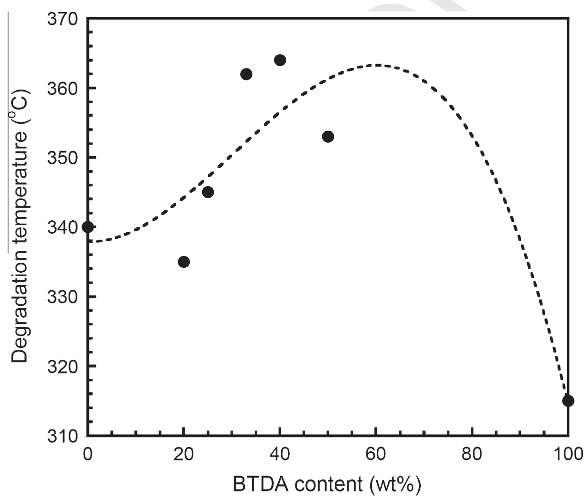


Fig. 15. Degradation temperature of the polybenzoxazine-dianhydride copolymer at various BA-a:BTDA molar ratios.

Recently, effect of aromatic tetracarboxylic dianhydrides, i.e. pyromellitic dianhydride (PMDA), 3,3′,4,4′ biphenyltetracarboxylic dianhydride (s-BPDA), or 3,3′,4,4′ benzophenonetetracarboxylic dianhydride (BTDA) on thermomechanical properties of poly(BA-a)-dianhydride copolymers were also investigated [42]. The authors have suggested that the obtained copolymers can be considered as potential candidates for high temperature materials with enhanced mechanical integrity. T_g of the copolymers was found to be in the order of poly(BA-a):PMDA > poly(BA-a):s-BPDA > poly(BA-a):BTDA. The difference in the T_g of the copolymers is connected to rigidity of the dianhydride components. Additionally, the degradation temperature at 10% weight loss (T_{d10}) of the neat poly(PBA-a) was 361 °C while the T_{d10} of the copolymers increased in the order of poly(PBA-a):PMDA (426 °C) > poly(PBA-a):s-BPDA (422 °C) > poly(PBA-a):BTDA (410 °C). In other words, the order of thermal stability like degradation temperature with respect to aromatic skeleton of acid dianhydride component is phenylene unit > biphenyl unit > benzophenone unit [40]. Furthermore, the degradation temperature (T_d) value of the neat poly(BA-a) film was observed to significantly increase with an incorporation of aromatic tetracarboxylic dianhydrides which lead to additional crosslinking sites via ester linkage between the anhydride group in the aromatic carboxylic dianhydride and hydroxyl group of the neat poly(PBA-a) thus clearly contributed this T_d enhancement.

4.2.6. Polybenzoxazine/poly(imide-siloxane) alloys

Ardhyanant et al. [43] have reported enhancement of thermal stability, mechanical property, flame resistance, and flexibility of bisphenol-A-aniline based polybenzoxazine (poly(BA-a)) by adding polydimethylsiloxane (PDMS) since polydimethylsiloxane (PDMS) is one of the most important silicones that have inorganic main chain, which shows not only flexibility but also unique properties such as good oxidative stability, low surface energy, high hydrophobicity, high gas permeability, and good biocompatibility [44]. The obtained poly(BA-a):PDMS alloy films at 7 wt% and 13 wt% of PDMS showed higher thermal stability, i.e. T_{d10} = 352 °C and 368 °C, respectively, than that of neat poly(BA-a), e.g. T_{d10} = 326 °C while T_g of the hybrid at the same content of PDMS determined from the maxima of E'' revealed two T_gs, lower T_g (63–72 °C) and higher T_g (176–185 °C) corresponding to the PDMS and poly(BA-a) components, respectively, suggesting that phase separation at micrometer-scale occurred in the alloy. Moreover, the weight residue at 850 °C of hybrids increased with the increase of the PDMS content (40–46%), indicating that the flame retardancy is also improved. They additionally reported that the obtained alloy film render higher tensile strength and elongation at break than neat poly(BA-a) because of the toughening effect of PDMS. Recently, the effect of pendant groups of polysiloxanes, e.g. PDMS, PMPS, and PDPS on thermal property have been investigated by Ardhyanant et al. [44]. The phenyl group of polysiloxanes as PMPS and PDPS enhanced their compatibility with poly(BA-a). The alloying could improve T_g due to the high crosslinking density of the poly(BA-a) by the plasticizing effect of the polysiloxanes that aid the polymerization of the poly(BA-a). Furthermore, The po(BA-a):PDMS alloy displayed the optimum enhancement of the degradation temperature, while the incorporation of PDPS into poly(-BA-a) was the most effective for the flame retardancy. Therefore, the thermal properties of the alloys can be controlled by various types of polysiloxanes.

To improve the phase separation of an alloy between poly(BA-a) and polysiloxanes, the poly(BA-a) alloyed with PDMS-containing polyimide as poly(imide-siloxane) with hydroxyl functionality (PI-Si(OH)) were studied [45]. They have confirmed that only one T_g was observed at ca. 300 °C caused by an AB-co-cross-linked polymer network is considered to be formed. Interestingly, in poly(-BA-a) alloyed with poly(imide-siloxane) without hydroxyl functionality (PISi), The synergistic behavior in char yield was reported at some content of PISi as shown in Fig. 16 [46]. This phenomenon could be related to a large amount of aromatic ring in the blends with some chemical bonding between polybenzoxazine and PISi.

4.2.7. Polybenzoxazine/poly(-caprolactone) blends

As previously reported that polybenzoxazine tend to be brittle, which is common for phenolic materials, and this feature limits their applications. Therefore, the flexural and impact properties of these resins are expected to improve upon the incorporation of a component having a low glass transition temperature (T_g). Therefore, Huang and Yang [47] investigated the thermal behaviors and dynamic mechanical properties of the blends between bisphenol-A-methylamine based benzoxazine resin (BA-m) and poly(ε-caprolactone) (PCL) via solution blending method. They reported that the synergistic behavior of glass transition temperature (T_g) was found in low content of PCL ca. 10–40 wt%. As presented in Fig. 17, the T_g value from DSC thermograms of the blends is as high as ca. 206 °C, while those of poly(BA-m) and PCL are ca. 170 °C and -60 °C, respectively. This is due to the fact that in presence of PCL, higher polymerization conversion occurred, as shown by the Fourier transform infrared spectroscopy (FTIR) results. The FTIR spectra revealed intermolecular hydrogen bonding between the hydroxyl groups of PBZ and the carbonyl groups of PCL during polymerization, affecting the enhancement of T_g and misibility of PCL and poly(BA-m). This finding implies that the introduction of poly(ε-caprolactone) unit into polybenzoxazine can improve the properties of the polybenzoxazine at high temperature. Moreover, an improvement of the flexural properites of polybenzoxazine blended with poly(ε-caprolactone) was also reported by Ishida and Lee [48]. Phase separation of the blends was also discussed [49].

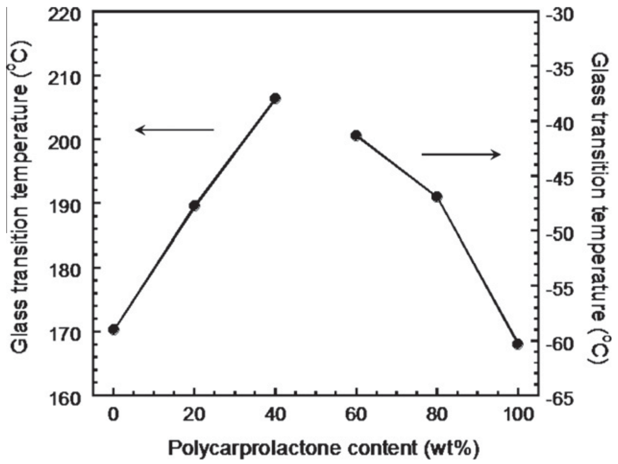


Fig. 17. Glass transition temperatures of poly(BA-m)/PCL systems at various content of PCL.

4.2.8. Polybenzoxazine/poly(N-vinyl-2-pyrrolidone) alloy

Su et al. [50] prepared the alloys between bishphenol-A-aniline type of polybenzoxazine (poly(BA-a)) and poly(N-vinyl-2-pyrrolidone) (PVP); the thermal properties and hydrogen bonding of the alloys were determined. The results revealed only one glass transition temperature (T_g) for all PVP contents, indicating complete miscibility in the alloy systems. The synergism of T_g was reported as shown in Fig. 18. The highest value of the T_g could be found at the weight ratio of 50:50. Furthermore, the research reveals that the hydrogen bonding in polybenzoxazine/poly(N-vinyl-2-pyrrolidone) alloy due to great interaction between the carbonyl group of PVP and hydroxyl group of polybenzoxazine, which is sufficient to induce rigidity and hinder the molecular mobility in the alloys, causing the T_g synergism.

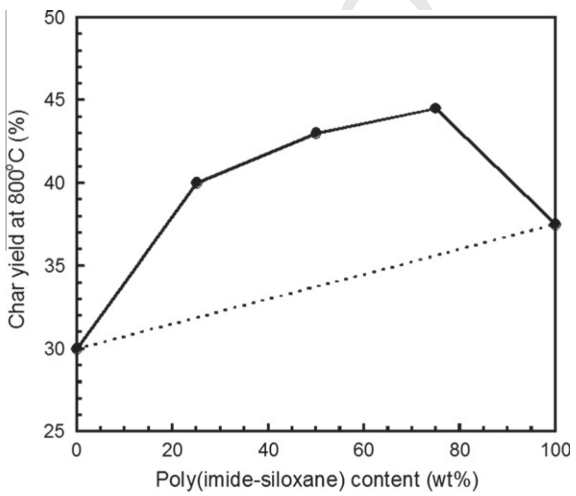


Fig. 16. Char yield of the polybenzoxazine/poly(imide-siloxane) alloys.

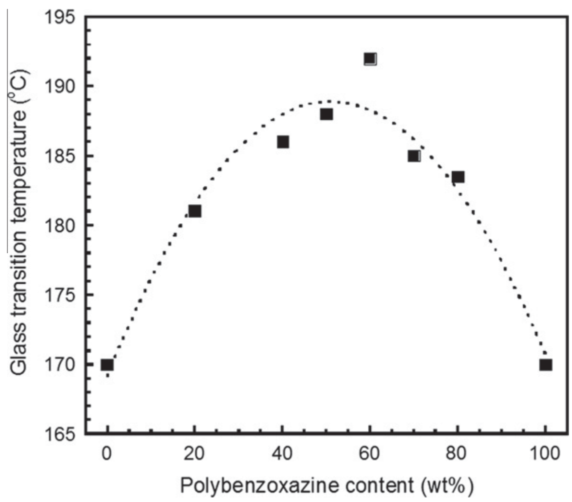


Fig. 18. Synergism of glass transition temperature in the alloy system between polybenzoxazine and poly(N-vinyl-2-pyrrolidone).

Please cite this article in press as: S. Rimdusit et al., React. Funct. Polym. (2012), http://dx.doi.org/10.1016/j.reactfunctpolym.2012.04.022

5. Manufacturing techniques and technologies

The manufacturing techniques for polybenzoxazine can be classified into two types, i.e. via solvent and solventless technologies. Typically, the benzoxazine monomeric resin can be synthesized by the dissolution of the initiating components (which are the phenolic derivative, aldehyde, and a primary amine) with the proper solvents such as dioxan, toluene, alcohol, and the compounds with similar chemical structure. The obtained product is then isolated from the solvent by the evaporation process or by the precipitation process of the obtained product to separate from the solvent via the addition of a proper non-solvent to the reaction mixture. As an example, the synthesis of 3,4-dihydro-1,3 benzoxazine resin can be carried out [51] in the suitable solvent such as dioxan, low aliphatic alcohol, water miscible alcohol (i.e. methyl alcohol, ethyl alcohol) for the reaction of the starting materials (para-formaldehyde, substituted phenols, and aliphatic amines). After the reaction, the isolation process has been performed to obtain the desired resin. As exhibited in the US patent numbers 5152939 [52] and 5266695 [53], the composites could be fabricated from the benzoxazine resin synthesized via solvent method.

Another technique is the solventless technology to synthesis benzoxazine compound, which was disclosed in US patent number 5543516. This method provides a clean resin without the need of solvent elimination or resin purification [6]. Furthermore, many beneficial aspects superior to the solvent method are regarded to the toxicity risk from solvent, and the cost for solvent elimination. Moreover, the solventless technique can be carried out with single step of synthesis process less consumption time and fewer byproducts. The comparison between the consumption time, the yield of the monomeric product, and the synthesis temperature were shown in Table 3. It could be noticed that the yield of the product and the operating temperature are similar for both method; however, the consumption for synthesis via solventless technique is significantly shorter than that via solvent technique. As example, the method of solventless reaction may be carried out by mixing all reactants (aldehyde, primary amine, and phenolic compound) which are in solid or liquid state, heating all components to their melting temperature, and keeping the temperature to obtain the desired product without the need of catalyst [6].

6. Future trends

6.1. Potential applications of polybenzoxazines alloys and blends

Polybenzoxazines have been developed for wide applications in many areas such as for fabricating molded and casted stuffs, as bonding particles, for ion exchange applications, for lamination and impregnation process, in manufacturing composites as well as electrical components, etc. due to its excellent ability to be alloyed with various existing resins or polymers as described in Section 4 thus further broaden the spectrum of its properties [6,54,55]. In addition, the benzoxazine resins are now commercially produced as the component in prepreg composites due to their excellent toughness and stability at high temperature, drastically low shrinkage improving equipment surface quality, and significantly long out-life. Moreover, liquid form of benzoxazine resins can be used in the process of vacuum assisted resin transfer molding (VARTM) and resin transfer molding (RTM) due to their good properties such as wide processing window, easiness to process in VARTM and RTM, long room temperature storage time, high modulus of resin, low shrinkage during cure. Another application of this resin is as film adhesive for composite bonding and high temperature composites. Furthermore, benzoxazine resins are a candidate to substitute phenolic resins due to toxicity before and upon cure as well as great fire retardant properties, high glass transition temperature, high mechanical properties, low moisture uptake. Therefore, the familiar uses of the polybenzoxazine are such as the prepreg for aircraft interior parts which must satisfy the stringent fire, smoke, and toxicity (FST) regulations. Recently benzoxazine resins have been developed and successfully introduced for the applications in the halogen free printed circuit board (PCB) industry because of their many intriguing properties as previously mentioned [56].

6.2. Commercialized polybenzoxazines

Nowadays, polybenzoxazine have been commercialized by many manufacturers. For instance, Huntsman Corporation produces the monomeric resins under the trademarks of Araldite® which is suitable for the civil engineering, oil exploration, aerospace, and electronics applications. Up till now, five types of benzoxazine resin of this company have been commercialized; the chemical structures of the Araldite® benzoxazine resins are shown in Table 4. Additionally, the recent invention of this company related to a halogen-free curable composition (which mainly composed of benzoxazine resin, and at least one epoxy resin in a solvent) has been commercialized; this new generation thermosetting materials possesses very high glass transition temperature and controlled reactivities. Furthermore, Gurit Group (2010) has developed the modified benzoxazine resin served as prepreg for aircraft interior parts. The prepreg could be curing without volatile at 140 °C (45 min) and 160 °C (15 min). In addition, Henkel Corporation has launched the resin under the tradename of Epsilon™, which is served as prepreg matrix resin, liquid resins for VARTM or RTM process, and film adhesives. Additionally, benzoxazine resins are manufactured by some companies such as Materials Americas Inc., Georgia Pacific Resins Inc. and Shikoku Chemical Corporation.

7. Sources of further information

7.1. Monographs and handbooks on polybenzoxazines

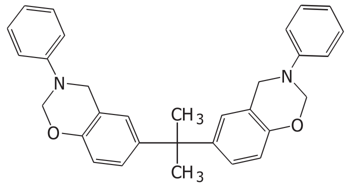
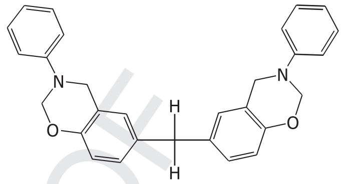
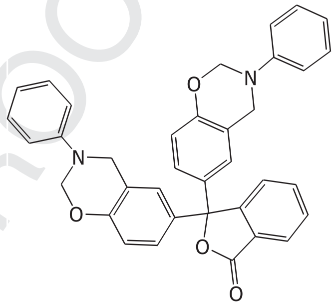
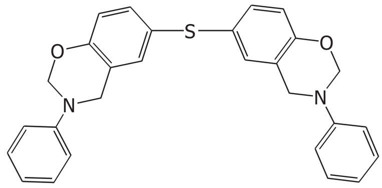
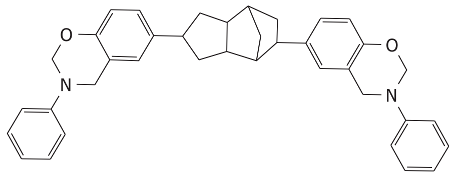
The overviews of the polymer including its advancement are provided in some articles such as the works of Yagci et al. [3], Ghosh et al. [2], and Nair [1]. In addition, further information could be obtained from the "Handbook of benzoxazine resins" by Hatsuo and Tarek [27]. This comprehensive handbook provides thorough Q3 coverage of the chemistry and applications of benzoxazine resins

Table 3
Comparison between two synthesis methods (synthesis time, approximately operating temperature, and percentage yield of benzoxazine resin).

Technique	Synthesis time	Approximately synthesis temperature (°C)	% Yield of benzoxazine resin	
			Type 1[a]	Type 2[b]
Solvent (in dioxane)	6 h	101	75	80
Solventless	10 min	110	75	83

[a] Type 1 = 2,2-bis(3,4-dihydro-3-toluidil-2H-1,3-benzoxazine)-propane.
[b] Type 2 = 2,2-bis(3,4-dihydro-3phenyl-2H-1,3-benzoxazine)-propane.

Table 4
Araldite® benzoxazine resins from Huntsman Corporation, 2009.

Product	Type of benzoxazine resin	Chemical structure
Araldite® MT35600	Bisphenol A based resin	
Araldite® MT35700	Bisphenol F based resin	
Araldite® MT35800	Phenolphthalein based resin	
Araldite® MT35900	Thiodiphenol based resin	
Araldite® MT36000	Dicyclopentadiene based resin	

with an evidence-based approach to enable chemists, engineers and material scientists to evaluate effectiveness. Additionally, the book named "Polybenzoxazine: Chemistry and Properties" by Kumar and Nair [5] gives the detailed information on many aspects of this polymers such as the synthesis of various polybenzoxazines, the degradation chemistry, and the potential areas of uses of this materials. This book is aimed to be a reference on the polymer for researcher in academic and industry.

7.2. Industrial sources for polybenzoxazines and related products

The sources of polybenzoxazines and related products are available from many companies such as Huntsman Corporation, Henkel Corporation, Gurit Group, Materials Americas Inc., Georgia Pacific Resins Inc. and Shikoku Chemical Corporation.

Acknowledgements

This research receives financial supports from Higher Education Research Promotion and National Research University Project of Thailand (AM1076A) and from the Rachadaphiseksomphot Endowment Fund Part of the "Strengthen CU's Researcher's Project." Additional funding is also provided by the research grants from New Researcher's Grant, Thailand Research Fund-Commission on Higher Education (TRF-CHE: MRG5380077) and by Matching Fund of SWU (2010-2012) as well as Research Grants of Faculty of Engineering and Graduate School of SWU (2011).

References

[1] C.P.N. Nair, Prog. Polym. Sci. 29 (2004) 401–498.
[2] N.N. Ghosh, B. Kiskan, Y. Yagci, Prog. Polym. Sci. 32 (2007) 1344–1391.
[3] Y. Yagci, B. Kiskan, N.N. Ghosh, J. Polym. Sci. Pol. Chem. 47 (2009) 5565–5576.
[4] T. Endo, A. Sudo, J. Polym. Sci. Pol. Chem. 47 (2009) 4847–4858.
[5] K.S.S. Kumar, C.P.R. Nair, Polybenzoxazines: Chemistry and Properties, iSmithers Rapra Publishing, England, 2010.
[6] H. Ishida, Process for Preparation of Benzoxazine Compounds in Solventlesssystems. US Patent 5543516, 1996.
[7] X. Ning, H. Ishida, J. Polym. Sci. Pol. Phys. 32 (1994) 921–927.
[8] S.B. Shen, H. Ishida, Polym. Compos. 17 (1996) 710–719.
[9] F.W. Holly, A.C. Cope, J. Am. Chem. Soc. 66 (1944) 875–1879.
[10] J. Liu, H. Ishida, A new class of phenolic resins with ring-opening polymerization', in: J.C. Salamone (Ed.), The Polymeric Materials Encyclopedia, CRC Press, Florida, 1996, pp. 484–494.
[11] M. Sponton, J.C. Ronda, M. Galia, V. Cadiz, Polym. Degrad. Stabil. 93 (2008) 2158–2165.
[12] S. Rimdusit, S. Pirstpindvong, W. Tanthapanichakoon, S. Damrongsakkul, Polym. Eng. Sci. 45 (2005) 288–296.
[13] H. Kimura, Y. Murata, A. Matsumoto, K. Hasegawa, K. Ohtsuka, A. Fukuda, J. Appl. Polym. Sci. 74 (1999) 2266–2273.

[14] H. Kimura, A. Matsumoto, H. Sugito, K. Hasfgawa, K. Ohtsuka, A. Fukuda, J. Appl. Polym. Sci. 79 (2001) 555–565.
[15] H. Ishida, S. Ohba, J. Appl. Polym. Sci. 101 (2006) 1670–1677.
[16] T. Takeichi, Y. Guo, S. Rimdusit, Polymer 46 (2005) 4909–4916.
[17] K.S.S. Kumar, C.P.R. Nair, K.N. Ninan, Eur. Polym. J. 45 (2009) 494–502.
[18] S.B. Shen, H. Ishida, J. Polym. Sci. Pol. Phys. 37 (1999) 3257–3268.
[19] H. Ishida, D.J. Allen, J. Polym. Sci. Pol. Phys. 34 (1996) 1019–1030.
[20] H. Ishida, H.Y. Low, Macromolecules 30 (1997) 1099–1106.
[21] Y.X. Wang, H. Ishida, J. Appl. Polym. Sci. 86 (2002) 2953–2966.
[22] H. Ishida, Y. Rodriquez, Polymer 36 (1995) 3151–3158.
[23] W.J. Burke, J. Am. Chem. Soc. 71 (1949) 609–612.
[24] W.J. Burke, J.L. Bishop, E.L.M. Glennie, W.N. Bauer, J. Org. Chem. 30 (1965) 3423–3427.
[25] T. Agag, T. Takeichi, Macromolecules 36 (2003) 6010–6017.
[26] H. Ishida, D.P. Sanders, J. Polym. Sci. Pol. Phys. 38 (2000) 3289–3301.
[27] H. Ishida, T. Agag, Handbook of Benzoxazine, Elsevier, New York, 2011.
[28] D.J. Allen, H. Ishida, J. Appl. Polym. Sci. 101 (2006) 2798–2809.
[29] S. Li, L. Wang, J. Appl. Polym. Sci. 99 (2006) 1359–1366.
[30] C.H. Lin, S.L. Chang, H.H. Lee, H.C. Chang, K.Y. Hwang, A.P. Tu, W.C. Su, J. Polym. Sci. Pol. Chem. 46 (2008) 4970–4983.
[31] R. Andereu, A.J. Reina, C.J. Ronda, J. Polym. Sci. Pol. Chem 46 (2008) 3353–3366.
[32] H. Ishida, Mod. Plast. Int. 6 (1998) 87–90.
[33] S. Rimdusit, W. Bangsen, P. Kasemsiri, J. Appl. Polym. Sci. 121 (2011) 3669–3678.
[34] S. Rimdusit, P. Kunopast, I. Dueramae, Polym. Eng. Sci. 51 (2011) 1797–1807.
[35] S. Rimdusit, H. Ishida, J. Polym. Sci. Pol. Phys. 38 (2000) 1687–1698.
[36] S. Rimdusit, H. Ishida, Polymer 41 (2000) 7941–7949.
[37] S. Rimdusit, T. Mongkhonsi, P. Kamonchaivanich, K. Sujirote, S. Tiptipakorn, Polym. Eng. Sci. 48 (2008) 2238–2246.
[38] T. Takeichi, Y. Guo, Polym. J. 33 (2001) 437–443.
[39] S. Rimdusit, C. Jubsilp, Polymer from anhydride modified polybenzoxazine. Thailand Patent pending. Issue Number 5543516, 2007.
[40] C. Jubsilp, T. Takeichi, S. Rimdusit, Polym. Degrad. Stabil. 96 (2010) 1047–1053.
[41] A. Tuzun, B. Kiskan, N. Alemdar, A.T. Erciyes, Y. Yagci, J. Polym. Sci. Polym. Chem. 38 (2010) 4279–4284.
[42] C. Jubsilp, B. Ramsiri, S. Rimdusit, Effects of aromatic carboxylic dianhydrides on thermalmechanical properties of polybenzoxazine-dianhydride copolymers, Polym. Eng. Sci., in press. Q4
[43] H. Ardhyanant, M.H. Wahid, M. Sasak, T. Agag, T. Kawauchi, H. Ismail, T. Takeichi, Polymer 49 (2008) 4585–4591.
[44] H. Ardhyananta, T. Kawauchi, H. Ismail, T. Takeichi, Polymer 50 (2009) 5959–5969.
[45] T. Takeichi, T. Agag, R. Zeidam, J. Polym. Sci. Pol. Chem. 39 (2001) 2633–2641.
[46] S. Tiptipakorn, S. Damrongsakkul, S. Ando, K. Hemvichian, S. Rimdusit, Polym. Degrad. Stabil. 92 (2007) 1265–1278.
[47] J.M. Huang, S.J. Yang, Polymer 46 (2005) 8068–8078.
[48] H. Ishida, Y.H. Lee, Polymer 42 (2001) 6971–6979.
[49] S. Zheng, H. Lu, Q. Guo, Macromol. Chem. Phys. 205 (2004) 1547–1558.
[50] Y.C. Su, S.W. Kuo, D.R. Yei, H. Xu, F.C. Chang, Polymer 44 (2003) 2187–2191.
[51] E.S. Lane, Benzoxazine Derivatives, UK Patent 694489, 1953.
[52] H. Ishida, Composite Densification with Benzoxazines, US Patent 5152939, 1992.
[53] H. Ishida, Composite Densification with Benzoxazines. US Patent 5266695, 1993.
[54] H. Ishida, Composition for Forming High Thermal Conductivity Polybenzoxazine-based Material and Method', US Patent 5900447, 1999.
[55] H. Ishida, S. Rimdusit, Ternary Systems of Benzoxazine, Epoxy, and Phenolicresins, US Patent 6207786, 2001.
[56] L.C. Chen, Halogen-free Varnish and Prepreg Thereof, US patent 7842401, 2010.

Symposium

BAEKELAND 2011

3rd International Symposium on Network Polymers

Program and Abstracts

September 11-14, 2011
Hotel Nikko Toyohashi
Toyohashi, Japan

BAEKELAND 2011

3rd International Symposium on Network Polymers

Program and Abstracts

September 11 – 14, 2011
Hotel Nikko Toyohashi
Toyohashi, JAPAN

Degradation kinetic of polybenzoxazine modified with aromatic tetracarboxylic dianhydride

Chanchira Jubsilp[1*], Tsutomu Takeichi[2] and Sarawut Rimdusit[3]

[1] *Department of Chemical Engineering, Faculty of Engineering, Srinakharinwirot University, Ongkharak, Nakhonnayok 26120, Thailand*

[2] *Department of Environmental and Life Sciences, Toyohashi University of Technology, 1-55 Hibarigaoka, Tempaku-cho, Toyohashi 441-8580, Japan*

[3] *Polymer Engineering Laboratory, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand*

**E-mail: chanchira@swu.ac.th*

Bisphenol-A-aniline type polybenzoxazine (PBA-a) modified with benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (BTDA) is attractive for those applications that require high thermal and mechanical properties with fire resistant characteristics as recently reported [1,2]. Therefore, it is important to investigate the changes that take place during the thermal degradation of PBA-a/BTDA system. In this work, the activation energy and the reaction mechanism of the degradation processes of the PBA-a/BTDA at 1.5:1 mole presented by thermogravimetric analysis under argon atmosphere have been estimated from non-isothermal kinetic results. The DTG thermograms of the PBA-a/BTDA at 1.5:1 mole exhibited five stages of thermal degradation reaction. The activation energy values obtained by Flynn-Wall-Ozawa method of five stages are 148-210 kJ/mol. Furthermore, the appropriate conversion model of the degradation processes was studied by Criado method as exemplification of the third stage shown in Fig. 1. The degradation reaction mechanism of five stages of the PBA-a/BTDA system is accounted by random nucleation model with one nucleus on the individual particle (F_1).

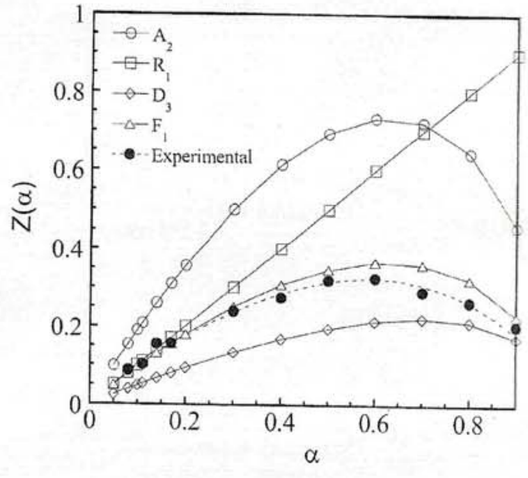


Fig.1 Master curves of Z(α) and experimental data in third stage of degradation processes.

References

1 C. Jubsilp, T. Takeichi, S. Rimdusit, accepted to Polym. Degrad. Stabili. Available online 5 April 2011.

2 B. Ramsiri, C. Jubsilp, S. Rimdusit, Proceeding of 2[nd] TJIA 2009, Kyoto, Japan, 20 Nov. 2008, p.81

Foreword

The inventor of Bakelite, Leo Hendrik Baekeland, was born in Sint-Martens-Latem near Ghent, Belgium in 1863. After getting his PhD from the University of Ghent at the age of 21, he was appointed associate professor of chemistry. In 1907, L. H. Baekeland took his first patent on the novel material based on phenol and formaldehyde, which was commercialized as the first fully synthetic plastic, "Bakelite". Therefore, the year of 1907 can be considered as the beginning of "the Age of Plastics".

Celebrating the centennial anniversary of the great invention, the first Baekeland symposium was successfully held in Ghent, Belgium in 2007 by the organization of Professor Eric Goethals. The second Baekeland symposium, Baekeland 2009 "2nd International Symposium on Thermosets", was held in Antalya, Turkey by the organization of Professor Yusuf Yagci. The second symposium was also a great success. Now, following the successful two symposiums, Baekeland 2011 "3rd International Symposium on Network Polymers" will be held in Toyohashi, Japan during September 11-14, 2011 at Hotel Nikko Toyohashi. It happened that this year is the centennial anniversary of the production of plastic in Japan, because Dr. Joukichi Takamine, a friend of L. H. Baekaland, produced Bakelite as the first plastic in Japan.

The purpose of the meeting is to review the present trends and developments in all types of network polymers, essentially from a R&D point of view.

The following topics have been selected:

1. New developments in network polymers

2. Modified resins and composite materials

3. Analysis and characterization of network polymers

4. Modelling, processing and shaping

5. New applications

The subtitle was changed from "thermosets" to "network polymers", because now we have various means to get three-dimensional networks other than thermal curing. Traditional phenolics and epoxies are still two main important players, but in this Baekeland 2011, we have presentations on various new concepts towards the construction of networks, on the hard and soft materials, on the quickly developing newcomers, and so on.

The symposium city, Toyohashi, and surrounding area are famous as the industrial and agricultural districts. Especially, this area is famous as the production and import / export center of automobiles.

We hope that all of you will enjoy the scientific program as well as Toyohashi and its surroundings.

Prof. Tsutomu Takeichi
Toyohashi University of Technology

Prof. Em. Eric Goethals
Ghent University

CONFERENCE COMMITTEES

Chair persons

Tsutomu TAKEICHI	*Toyohashi University of Technology, JAPAN*
Eric GOETHALS	*Ghent University, BELGIUM*

International Advisory Board

Ingo ALIG	*Deutsches Kunststoff-Institut, GERMANY*
Ramon BACARDIT	*Henkel, GERMANY*
Dirk BONTINCK	*Cytec Surface Specialties, BELGIUM*
Virginia CADIZ	*Universitat Rovira i Virgili, SPAIN*
John W. CONNELL	*NASA Langley Research Center, USA*
Wayne D. COOK	*Monash University, AUSTRALIA*
Takeshi ENDO	*Kinki University , JAPAN*
Kazuhisa HIRANO	*Sumitomo Bakelite Co., Ltd., JAPAN*
Ton LOONTJENS	*DSM & RU Groningen, NETHERLANDS*
Libor MATEJKA	*Academy of Sciences of the Czech Republic, CZECH REPUBLIC*
Bruno Van MELE	*Vrije Universiteit Brussel, BELGIUM*
Osama MUSA	*International Speciality Products, USA*
Eckart NAUSCH	*European Phenolic Resins Association, GERMANY*
Mitsukazu OCHI	*Kansai University, JAPAN*
Louis PILATO	*Pilato Consulting, USA*
Mark D. SOUCEK	*University of Akron, USA*
Toshikazu TAKATA	*Tokyo Institute of Technology, JAPAN*
Yusuf YAGCI	*Istanbul Technical University , TURKEY*
Yichu YIN	*Shanghai Research Institute of Synthetic Resins, CHINA*

Organizing Committee

Tetsurou AGAWA	*DIC Corporation, JAPAN*
Akira AKIMOTO	*Starlite Co., Ltd., JAPAN*
Yasushi ARITA	*Sumitomo Bakelite Co., Ltd., JAPAN*
Sumitoshi ASAKUMA	*Sumitomo Bakelite Co., Ltd., JAPAN*
Miyuki HARADA	*Kansai University, JAPAN*
Naoki HARAGUCHI	*Toyohashi University of Technology, JAPAN*
Shigeru HAYASHIDA	*Hitachi Chemical Co., Ltd., JAPAN*
Shinichi ITSUNO	*Toyohashi University of Technology, JAPAN*
Masashi KAJI	*Nippon Steel Chemical Co., Ltd., JAPAN*
Takehiro KAWAUCHI	*Toyohashi University of Technology, JAPAN*

Conference Secretariat

Akihiko MATSUMOTO (Secretary-General, Treasurer)
Takehiro KAWAUCHI (Secretary)
Department of Environmental and Life Sciences,
Toyohashi University of Technology,
Tempaku-cho, Toyohashi 441-8580, JAPAN
E-mail: baekeland2011@tutms.tut.ac.jp

THE 6th PURE AND APPLIED CHEMISTRY INTERNATIONAL CONFERENCE 2012

PACCON 2012– CHEMISTRY BEYOND BOUNDARIES

11 - 13 JANUARY 2012, THE EMPRESS CONVENTION CENTER
CHIANG MAI, THAILAND

PROGRAM & HIGHLIGHTS

DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, CHIANG MAI UNIVERSITY
& THE CHEMICAL SOCIETY OF THAILAND UNDER THE PATRONAGE OF
HER ROYAL HIGHNESS PRINCESS CHULABHORN MAHIDOL

PACCON 2012

Department of Chemistry,
Faculty of Science,
Chiang Mai University
Tel. +66 5394 3341-5
Fax. +66 5389 2277

www.paccon2012.com

Report by

PROFESSOR DR. PONGSAK ANGKASITH

President, Chiang Mai University
Chairman of the Organizing Committee

Opening Ceremony of the 6^{th} Pure and Applied Chemistry International Conference 2012 (PACCON 2012)

Wednesday 11^{th} January 2012

May It Please Your Royal Highness,

On behalf of the Organizing Committee of the 6th Pure and Applied Chemistry International Conference (PACCON) 2012, and all those convened here today, may I humbly express my deepest gratitude to Your Royal Highness for having graciously consented to preside over this Opening Ceremony.

PACCON has become an annual flagship scientific meeting among chemists and related scientists where recent developments can be shared, ideas and interests can be exchanged, new directions can be explored and new research collaboration can be initiated. This year, PACCON 2012 has been jointly organized by Chiang Mai University and the Chemical Society of Thailand under the Patronage of Her Royal Highness Princess Chulabhorn Mahidol with support from several other local agencies. This conference also celebrates the completion this month of the 4th cycle (48 years) of Chiang Mai University since its founding in January 1964 as the first provincial university in Thailand, outside of the capital Bangkok.

The theme of this conference – "Chemistry Beyond Boundaries" – reflects the relevance and importance of modern-day chemistry to a wide range of related fields. These widening scientific horizons are leading to new and exciting discoveries that are improving the quality of life. This theme is therefore well chosen and is in keeping with the multidisciplinary nature of modern scientific research.

The conference is being attended by more than 1,400 participants from 10 different countries. Three plenary lectures and 36 invited lectures will be given by internationally renowned scientists from all areas of chemistry. Some of the most recent advances in chemistry will be presented in eight oral sessions, three symposia and four poster sessions. An open panel discussion on the topic of global interest in relation to chemistry will also be hold by four executives from ones of the most renowned private and government sectors.

The organization of a large meeting as the one today inevitably involves a great deal of time and effort on the part of many staff. For this, I thank my colleagues in the Organizing Committee and join them in hoping that the conference will lead to furthering fruitful academic development and research collaboration, not only in this region, but also in nation and worldwide. This conference provides a valuable opportunity for young scientists to meet and interact with internationally recognized authorities in their respective fields and to allow the passing on of research experience from generation to generation.

Your Royal Highness, the auspicious moment has now arrived. May I humbly request Your Royal Highness to open officially this Pure and Applied Chemistry International Conference PACCON 2012.

Introduction of

PROFESSOR DR. HER ROYAL HIGHNESS PRINCESS CHULABHORN

by

ASSOCIATE PROFESSOR DR. JINTANA SIRIPITAYANANON

Head of Chemistry Department, Faculty of Science,
Chiang Mai University

Opening Ceremony of the Pure and Applied Chemistry
International Conference 2012 (PACCON 2012)

Wednesday 11th January 2012

Your Royal Highness,

On behalf of the organizers of the 6th Pure and Applied Chemistry International Conference 2012, may I humbly express my deepest gratitude to Your Royal Highness for graciously presenting a Special Keynote Lecture at this conference.

For many years now, Your Royal Highness has been heavily involved in the promotion of scientific research here in Thailand and in establishing international collaborations. As an inspirational researcher, Your Royal Highness has founded and served as the President of the Chulabhorn Research Institute to support Thailand's development through the Institute's mission of the "Application of Science and Technology to Improve the Quality of Life". In addition, the prestigious Chulabhorn Graduate Institute was established in 2005.

Your Royal Highness has received numerous international awards in recognition of many outstanding scientific achievements including the UNESCO Einstein Medal in 1986 for promoting scientific collaboration, Honorary Fellowship of the Royal Society of Chemistry in the United Kingdom, the Albert Hofmann Centennial Gold Medal and Golden Honour Ring in 2007, the Windaus Award and the Ramazzini Award in 2009, and the Distinguished Women in Chemistry and Chemical Engineering Award from IUPAC in 2011.

It is therefore a great honour for Chiang Mai University to have Your Royal Highness reside this Opening Ceremony and to be the Special Keynote Lecturer in this Pure and Applied Chemistry International Conference PACCON 2012.

If it pleases Your Royal Highness, may I now humbly request Your Royal Highness to deliver a Special Keynote Lecture.

Congratulatory Message from

The President of Chiang Mai University

PROFESSOR DR. PONGSAK ANGKASITH

On behalf of Chiang Mai University, may I extend a very warm welcome to you all to the Sixth Pure and Applied Chemistry International Conference 2012 (PACCON 2012) here in Chiang Mai. This is the first time that we have been given the honor of hosting PACCON – a very important and much anticipated annual event for chemists and scientists of related disciplines. It is particularly timely that PACCON 2012 has come to Chiang Mai this year since Chiang Mai University is celebrating its 4th cycle (48 years) since its establishment in January 1964.

This conference, jointly organized by Chiang Mai University and the Chemical Society of Thailand under the Patronage of Her Royal Highness Princess Chulabhorn Mahidol, has attracted both local and international scientists and provides an ideal forum for the exchange of new knowledge and ideas. This year, PACCON 2012 comprises eight parallel multidisciplinary sessions, three symposia and a panel discussion on the cutting edge topic. Under the theme of "Chemistry Beyond Boundaries", the conference provides an excellent opportunity for participants to expand their scientific horizons.

Outside of the academic program, it is hoped that you will be able to find time to enjoy some of the many attractions that the city of Chiang Mai has to offer. Chiang Mai is a myriad of Lanna culture and is a city that has successfully combined the old with the new. Your visit to Chiang Mai would not be complete without sampling at least some of these attractions.

Finally, I hope that you will find your participation in PACCON 2012 to be well worthwhile, both academically and socially. Conferences such as this do much to promote the development of chemistry and its related areas, not only in Thailand but also internationally.

I wish you all a successful meeting and a memorable stay here in Chiang Mai.

Professor Dr. Pongsak Angkasith
President, Chiang Mai University

Message from

The President of The Chemical Society of Thailand Under The Patronage of Her Royal Highness Princess Chulabhorn Mahidol

ASSOCIATE PROFESSOR DR. SUPAWAN TANTAYANON

On behalf of the Chemical Society of Thailand (CST) under the Patronage of Her Royal Highness Princess Chulabhorn Mahidol, I am grateful to Her Royal Highness Princess Chulabhorn for graciously presiding over the opening of Pure and Applied Chemistry Conference 2012 (PACCON 2012). This is the sixth of its kind.

The Chemical Society of Thailand under the Patronage of Her Royal Highness Princess Chulabhorn Mahidol has been established in 1980. We organize many meetings, trainings, seminars, short courses, workshops and conferences with the aim to disseminate the advancement of chemistry as well as the standard practice for working personnel. It also undertakes many activities that promote education in chemistry in both school and university levels, and public understanding of chemistry. The society has had the strong international collaboration with the Federation of Asian Chemical Societies for decades and will extend such collaboration to other international organizations.

If chemists increasingly direct their strengths to contribute to a sustainable development, chemistry will become more worthy of public support for improving the quality of life without damaging the globe for future generations. Although the celebration of "The International Year of Chemistry" is going to end soon, it has already made the public worldwide recognize the importance of chemistry to our life and to our future. These messages will continue to widespread from generations to generations. To do all these tasks, the Chemical Society of Thailand certainly requires the strong support and contribution from Thai chemists. We, therefore look forward to welcoming all Thai chemists becoming our members soon.

As PACCON 2012 is the one of our significant activities, it gives us great honor indeed to co-organize and welcome all of you to this conference. We trust that the conference theme, "Chemistry Beyond Boundaries", will draw the attention from the participants in diverse fields within chemistry and applied chemistry, both locally and internationally. By sharing and understanding the recent progress in chemistry, we will be updated on the latest trends in chemistry as well as be informed about innovative research strategies to empower our students and people in this world to live well in this fast changing world. We also trust that this event will be an important meeting place for professionals, educators, and researchers to exchange ideas and consider further collaboration.

I appreciate the keynote, plenary and invited lecturers as well as all other participants who contributed to the conference, particularly those from oversea. I would also like to extend my sincere thank and congratulation to the Department of Chemistry, Faculty of Science, Chiang Mai University as the main organizer of this conference.

I wish PACCON 2012 a fruitful success, and hope that all of you enjoy the sharing and exchanging of your expertise.

Assoc. Prof. Dr. Supawan Tantayanon
President, the Chemical Society of Thailand

Message from

The Dean of the Faculty of Science

ASSOCIATE PROFESSOR DR. SAMPAN SINGHARAJWARAPAN

On behalf of the Faculty of Science, may I first of all wish you a very warm welcome to Chiang Mai and to this 6th Pure and Applied Chemistry International Conference 2012 (PACCON 2012). To be the host for such a prestigious conference as this is an honor and a privilege not only for the Chemistry Department in particular but for the Faculty of Science in general. In line with the vision of Chiang Mai University as a whole, we in the Faculty of Science consider ourselves to be a research-driven Faculty, emphasizing research for the benefit of society, and the Chemistry Department's chosen theme of Chemistry Beyond Boundaries for PACCON 2012 reflects this approach.

Our hosting of this year's PACCON Conference is also very timely in that this year 2012 coincides with the 48th anniversary (4th cycle) of our Faculty of Science as one of the 3 founding faculties of Chiang Mai University in 1964. And, of course, this month of January 2012 also follows on immediately after the nation's celebration of His Majesty the King's 84th birthday (7th cycle) in December 2011.

Therefore, 2012 is an auspicious year for Chiang Mai University and we in the Faculty of Science are pleased to be able to contribute to the year's celebrations by starting off the year with such an important international event as this. With over 1400 registered participants, I must congratulate and thank all of the organizing staff, especially in the Chemistry Department, for all their hard work over the past few months.

To all participants, both from within Thailand and from abroad, please enjoy all of the attractions that PACCON 2012 and the city of Chiang Mai have to offer during your stay. We sincerely hope that your visit here to the north of Thailand will be a memorable one.

Associate Professor Dr. Sampan Singharajwarapan
Dean, Faculty of Science
Chiang Mai University

Message from

The Chairperson of the Local Organizing Committee

ASSOCIATE PROFESSOR DR. JINTANA SIRIPITAYANANON

As the local organizer of the Pure and Applied Chemistry International Conference 2012 (PACCON 2012), co-hosted with the Chemical Society of Thailand (CST) under the Patronage of Her Royal Highness Princess Chulabhorn Mahidol, it is our great pleasure and honor to welcome you to Chiang Mai.

Chiang Mai University, this month celebrating its 48th anniversary, was the first provincial university to be established in Thailand outside the capital Bangkok. The Chemistry Department is in the Faculty of Science which was one of the 3 founding faculties in January 1964. In keeping with the interdisciplinary nature of our teaching curriculum, we have widened the scope of PACCON 2012 to reflect the central role and importance of Chemistry to a range of interrelated and cutting-edge fields of discovery. With the theme, "Chemistry Beyond Boundaries", PACCON 2012 aims to highlight how Chemistry in combination with these other related fields, such as materials science and nanotechnology, is widening scientific horizons and leading to exciting new discoveries.

PACCON 2012 therefore provides a forum in which chemists and related scientists from around the world can meet and present their work alongside nationally and internationally renowned scientists. We hope that this will inspire our young chemists especially to believe that they too can go on to achieve great things in the future.

In addition to the diverse scientific program, there is a range of social activities through which participants will be able to enjoy the charm of Chiang Mai □ a city rich in culture and tradition. It is with these aims in mind that the Local Organizing Committee have dedicated themselves to making PACCON 2012 not just a successful conference but a truly memorable event.

As the Chairperson of this Committee, may I thank all my colleagues most sincerely for their hard work over many months and thank you, the participants, for your support. On behalf of the Committee, I wish you all an enjoyable and rewarding conference and a very pleasant stay here in Chiang Mai.

Jintana Siripitayananon

Associate Professor Dr. Jintana Siripitayananon
Head of Department of Chemistry, Chiang Mai University
Chairperson of Local Organizing Committee

PLENARY LECTURERS

Prof. Vicharn Panich

Chairman, The Knowledge Management Institute Foundation, Thailand

Prof. Young Joon Surh

Director, Tumor Microenvironmental Research Center, Seoul National University, Korea

Dr. A. Maureen Rouhi

Deputy Editor-in-chief, Chemical & Engineering News, American Chemical Society

PANEL DISCUSSION

Prof. Malyn Chulasiri

Director,
S&J International Enterprises Public Company Limited
Thailand

Dr. Songpope Polachan

Director General,
Department of Mineral Fuels Ministry of Energy, Thailand

Mr. Suraphong Iamchula

Executive Vice President,
Domestic Assets Group & Acting Senior Vice President
PTT Exploration and Production Public Company Limited
Thailand

Dr. Royol Chitradon

Director, Hydro and Agro Informatics Institute
Thailand

INVITED SPEAKERS

ADVANCES IN FLOW ANALYSIS & SENSORS

Assoc. Prof. Ian McKelvie
The university of Melbourne
Australia

Prof. Hiroyuki Ukeda
Kochi University
Japan

Assoc. Prof. Proespichaya Kanatharana
Prince of Songkla University
Thailand

CHEMISTRY FOR HEALTH SCIENCE & TECHNOLOGY

Prof. Jae Hyoun Kim
Dongduk's Women University
Korea

Prof. Masataka Nagaoka
Nagoya University
Japan

Assoc. Prof. Chanan Angsuthanasombat
Mahidol University
Thailand

INVITED SPEAKERS

CHEMISTRY FOR HEALTH SCIENCE & TECHNOLOGY

Dr. John Ogbaji Igoli
University of Strathclyde
Scotland

CHEMISTRY FOR GLOBAL WARMING, GREEN ENERGY & ENVIRONMENT

Prof. Vincent Remcho
Oregon State University
USA

Prof. Dana Boyd Barr
Emory University
USA

CHEMISTRY IN FOOD & AGRICULTURAL SCIENCE & CHEMISTRY FOR SPA & COSMETICS

Prof. Ken Izumori
Kagawa University
Japan

Assoc. Prof. Neti Waranuch
Naresuan University
Thailand

Prof. Nuntavan Bunyapraphatsara
Mahidol University
Thailand

INVITED SPEAKERS

SYNTHETIC CHEMISTRY

Prof. Roderick W. Bates
Nanyang Technological University
Singapore

Prof. Stephen Geoffrey Pyne
University of Wollongong
Australia

PLATFORM CHEMISTRY

Dr. Keiro Higuchi
Ogawa Co. Ltd. & Kochi University
Japan

Asst. Prof. Siriporn Jungsuttiwong
Ubon Ratchathani University
Thailand

CHEMISTRY FOR MATERIALS & NANOTECHNOLOGY

Prof. Pramuan Tangboriboonrat
Mahidol University
Thailand

Dr. Katerina Aifantis
Michigan Technological University
USA

INVITED SPEAKERS

CHEMISTRY FOR MATERIALS & NANOTECHNOLOGY

Assoc. Prof. Vinich Promarak
Ubon Ratchathani University
Thailand

Assoc. Prof. Sukon Phanichphant
Chiang Mai University
Thailand

Asst. Prof. Pierre-Henri Aubert
University of Cergy-Pontoise
France

Asst. Prof. Teerakiat Kerdcharoen
Mahidol University
Thailand

Asst. Prof. Arnon Chaipanich
Chiang Mai University
Thailand

Assoc. Prof. Taweechai Amornsakchai
Mahidol University
Thailand

Assoc. Prof. Pisith Singjai
Chiang Mai University
Thailand

INVITED SPEAKERS

CHEMISTRY FOR MATERIALS & NANOTECHNOLOGY

Dr. Adisorn Tuantranont
National Electronics and Computer
Technology Center, Thailand

BIOMATERIALS, BIOPLASTICS & BIONANOTECHNOLOGY

Prof. Pornprom Muangman, MD
Mahidol University
Thailand

Prof. Doo Sung Lee
SungKyunKwan University
Korea

Prof. Suwabun Chirachanchai
Chulalongkorn University
Thailand

Assoc. Prof. Matsuzaki Michiya
Osaka University
Japan

INVITED SPEAKERS

BIOMATERIALS, BIOPLASTICS & BIONANOTECHNOLOGY

Assoc. Prof. John Foster
The University of New South Wales
Australia

Dr. Vivan Thammongkol
PTT (RTI), Thailand

Mr. Derek Atkinson
PURAC (Thailand)

Asst. Prof. Toemsak Srikhirin
Mahidol University
Thailand

Assoc. Prof. Voravee P. Hoven
Chulalongkorn University
Thailand

Asst. Prof. Winita Punyodom
Chiang Mai University
Thailand

INVITED SPEAKERS

CHEMISTRY FOR ENGINEERING & INDUSTRY

Prof. Momoji KUBO
Tohoku University
Japan

Prof. Teruyuki Kondo
Kyoto University
Japan

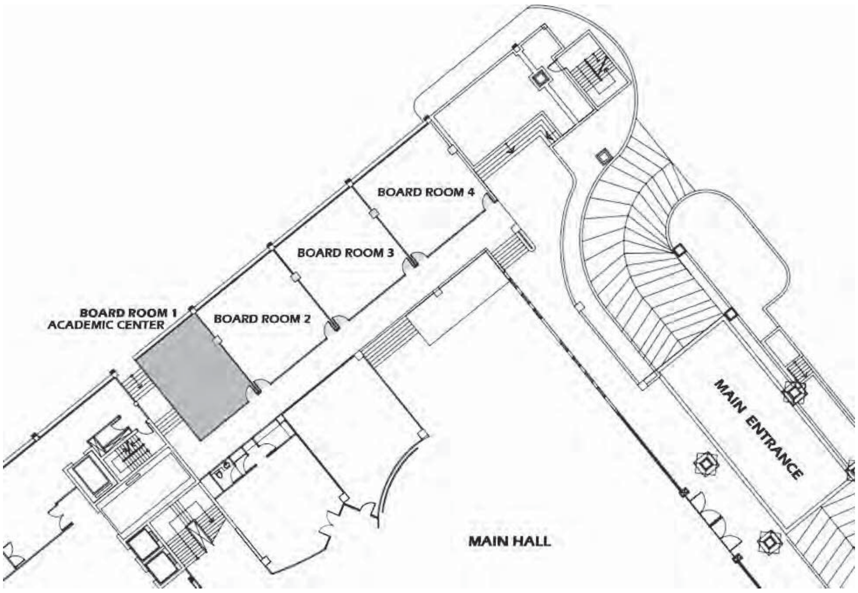
Prof. Tsugio Sato
Tohoku University
Japan

Prof. Shiro Saka
Kyoto University
Japan

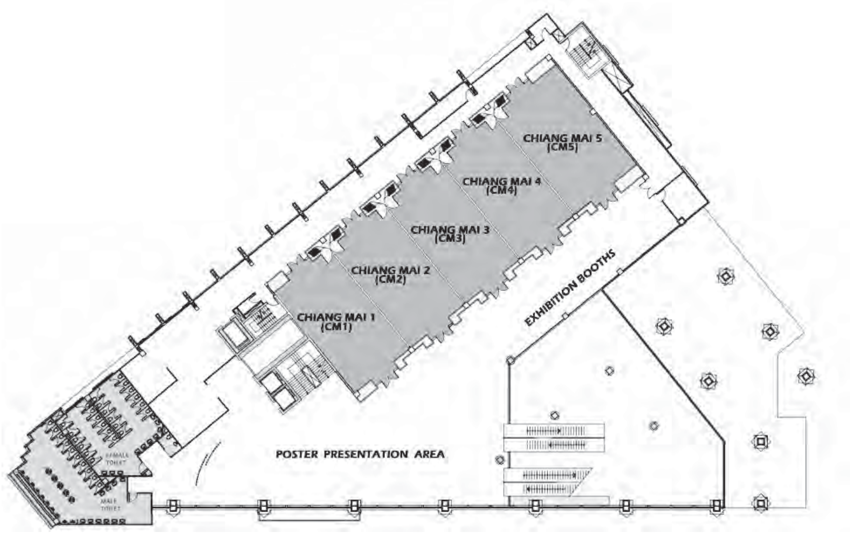
Prof. Heiko Hessenkemper
University of Freiberg
Germany

Dr. Sumate Charoenchaidet
Thai Polyethylene Co., Ltd.
Thailand

Dr. Thevarak Rochanapruk
PTT Phenol Co., Ltd.
Thailand

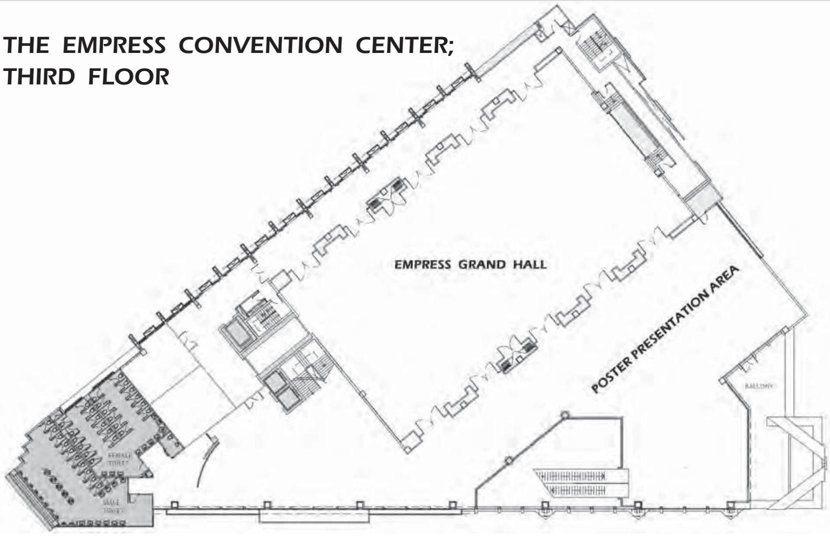


THE EMPRESS CONVENTION CENTER; FIRST FLOOR

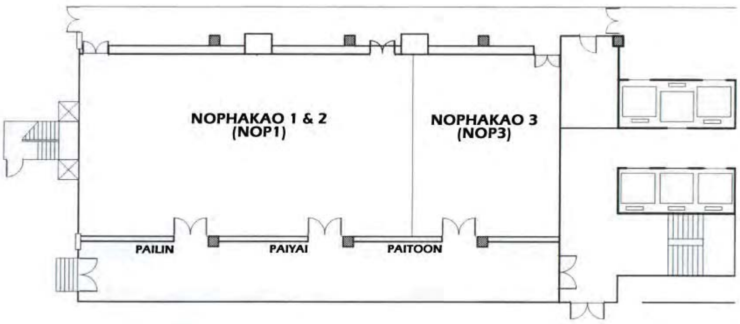


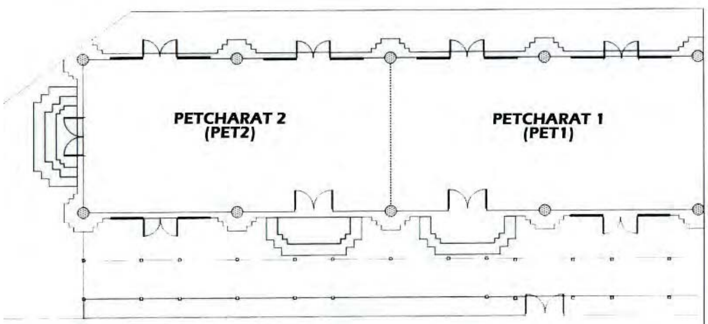
THE EMPRESS CONVENTION CENTER; SECOND FLOOR

THE EMPRESS CONVENTION CENTER; THIRD FLOOR



THE EMPRESS HOTEL





GENERAL INFORMATION

REGISTRATION DESK

Registration desk is located on the first floor of the Empress Convention Center. Additional registration point is also available at the lobby of the Hotel during the morning session of the first day of the conference.

EXHIBITIONS

Exhibition booths are located on the second floor of the Empress Convention Center.

INTERNET ACCESS

Free internet access is available for public use at the Empress Convention center. However it may be subjected to a slow down and interruption when there are too many concurrent users. The transmitted data may not be protected. Personal PCs are welcome, yet there will be no public PCs available.

FIRST AID SERVICE

The first aid service is available, if required, on the first floor of the Empress Convention Center with on-site ambulance sponsored by the Central Chiangmai Memorial Hospital.

INFORMATION FOR AUTHORS & PRESENTERS

OFFICIAL LANGUAGE

The official language of the PACCON 2012 is English.

ORAL PRESENTATIONS

A set of notebook (MS Power Point 2007 or MS Power Point 2010) and LCD projectors with laser pointer are available in each room. All presenters are kindly requested to submit and check the presentation files (MS Power Point) at the front desk located on the first floor of the Empress Convention Center, at least two hours before the start of the presenting session or during the break time prior to the session. The time slot of 20 minutes including 5 minutes of Q&A is allocated for each invited speakers, while 15 minutes including the 5 minutes of Q&A is for each oral presentation.

POSTER PRESENTATIONS

There are four poster sessions for the PACCON 2012, designated P1 (brown), P2 (red), P3 (pink) and P4 (purple). For convenience, each session is coded by color as shown in the brackets. Due to a large number of poster contributions, the presenters are kindly requested to mount up and take off the posters strictly following the appointed schedule;

	Installation Date/Time	Removal Date/Time
P1 (brown) • EDU • FAS • HST • PLA • SPC	10.01.2012/15.00-18.00 h P1-EDU-000 P1-FAS-000 P1-HST-000 P1-PLA-000 P1-SPC-000	11.01.2012/Before 17.00 h
P2 (red) • IEN • GCE • AFA • SYN	11.01.2012/17.00-18.00 h P2-IEN-000 P2-GCE-000 P2-AFA-000 P2-SYN-000	12.01.2012/11.30-12.00 h
P3 (pink) • MNT • BIP	12.01.2012/12.00-12.30 h P3-MNT-000 P3-BIP-000	12.01.2012/15.30-16.00 h
P4 (purple) • MNT	12.01.2012/16.00-16.30 h P4-MNT-000	13.01.2012/Before 10.15 h

For the posters which are not taken down according to the assigned duration, the posters will be removed by staff and can be fetched from the academic staff center (Board room 1 on the first floor of the Empress Convention Center).

Mounting materials and poster presentation ID as well as map for each session are available in the poster presentation areas: <u>the second and third floor of the Empress Convention Center</u>. Although the ID will be attached to your poster wall, it will be more convenient if you could find your poster ID in the program book (Poster Sessions) before hand.

ARTICLE & PRESENTATION CODES

For ease of communication, TWO codes have been assigned for each presentation, *i.e.* ARTICLE CODE and PRESENTATION CODE. The article code is in the form of

AAA – O – 000 for <u>Oral</u> presentation, and

AAA – P – 000 for <u>Poster</u> presentation where AAA is the abbreviation for conference session or symposium (AFA, BIP, EDU, FAS, GCE, HST, IEN, MNT, PLA, SYN, SPC) and 000 is an identification number for each article (starting from 001, 002, 003 ...).

For oral presentation code, information on presentation time, room, session and presentation type is included. Definition for each part of the code is as follows;

Time code					
Code	Date	Starting time	Code	Date	Starting time
C1	11.01.2012	13.45	C2	12.01.2012	14.00
D1	11.01.2012	16.15	D2	12.01.2012	15.45
E2	12.01.2012	11.00	A3	13.01.2012	8.30
			B3	13.01.2012	10.15
Room code					
CM1	Chiang Mai 1		NOP1	Nophakao 1 & 2	
CM2	Chiang Mai 2		NOP3	Nophakao 3	
CM3	Chiang Mai 3		PET1	Petcharat 1	
CM4	Chiang Mai 4		PET2	Petcharat 2	
CM5	Chiang Mai 5				
Session code					
AFA	Advances in Flow Analysis and Sensors		IEN	Chemistry for Engineering & Industry	
BIP	Biomaterials, Bioplastics & Bionanotechnology		MNT	Chemistry for Materials & Nanotechnology	
EDU	Chemical Education & Knowledge Management		PLA	Platform Chemistry	
FAS	Chemistry in Food & Agricultural Science		SYN	Synthetic Chemistry	
GCE	Chemistry for Global Warming, Green Energy & Environment		SPC	Chemistry for Spa & Cosmetics	
HST	Chemistry for Health Science &Technology				

The code for oral and poster contributions may be illustrated by the following examples; C1-CM1-MNT-I1, D1-CM1-MNT-O1 and C2-CM4-GCE-O3 for oral contributions, and P1-HST-001 and P3-MNT-001 for poster presentations.

For those who cannot find codes for either poster or oral presentations in the program book, this may be due to the incomplete payment of registration fee or the belated payment than the due date.

WEDNESDAY: January 11^{th}, 2012 (Morning Sessions)

Empress Grand Hall, 3^{rd} Floor	
08.00-09.00	Registration (1^{st} Floor)
08.30-09.00	Coffee Break
	OPENING CEREMONY
9.00	Guests are requested to be seated in the room
10.00	Arrival of Professor Dr. Her Royal Highness Princess Chulabhorn
	Present the Conference Package to Professor Dr. HRH Princess Chulabhorn by the President of Chemical Society of Thailand
	Report by the President of Chiang Mai University, the Chairperson of the PACCON2012 Organizing Committee
	Presentation of Plenary Lectures and Sponsors to receive plaques from Professor Dr. HRH Princess Chulabhorn by the Dean of Faculty of Science, Chiang Mai University
	Professor Dr. HRH Princess Chulabhorn graciously presents the Plaques of appreciation to Plenary Lectures and Sponsors
12.00	Presentation of the recipients of the CST Awards to receive plaques from Professor Dr. HRH Princess Chulabhorn by the President of Chemical Society of Thailand
	Professor Dr. HRH Princess Chulabhorn graciously presents the Plaques of appreciation to the recipients of The CST Awards
	Royal Opening Address by Professor Dr. HRH Princess Chulabhorn
	Introduction of Professor Dr. HRH Princess Chulabhorn by the Head of Chemistry Department, Chiang Mai University
	Special Keynote Lecture by Professor Dr. HRH Princess Chulabhorn
	Professor Dr. HRH Princess Chulabhorn has photographs taken with two groups of organizing committee
	Departure of Professor Dr. HRH Princess Chulabhorn

WEDNESDAY: January 11th, 2012 (Afternoon Sessions)

ROOM		E1 12.45	C1 13.45		D1 16.15
GRAND HALL	CST Annual Meeting* / LUNCH 12.00 h	PLENARY 1		POSTER P1 / BREAK 15.15 h	
CHIANG MAI 1 (CM1)			(MNT) C1-CM1-MNT		(MNT) D1-CM1-MNT
CHIANG MAI 2 (CM2)			MNT C1-CM2-MNT		MNT D1-CM2-MNT
CHIANG MAI 3 (CM3)			(SYN) C1-CM3-SYN		(SYN) D1-CM3-SYN
CHIANG MAI 4 (CM4)			(FAS) C1-CM4-FAS		(FAS) D1-CM4-FAS
CHIANG MAI 5 (CM5)			CST Awards Lectures		(HST) D1-CM5-HST
BOARD ROOM 4			Meeting of Heads of Department of Chemistry (13.45-16.45)		

* CST Annual Meeting during lunch break at Petcharat room

Thursday: January 12th, 2012 (Morning Sessions)

ROOM	A 2 8.30		B2 10.15	E2 11.00	
GRAND HALL	PLENARY 2 & 3	POSTER P2 / BREAK 10.00 h	PANEL DISCUSSION		LUNCH 12.00 h
CHIANG MAI 1 (CM1)				(HST/SPC) E2-CM1-SPC	
CHIANG MAI 2 (CM2)				(HST) E2-CM2-HST	
CHIANG MAI 3 (CM3)				(GCE) E2-CM3-GCE	

Thursday: January 12th, 2012 (Morning Sessions)

ROOM	A 2 8.30		B2 10.15	E2 11.00	
CHIANG MAI 4 (CM4)		POSTER P2 / BREAK 10.00 h		(GCE) E2-CM4-GCE	LUNCH 12.00 h
CHIANG MAI 5 (CM5)				(AFA) E2-CM5-AFA	
NOPHAKAO 1 & 2 (NOP1)	(MNT) A2-NOP1-MNT			(MNT) E2-NOP1-MNT	
NOPHAKAO 3 (NOP3)	(MNT) A2-NOP3-MNT			MNT E2-NOP3-MNT	
PETCHARAT 1 (PET1)	(BIP) A2-PET1-BIP			(BIP) E2-PET1-BIP	
PETCHARAT 2 (PET2)	(IEN) A2-PET2-IEN			(IEN) E2-PET12-IEN	

Thursday: January 12th, 2012 (Afternoon Sessions)

ROOM			C2 14.00		D2 15.45	
CHIANG MAI 1 (CM1)	LUNCH 12.00 h	POSTER P3 13.00 h	(HST) C2-CM1-HST-I1	BREAK 15.30 h	(HST) D2-CM1-HST-I1	POSTER P4 17.15 h
CHIANG MAI 2 (CM2)			(GCE) C2-CM2-GCE		(GCE) D2-CM2-GCE	
CHIANG MAI 3 (CM3)			(PLA) C2-CM3-PLA		(PLA) D2-CM3-PLA	
CHIANG MAI 4 (CM4)			(GCE) C2-CM4-GCE		(GCE) D2-CM4-GCE	
CHIANG MAI 5 (CM5)			(AFA) C2-CM5-AFA		(AFA) D2-CM5-AFA	
NOPHAKAO 1 & 2 (NOP1)			(MNT) C2-NOP1-MNT			

Thursday: January 12th, 2012 (Afternoon Sessions)

ROOM	LUNCH 12.00 h	POSTER P3 13.00 h	C2 14.00	BREAK 15.30 h	D2 15.45	POSTER P4 17.15 h
NOPHAKAO 3 (NOP3)			(MNT) C2-NOP3-MNT		(MNT) D2-NOP3-BIP	
PETCHARAT 1 (PET1)			(BIP) C2-PET1-BIP		(BIP) D2-PET1-BIP	
PETCHARAT 2 (PET2)			(IEN) C2-PET2-IEN		(IEN) D2-PET2-IEN	
BOARD ROOM 4			Hand-on Small Scale Chemistry Workshop (14.00-16.30)			

Friday: January 13th, 2012 (Morning Sessions)

ROOM	A3 8.30	BREAK 10.00 h	B3 10.15	LUNCH
CHIANG MAI 1 (CM1)	(MNT) A3-CM1-MNT			
CHIANG MAI 2 (CM2)	(MNT) A3-CM2-MNT			
CHIANG MAI 3, 4 & 5			CLOSING CEREMONY	

HANDS-ON SMALL SCALE CHEMISTRY WORKSHOP

Small-scale chemistry focuses on the reduction of waste and student exposure to chemicals. The goal of this workshop is to provide information and practical hands-on experimentation to better promote the practice of small-scale chemistry in education.

WORKSHOP CONDUCTORS

- Supawan Tantayanon, Ph.D.
  Associate Professor of Chemistry, Faculty of Science,
  Chulalongkorn University, Bangkok 10330, Thailand

- Zuriati Zakaria, Ph.D.
  Professor of Chemistry, Kebangsaan University,
  Kuala Lumper, Malaysia.

SCHEDULE

Thursday, November 12, 2012
14:00-14:20: Introduction to Small Scale Chemistry
14:20-16:30: Hands-on experiments

Workshop has been sponsored by Federation of Asian Chemical Societies (FACS), and Chemical Society of Thailand.

ADVANCES IN FLOW ANALYSIS AND SENSORS

DATE : 12.01.2012 TIME SLOT : E2			ROOM : CHIANG MAI 5	
11.00-11.20	E2-CM5-AFA-I1	-	I. D. McKelvie	UTILIZATION OF EVERYDAY IT AND COMMUNICATION DEVICES IN MODERN ANALYTICAL CHEMISTRY
11.20-11.40	E2-CM5-AFA-I2	-	H. Ukeda	RAPID AND CONVENIENT FLOW-BASED ANALYSIS FOR FOOD FUNCTION
11.40-11.55	E2-CM5-AFA-O1	AFA-O-001	W. Wongwilai	A NETWORK USING MODERN INFORMATION TECHNOLOGY FOR ANALYTICAL CHEMISTRY LABS
11.55-12.10	E2-CM5-AFA-O2	AFA-O-003	P. Klayprasert	DEVELOPMENT OF FLOW INJECTION AMPEROMETRIC METHOD USING TRIIODIDE ION AS REAGENT FOR ESTIMATION OF ANTIOXIDANT ACTIVITY

DATE : 12.01.2012 TIME SLOT : C2			ROOM : CHIANG MAI 5	
14.00-14.20	C2-CM5-AFA-I1	-	P. Kanatharana	DEVELOPMENT OF COST EFFECTIVE/GREEN TRACE ANALYSIS METHOD
14.20-14.35	C2-CM5-AFA-O1	AFA-O-012	S. Chan-Eam	ABTS ASSAY WITH AMPEROMETRIC SEQUENTIAL INJECTION: AN ECONOMIC AND EFFECTIVE TOOL FOR EVALUATION OF TOTAL ANTIOXIDANT CAPACITY IN GINGER DRINK
14.35-14.50	C2-CM5-AFA-O2	AFA-O-004	S. Liawruangrath	LAB-ON-A-CHIP IN CHIANG MAI
14.50-15.05	C2-CM5-AFA-O3	AFA-O-013	A. Apilux	SILVER NANOPARTICLES FOR COLORIMETRIC DETECTION OF MERCURY(II) ION USING PAPER-BASED DEVICE

DATE : 12.01.2012				
TIME SLOT : C2		ROOM : CHIANG MAI 5		
15.05-15.20	C2-CM5-AFA-O4	AFA-O-005	Pornwilard M-M	FLOW FIELD-FLOW FRACTIONATION FOR SIZE CHARACTERIZATION OF SELENIUM NANOPARTICLES IN GASTROINTESTINAL CONDITIONS
15.20-15.35	C2-CM5-AFA-O5	AFA-O-009	T. Kanyanee	DEVELOPMENT OF LIQUID DROP/FILM AS LOW-COST ANALYTICAL CHEMISTRY APPROACH IN THAILAND

DATE : 12.01.2012				
TIME SLOT : D2		ROOM : CHIANG MAI 5		
15.45-16.00	D2-CM5-AFA-O1	AFA-O-011	C. Buranachai	RECONFIGURABLE LABELED OPTICAL BIOSENSOR BASED ON APTAMER - DNA MOLECULAR BEACON
16.00-16.15	D2-CM5-AFA-O2	AFA-O-010	S. Janthai	DISPOSABLE CHEMICAL SENSOR FOR DETERMINATION OF CADMIUM BASED ON BISMUTH DEPOSITED MULTIWALLED CARBON NANOTUBE LINKED CHITOSAN
16.15-16.30	D2-CM5-AFA-O3	AFA-O-002	K. Wechakorn	DEVELOPMENT OF HIGHLY SELECTIVE FLUORESCENT SENSORS BASED ON TRIAZOLE MOIETY FOR DETECTION OF METAL IONS AND ITS APPLICATION IN LIVING CELLS
16.30-16.45	D2-CM5-AFA-O4	AFA-O-006	W. Tangkawsakul	INVESTIGATING IMMOBILIZED ALLERGEN ANTIGEN ON DEXTRAN SURFACE FOR DETECTION OF *IGE* ANTIBODY ON FOOD ALLERGY BY SURFACE PLASMON RESONANCE (SPR) TECHNIQUE
16.45-17.00	D2-CM5-AFA-O5	AFA-O-007	K. Sudprasert	INVESTIGATION OF LEWIS BLOOD TYPING BY SURFACE PLASMON RESONANCE IMAGING (SPRI)
17.00-17.15	D2-CM5-AFA-O6	AFA-O-008	W. Wangwattanapan	MODIFICATION OF GLASSY CARBON ELECTRODE BY BISMUTH AMALGAM/CARBON NANOTUBE/CHITOSAN FOR DETECTION OF LEAD IN HONEY PRODUCTS

BIOMATERIALS, BIOPLASTICS AND BIONANOTECHNOLOGY

DATE : 12.01.2012				
TIME SLOT : A2			ROOM : PETCHARAT 1	
8.30-8.50	A2-PET1-BIP-I1	-	D. Atkinson	PURAC'S CONTRIBUTION TO A SUSTAINABLE WORLD
8.50-9.10	A2-PET1-BIP-I2	-	W. Punyodom	FROM LACTIC ACID TO POLY(LACTIC ACID): REACTION PATHWAY AND KINETICS
9.10-9.25	A2-PET1-BIP-O1	BIP-O-073	M. Sriyai	KINETIC STUDIES BY DSC OF THE RING-OPENING POLYMERISATION OF *L*-LACTIDE USING TIN(II) OCTOATE/n-ALCOHOLS AS INITIATING SYSTEMS
9.25-9.40	A2-PET1-BIP-O2	BIP-O-068	P. Khomein	SYNTHSIS OF POSITIVE-CHARGES POLY(LACTIC ACID)
9.40-9.55	A2-PET1-BIP-O3	BIP-O-071	W. Sontising	MECHANISM AND KINETIC STUDIES OF TIN(II) n-BUTOXIDE INITIATED RING-OPENING POLYMERIZATION OF CYCLIC ESTERS: A THEORETICAL STUDY
9.55-10.10	A2-PET1-BIP-O4	BIP-O-070	N. Lawan	HIGH ACCURACY CALCULATION OF POLY(L-LACTIDE) SYNTHESIS BY THE RING-OPENING POLYMERIZATION OF *L*-LACTIDE USING TIN(II) ALKOXIDES AS INITIATORS

DATE : 12.01.2012				
TIME SLOT : E2			ROOM : PETCHARAT 1	
11.00-11.20	E2-PET1-BIP-I1	-	V. Thammongkol	HOW CHEMISTRY STRENGTHENS THE BIOPLASTIC INDUSTRY IN THAILAND
11.20-11.35	E2-PET1-BIP-O1	BIP-O-065	K. Suthapakti	ENVIRONMENTALLY DEGRADABLE POLYESTER BLENDS BASED ON POLY(LACTIC ACID) AND ITS COPOLYMER WITH CAPROLACTONE
11.35-11.50	E2-PET1-BIP-O2	BIP-O-063	N. Pinsurong	MORPHOLOGY AND MECHANICAL PROPERTIES OF THE TERTIARY BLEND OF POLY(LACTIC ACID)/THERMOPLASTIC STARCH/SOY PROTEIN CONCENTRATE

DATE : 12.01.2012				
TIME SLOT : E2			ROOM : PETCHARAT 1	
11.50-12.05	E2-PET1-BIP-O3	BIP-O-064	A. Promjun	POLYPYRROLE-CELLULOSE COMPOSITE AND THE USE AS CONDUCTING FILLER IN BIOPOLYMERS
12.05-12.20	E2-PET1-BIP-O4	BIP-O-069	C. Worrarat	PINEAPPLE FIBER-REINFORCED POLY (LACTIC ACID) COMPOSITES : MECHANICAL PROPERTIES AND MORPHOLOGY ANALYSIS

DATE: 12.01.2012				
TIME SLOT : C2			ROOM : PETCHARAT 1	
14.00-14.20	C2-PET1-BIP-I1	-	L. Foster	BIOPEGYLATION OF POLYHYDROXYALKANOATES AND THEIR POTENTIAL AS NEW BIOMATERIALS
14.20-14.40	C2-PET1-BIP-I2	-	P. Muangman	CLINICAL APPLICATIONS OF ADVANCED WOUND DRESSING, BIOMATERIALS AND TISSUE ENGINEERING FOR WOUND MANAGEMENT
14.40-14.55	C2-PET1-BIP-O1	BIP-O-061	O. Sukjai	EFFECT OF SERICIN PROTEIN ON GROWTH OF HYDROXYAPATITE OVER SURFACE OF SILK FIBERS USING SIMULATED BODY FLUID
14.55-15.10	C2-PET1-BIP-O2	BIP-O-072	D. Daranarong	IN VITRO BIOCOMPATIBILITY OF COLLAGEN-POLY(L-LACTIDE-CO-CAPROLACTONE) NERVE GUIDE CONDUITS FOR PERIPHERAL NERVE REPAIR
15.10-15.25	C2-PET1-BIP-O3	BIP-O-067	P. Wongpanit	COCONUT OIL-INCORPORATED PLURONIC F-68/SILK FIBROIN SHEET WITH ANTIBACTERIAL ACTIVITIES FOR POSSIBLE USE AS WOUND DRESSING MATERIAL

DATE : 12.01.2012				
TIME SLOT : D2			ROOM : PETCHARAT 1	
15.45-16.05	D2-PET1-BIP-I1	-	M. Matsuzaki	DEVELOPMENT OF 3D-VASCULARIZED TISSUE MODELS FABRICATED BY LAYER-BY-LAYER NANOFILM COATING

DATE : 12.01.2012		TIME SLOT : D2		ROOM : PETCHARAT 1
16.05-16.25	D2-PET1-BIP-I2	-	S. Chirachanchai	FROM HOST-GUEST MOLECULAR ASSEMBLY TO NANOCONFINED MORPHOLOGICAL ARRANGEMENT
16.25-16.45	D2-PET1-BIP-I3	-	V. P. Hoven	SURFACE-IMMOBILIZED N-CADHERIN MEDIATED CYCLIC PEPTIDE: A NOVEL PLATFORM FOR STEM CELL
16.45-17.00	D2-PET1-BIP-O1	BIP-O-058	M. Baru	PREPARATION AND CHARACTERISATION OF A NOVEL INJECTABLE RESPONSIVE HYDROGEL BASED CHITOSAN
17.00-17.15	D2-PET1-BIP-O2	BIP-O-066	M. Matsumoto	DEVELOPMENT OF BIODEGRADABLE PEPTIDE NANOSPHERE COVERED WITH DETACHABLE AND ATTACHABLE HIGH-DENSITY PEG BRUSHES
17.15-17.30	D2-PET1-BIP-O3	BIP-O-075	T. Leeteera	FABRICATION AND CHARACTERIZATION OF SILK FIBROIN PROTEIN HYDROGEL

DATE : 12.01.2012		TIME SLOT : D2		ROOM : NOPHAKAO 3
15.45-16.05	D2-NOP3-BIP-I1	-	D. S. Lee	DESIGN OF pH AND TEMPERATURE SENSITIVE BLOCK COPOLYMERS FOR DRUG DELIVERY AND MOLECULAR IMAGING
16.05-16.25	D2-NOP3-BIP-I2	-	T. Srikhirin	DEVELOPMENT OF SURFACE PLASMON RESONANCE IMAGING (SPRI) PROTEIN ARRAY FOR THE HIGH THROUGHPUT CLINICAL AND BILOGICAL SCREENING
16.25-16.40	D2-NOP3-BIP-O1	BIP-O-001	N. Nakthong	THE BIOCOMPATIBLE EPOXY-CLAY NANOCOMPOSITE FOR IMPLANTED ELECTRONIC DEVICE ENCAPSULATION
16.40-16.55	D2-NOP3-BIP-O2	BIP-O-059	T. Wangkam	APPLICATIONS OF SURFACE PLASMON RESONANCE TECHNIQUE FOR MEDICAL SENSOR : MITE ALLERGY DETECTION
16.55-17.10	D2-NOP3-BIP-O3	BIP-O-062	N. Woramongkolchai	siRNA DELIVERY INTO A HUMAN CERVICAL CANCER CELL USING A CATIONIC NANOPARTICLE-POLYETHYLENEIMINE-INTRODUCED CHITOSAN SHELL/POLY(METHYL METHACRYLATE) CORE NANOPARTICLES
17.10-17.25	D2-NOP3-BIP-O4	BIP-O-074	K. Karnpakdee	POTENTIAL DEGRADATION OF r-PMMA/PMMA-BLENS-PU/ECOFLEX SHEET IN CASTING CAST PROCESS

CHEMISTRY FOR ENGINEERING & INDUSTRY

DATE : 12.01.2012				
TIME SLOT : A2			ROOM : PETCHARAT 2	
08:30-08:50	A2-PET2-IEN-O1	ENG-O-002	J. Phromprasit	SORPTION ENHANCED BIOGAS STEAM REFORMING FOR HYDROGEN PRODUCTION USING NICKEL OVER ALUMINA CATALYST AND CALCIUM OXIDE
08:50-09:10	A2-PET2-IEN-O2	ENG-O-008	K. Tangpanithandee	KINETIC STUDIES OF ISOMERIZATION OF 1-BUTENE TO TRANS- AND CIS-2-BUTENE OVER CAO CATALYST
09:10-09:40	A2-PET2-IEN-I1	-	S. Saka	RECENT PROGRESS IN NON-CATALYTIC BIODIESEL PRODUCTION BY SUPERCRITICAL FLUID TECHNOLOGIES
09:40-10:10	A2-PET2-IEN-I2	-	T.Rochanapruk	THE CHALLENGE OF DOING AN EPC PROJECT IN THAILAND
10:10-10:40	A2-PET2-IEN-I3	-	S. Charoenchaidet	A TREND OF POLYOLEFIN CATALYST DEVELOPMENT FOR FUTURE PRODUCTION IN THAILAND

DATE : 12.01.2012				
TIME SLOT : E2			ROOM : PETCHARAT 2	
11:00-11:30	E2-PET2-IEN-I1	-	T. Kondo	RUTHENIUM-CATALYZED OLIGOMERIZATION AND CO-OLIGOMERIZATION OF ALKENES WITH HIGH ATOM-EFFICIENCY
11:30-11:50	E2-PET2-IEN-O1	ENG-O-009	W. Wibowo	CATALYTIC REACTION OF CASHEW NUT SHELL LIQUID WITH METHANOL USING KNAX ZEOLITE AS CATALYST FOR THE APPLICATION OF BIOLUBRICANT
11:50-12:10	E2-PET2-IEN-O2	ENG-O-010	N. Malailak	HYDRODESULFURIZATION OF DIBENZOTHIOPHENE OVER CoMo SUPPORTED ON Al_2O_3-TiO_2 MIXED OXIDE SUPPORTS

DATE : 12.01.2012	TIME SLOT : C2			ROOM : PETCHARAT 2
13:00-13:20	C2-PET2-IEN-O1	ENG-O-005	S. Sangribsub	REACTIVE COMPATIBILIZER FROM POLYETHYLENE WAX OBTAINED AS BY-PRODUCT IN HIGH DENSITY POLYETHYLENE PLANT
13:20-13:50	C2-PET2-IEN-I1	-	M. Kubo	QUANTUM CHEMICAL MOLECULAR DYNAMICS SIMULATIONS ON CHEMICAL REACTION DYNAMICS IN MECHANICAL SYSTEM
13:50-14:10	C2-PET2-IEN-O2	ENG-O-001	L. Baingam	STUDY ON MECHANISM OF MAGNESIUM SULFATE ATTACK ON HARDENED CEMENTITIOUS SYSTEM BY USING COMPUTATION METHODS
14:10-14:30	C2-PET2-IEN-O3	ENG-O-004	A. Thirasak	BRIDGING FUNDAMENTAL TO INDUSTRIAL APPROACH: THE APPLICATION OF QUANTUM MECHANICS SIMULATION FOR SOLVENT SCREENING METHOD OF EXTRACTIVE DISTILLATION
14:30-14:50	C2-PET2-IEN-O4	ENG-O-012	K. Pornsuksawang	REGRESSION MODEL OF THERMAL CRACKING FOR OLEFINS PRODUCTION

DATE : 12.01.2012	TIME SLOT : D2			ROOM : PETCHARAT 2
15:00-15:30	D2-PET2-IEN-I1	-	T. Sato	DESIGN AND FABRICATION OF CERIA-BASED CERAMIC MATERIAL FOR ENVIRONMENT CLEAN-UP
15:30-16:00	D2-PET2-IEN-I2	-	H. Hessenkemper	NEW DEVELOPMENTS IN GLASS TECHNOLOGY
16:00-16:20	D2-PET2-IEN-O1	ENG-O-013	I. Hastiawan	THE COMPARISON OF CYANIDATION AND CHLORINATION GOLD RECOVERY FROM GOLD ORE OF HALMAHERA INDONESIA
16:20-16:40	D2-PET2-IEN-O2	ENG-O-003	N. Lertlukkanasuk	REACTIVE DISTILLATION FOR SYNTHESIS OF GLYCEROL CARBONATE VIA GLYCEROLYSIS OF UREA
16:40-17:00	D2-PET2-IEN-O3	ENG-O-011	W.Uraisakul	IMPROVEMENT OF DEHYDROGENATION REACTION IN ISOPROPANOL/ACETONE/HYDROGEN CHEMICAL HEAT PUMP USING REACTIVE DISTILLATION SYSTEM BY FLUIDIZATION
17:00-17:20	D2-PET2-IEN-O4	ENG-O-006:	T. Therdjittoam	PREPARATION OF POLYIMIDE COPOLYMER BASED FOR NANOPOROUS POLYIMIDE FILM
17:20-17:40	D2-PET2-IEN-O5	ENG-O-007	K. Peeraporntam	HIGH THERMAL CONDUCTIVITY OF POLYIMIDE/SILICON NITRIDE COMPOSITE FILMS