รายงานวิจัยฉบับสมบูรณ์

โครงการ การพัฒนาวัสดุทดแทนไม้จากระบบสารเติมปริมาณสูงของผงไม้และเบนซอกซาซีนเรซิน

โดย ผศ.ดร. ศราวุธ ริมดุสิตและคณะ

กรกฎาคม พ.ศ. 2547

สัญญาเลขที่ TRG4580048

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ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์
จุฬาลงกรณ์มหาวิทยาลัย

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

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ชื่อโครงการ การพัฒนาวัสดุทดแทนไม้จากระบบสารเติมปริมาณสูงของผงไม้และเบนซอกซาซีนเรซิน

ชื่อนักวิจัย : ผศ.ดร. ศราวุธ ริมดุสิต (Dr. Sarawut Rimdusit)
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
โทรศัพท์ 0-218-6862, 0-9449-7598 โทรสาร 0-2218-6877

E-mail Address: sarawut.r@chula.ac.th

ระยะเวลาโครงการ : 1 กรกฎาคม พ.ศ. 2545- 30 มิถุนายน พ.ศ. 2547

งานวิจัยนี้เป็นการพัฒนาวัสดุประกอบแต่งสำหรับทดแทนไม้จากพอลิเบนซอกซาซีนซึ่งทำหน้าที่เป็นเมตริกซ์ และใช้ผงไม้ยางพาราเป็นสารเติม ซึ่งวัสดุประกอบแต่งประเภทที่ใช้ผงไม้หรือขี้เลื่อยเป็นสารเติมจะสามารถทำให้ลดต้นทุนในการผลิตและเพิ่มมูลค่าของวัสดุเหลือใช้หรือวัสดุที่ใช้แล้วและนำกลับมาใช้ใหม่ ผลของขนาดอนุภาคและปริมาณของผงไม้ยางพาราต่อสมบัติทางความร้อน สมบัติทางกล และสมบัติทางกายภาพของวัสดุพอลิเมอร์ประกอบแต่งที่ได้ พบว่า คุณสมบัติทางความร้อน คือ ค่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วและอุณหภูมิการสลายตัว (Tg, Td) มีค่าสูงถึง 200 และ 275 องศาเซลเซียสตามลำดับ ปริมาณของเถ้ามีค่าเพิ่มขึ้นอยู่ในช่วง 33.7-36.3 เปอร์เซ็นต์ เมื่อเปรียบเทียบกับพอลิเบนซอกซาซีนซึ่งมีค่าเท่ากับ 27.7 เปอร์เซ็นต์ สำหรับคุณสมบัติทางกล คือ ค่าสโตเรจมอดูลัสมีค่าค่อนข้างสูง เมื่อเปรียบเทียบกับกรณีที่ไม่ได้เติมผงไม้ในพอลิเบนซอกซาซีน (เช่น สโตเรจมอดูลัสมีค่าเป็น 3.85 GPa กรณีเติมผงไม้เท่ากับ 75 เปอร์เซ็นต์โดยน้ำหนัก และ 2.33 GPa ในกรณีไม่เติมผงไม้) และเมื่อขนาดของอนุภาคและปริมาณสารเติมเพิ่มขึ้น พบว่า ค่าสโตเรจมอดูลัสและค่ามอดูลัสของการดัดโค้งจะมีค่าเพิ่มสูงขึ้น ส่วนในกรณีของค่าความแข็งแรงในการดัดโค้งมีแนวโน้มลดลงเมื่อปริมาณผงไม้เพิ่มขึ้น ค่าการดูดซึมน้ำต่ำประมาณ 17 เปอร์เซ็นต์โดยน้ำหนัก ที่สภาวะอิ่มตัว เมื่อเทียบกับไม้ธรรมชาติซึ่งมีความสามารถในการดูดซึมน้ำได้สูงถึง 30-200 เปอร์เซ็นต์โดยน้ำหนัก และปริมาณผงไม้ที่เติมได้สูงสุดโดยชิ้นงานยังสามารถรับแรงได้เทียบเท่ากับไม้ธรรมชาติเท่ากับ 75 เปอร์เซ็นต์โดยน้ำหนัก (ประมาณ 50 เปอร์เซ็นต์โดยปริมาตร) รูปจากกล้องจุลทรรศน์แบบส่องกราดแสดงให้เห็นว่าผงไม้และพอลิเบนซอกซาซีนเมตริกซ์สามารถยึดเกาะกันได้ดี จึงส่งผลต่อค่ามอดูลัสและความเสถียรทางความร้อนที่สูงดังกล่าว

คำหลัก : Wood composites, Highly filled systems, Polybenzoxazine

Project Code : TRG4580048

Project Title : Development of wood-substituted materials based on highly filled systems of wood flour and benzoxazine resin

Investigator : Asst. Prof. Sarawut Rimdusit), Ph.D.

Dept. Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330

Tel: 0-218-6862, 0-9449-7598 Fax: 0-2218-6877

E-mail Address: sarawut.r@chula.ac.th

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In this study, composites made from a polybenzoxazine matrix and woodflour have been prepared and tested. The objectives of the study are to determine the influence of the particle size and percent filler content of woodflour on their thermal, mechanical (flexural test) and some important physical properties. The glass transition temperature and the degradation temperature of these woodflour-filled polybenzoxazine composites were found to have relatively high values up to 200°C and 273°C, respectively. The char yield of woodflour-filled polybenzoxazine composite is up to 33.8-36.3 % which is significantly higher compared to that of the neat resin, i.e. 27.7 %. The mechanical properties of the composites were also strongly affected by the woodflour content, i.e. having the storage modulus of 3.85 GPa in the 75 % by weight filled systems vs. 2.33 GPa of the unfilled system. The storage modulus and flexural modulus were found to increase with the filler content and particle size of woodflour whereas the flexural strength decreases. Water absorption shows the value of about 17 % by weight at saturation when compare to that of natural wood, i.e. between 30 and 200 % by weight. The maximum filler content which the specimen can still support the load at the level comparable to the natural wood is approximately 75 % by weight or 50 % by volume of woodflour. The good interfacial adhesion of woodflour and polybenzoxazine matrix is one key contribution to the desirable high modulus and high thermal stability of the resulting composite and was also confirmed by the SEM micrograph.

Keywords : Wood composites, Highly filled systems, Polybenzoxazine

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INTRODUCTION

General Introduction

Wood is an important raw material, which has been used by human beings since early years. The reason for its diverse and great utilization is related to its good physical strength, aesthetically pleasing characters, and low processing cost (Deka and Saikia, 2000). As the world economy ascends to a new stage, demand for wood increases proportionally. Current statistics show that the timber trade in the world market has exceeded 1,500 million m^3. The demand for good-quality timber will lead to nonrenewable logging of tropical hardwood forests in many developing countries, and give rise to serious global concern, especially in Asian countries. Indonesia's current dominance of export market is expected to end within 20 years at present rates of logging, while Thailand has banned all commercial logging in its hardwood forests. Therefore, a rise in the cost of natural timber products is expected in the near future (Chen et al., 1998). The development of new materials with the natural wood's properties to be used for substituting natural wood can partially reduce the consumption of natural wood.

Wood composite provide a unique combination of material properties and; therefore, can substitute many conventional materials. The combination of three driving forces has created an opportunity for advanced composite materials (Simonsen, 1996). The first driving force is the continuing population explosion, which has created a growing worldwide demand for building materials. The second driving force is the municipal solid waste crisis. Probably the most popular response to the municipal solid waste problem has been recycling, i.e., paper, glass, and metals. The third driving force creating an opportunity for composites is the increase in price and decrease in the availability of wood. Polymeric matrices reinforced with special wood fillers are enjoying rapid growth due to their many advantages (Glasser et al., 1999), such as light weight, reasonable strength, and stiffness. The processing is flexible, and economical. On the other hand, the use of waste wood will help solving the severe environmental problem.

There are two types of matrices for wood-polymer composite. The first type is thermoplastic i.e. polyethylene, polypropylene, polystyrene, polyvinyl chloride, and ABS, in which the filler in a form of wood particle, is dispersed into a thermoplastic matrix. Many researches in recent years have gained much attention in this type of matrix due to

its ability to give promise for improved performance composites that may be produced from recycled materials (Simonsen, 1996). However, the main problem encountered in using this type of matrix is its rather poor interfacial adhesion between the untreated wood particle and the matrix. This behavior results in its characteristics of low strength, low stiffness and high moisture sorption. Another major shortcoming of this type of matrix is that relatively low filler content of less than 50-60 % by weight can be added into the matrix (Takeyasu, 1999). To obtain higher filler content, a modification at the interface between the wood particle and the matrix is required by using some physical and chemical treatments (Bledzki et al., 1998). The effect of treatment wood particle can be improved the interfacial adhesion between wood particle filler and the matrix.

The second type, which has been increasingly used, is thermosetting matrix. This type of matrix is generally used with an introduction of some reinforcement fillers, such as natural fibers and/or particles, to the polymeric matrix (Kharade and Kale, 1998). The thermosetting matrix was first introduced for a commercial purpose in the early 1900s under the trade name ′Bakelite′ which is composed of phenol- formaldehyde and woodflour (Pinchot, 2002). Many efforts have continued on studying in this field over the past decade both from the academic and application points of view. The main application of thermosetting matrix is found in composites, particularly, in the production of particleboard. The addition, it shows promising application in packaging, construction, and automotive industrials. However, due to the problem in shortage of high-quality wood at present, the reconstituted wood materials become the important products of wood-based industries (Marcovich et al., 2001).

Filler particles are often incorporated into polymers to modify their properties to meet performance requirements. A wide variation of mechanical, thermal, and physical properties can be developed through an appropriate compounding of polymer and fillers (Balasuriya et al., 2001). For polymeric matrices, phenolic resin was the first synthetic polymer derived from a condensation of phenol and formaldehyde in the presence of acid or alkaline catalysts and up to now is one of the most widely used thermosetting resins (Antony and Pillai, 1994). The major advantages of phenolics are; high temperature resistance, flame retardancy, chemical resistance, dimension stability, and electrical insulation properties. Thus, traditional phenolic resins have been used in many applications such as construction and automotive industries. However, traditional phenolic resins still have many shortcomings. These include the need of strong acid or

alkaline catalysts in the synthesis step, the release of by-product such as water or ammonia during the processing step, and their brittleness and limited shelf-life (Jang and Yang, 2000). A polymer that we choose as a matrix in this wood-substituted composite is polybenzoxazine.

Polybenzoxazine or oxazine-based phenolic resins are an alternative to traditional phenolics. It is synthesized by the ring-opening polymerization of aromatic oxazines, which can be modified by changing the functional groups on the backbone. Furthermore, it does not produce reaction by-products and can be synthesized via a simple (without strong acid or alkaline catalysts) solventless technology. The resin has been reported to possess some intriguing properties such as low viscosity, low water absorption, high-temperature properties, near-zero volumetric changes upon polymerization, and ease of processing due to self-polymerization upon heating via ring-opening polymerization. The latter property renders no volatile by-products; therefore, giving no void formation in the curing step (Ning and Ishida, 1994a,1994b). Low melt viscosity is one of the outstanding properties of polybenzoxazine which results in the ability to accommodate relatively large quantity of filler. Ishida and Rimdusit (1998) studied the effect of particle size and its distribution on thermal conductivity of boron nitride-filled polybenzoxazine. The authors used large aggregates of flake-like boron nitride crystals and were able to make a composite with a maximum filler content up to 78.5 % by volume (88 % by weight). The extraordinary high thermal conductivity value of 32.5 W/mK at the maximum filler content was achieved.

The Purposes of the Present Study

The objective of this study is to develop a wood composite for high mechanical properties and high thermal stability applications based on a highly-filled polybenzoxazine system. The effect of the particle size and the filler content on thermal, mechanical and some important physical properties of the resulting composites will be evaluated. The investigation utilizes a low viscosity of benzoxazine resin that offers an ability to add greater amount of filler while maintaining processibility of the molding compound. Moreover, the polar nature of both polybenzoxazine and woodflour should render a substantial bonding between the two components thus expected to give good overall composite properties. The good interfacial adhesion of woodflour and polybenzoxazine is one key contribution to the desirable high modulus and high thermal stability of the resulting composites.

EXPERIMENTAL

2.1 Materials

Woodflour (*Hevea brasiliensis*) was supplied by Department of Corrections, Nakorn Si Thammarat Province, Thailand. Bisphenol-A (Commercial grade) was kindly denoted by Thai Polycarbonate Co.,Ltd. (TPCC). Para-formaldehype (AR grade) was purchased from Merck Company, and aniline (AR grade) was from APS Finechem Company. All chemicals were used without further purification.

2.2 Instruments and Equipment

2.2.1 Composition and Density Measurement

The density of woodflour was determined using a gas pycnometer while the composite specimens were tested for the density by using water displacement method (ASTM D972-91). The specimens were disk-shaped with a 51 mm diameter and a 2.0 mm thickness.

2.2.2 Water Absorption

Water absorption measurements were conducted following ASTM D570 using disk-shaped specimens. The dimension of the specimens is 51 mm in diameter and a 3.2 mm in thickness. The composite specimens were first dried and then weighed in an analytical balance (± 0.001g). The determination of moisture content was performed on three specimens at different filler content.

2.2.3 Bending Test

Three point bending tests were carried out at room temperature at a crosshead speed of 1 mm/min and tested by using the support span of 40 mm in a LLOYD Instruments, universal testing machine, Model 2000R. The bending tests or flexural testing was performed according to the procedure of ASTM standard (ASTM D790-92).

2.2.4 Dynamic Mechanical Analysis (DMA)

Polymer laboratories (model DMTA Mk III) was used in these experiments to obtain the glass transition temperature, the storage modulus (E′), and loss tangent (tan δ) of the samples. The tests were carried out by using the temperature scan mode, and the single cantilever bending fixture. The dimensions of the specimen were about 25×5.0×2.0 mm^3. The Amplitude is 16 micron peak-peak, the average strain is 0.016% R.M.S, and the frequency of the forced oscillations was fixed in 1 Hz in the temperature sweep experiment. The specimens were heated at a rate of 2^oC/min from the room temperature to the temperature beyond the glass transition temperature of each composite.

2.2.5 Scanning Electron Microscopy (SEM)

The fracture surface of the composite samples was studied with ISM-5400 Scanning Microscope at an acceleration voltage of 10 kV. The micrograph was used to investigate the adhesion between woodflour filler and polybenzoxazine matrix. The samples were coated with thin film of gold using JEOL model JFC-1100E Ion Sputtering Device before obtaining the micrograph.

2.2.6 Thermogravimetric Analysis (TGA)

The weight loss of the sample as a function of temperature was determined by using TGA. Mettler-Toledo (Model TGA/SDTA851^e). The weight of sample was measured to be 15-20 mg. The specimens were heated at a rate of 20^oC/min from 30^oC to 800^oC under nitrogen purging. The oven was continuously purged with nitrogen during the experiment to remove the released gases and maintain inert conditions.

2.2.7 Differential Scanning Calorimetry (DSC)

Curing behaviors and thermal transitions of the filled and unfilled sample were measured using a differential scanning calorimeter (DSC) model 2910 from TA Instruments. Samples (5-10 mg.) were sealed in aluminum pans. The heating rate used was 10^oC/min from room temperature to 300 ^oC. The experiment was performed under nitrogen purging.

2.2.8 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra were obtained on a Bruker Veotor 33 Spectrometer with 32 scans at a resolution of 4 cm^{-1}. A frequency range of 4000-400 cm^{-1} was observed using a deuterated triglycinesulfate detector (DTGS).

2.2.9 Compression Molding

A hydraulic compression molder was used to fabricate a woodflour filled-polybenzoxazine. All specimens were under a curing of 180 ^{o}C for 2 hr. The spacer used in this work is a stainless steel mold which was cut into various dimensions depending upon types of experiments.

2.3 Methodology

2.3.1 Monomer Preparation

The chemical structure of benzoxazine resin used in this work is shown in Fig. 4.1 and Fig. 4.2. The IUPAC notation of this compounds is bis (3,4-dihydro-2*H*-3-phenyl-1,3-benzoxazinyl) isopropane (abbreviated as BA-a).

This bifunctional benzoxazine monomer is based on bisphenol-A and aniline. The molar ratio of bisphenol-A: para-formaldehyde: aniline was 1:4:2. The benzoxazine monomer is solid at the room temperature. It was ground into fine powder and kept in a refrigerator. The benzoxazine monomer was obtained as a yellow powder. This monomer was synthesized according to the following schemes in Fig. 4.1 and Fig. 4.2 respectively.

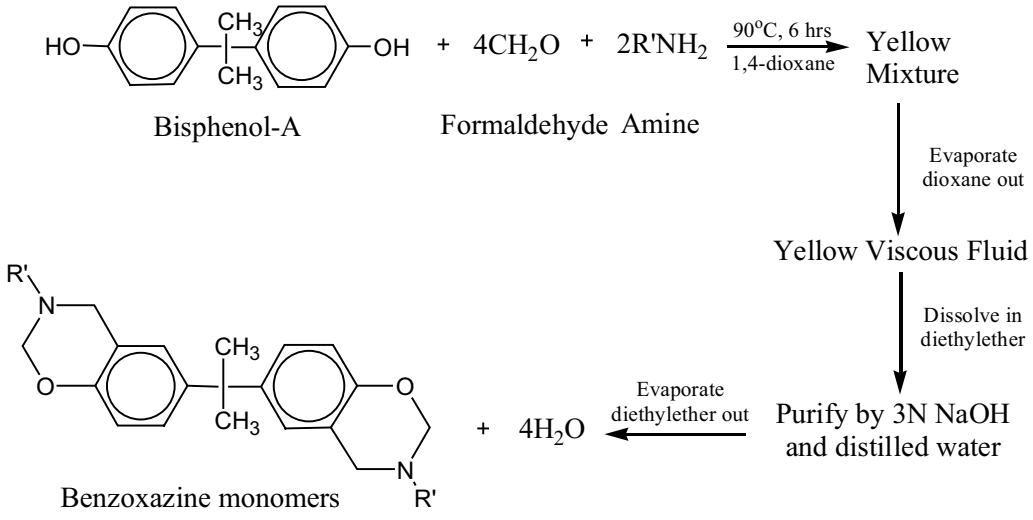

Figure 2.1 Preparation of Benzoxazine-Based Bisphenol-A (BA-a).

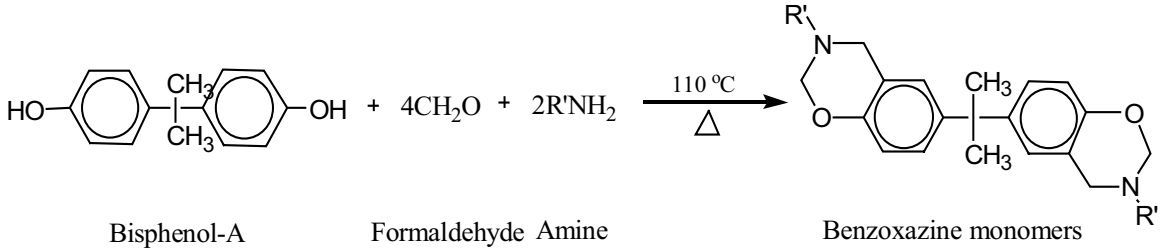

Figure 2.2 Preparation of Benzoxazine-Based Bisphenol-A (BA-a) by using solventless technology.

2.3.2 Preparation of Woodflour

The woodflour from *hevea brasiliensis* was selected for this work because of its availability and this wood is widely grown in Thailand. The density of the woodflour determined by using a gas pycnometer is 1.49 g/cm^3. The particles that pass through a sieve of less than 149 μm, 250-297 μm, and 420-595 μm were used in this study. The over size wood particle was crushed using ball mill apparatus in order to reducing its particle size. All woodflour was dried at 105 ^{o}C for 24 hr in a vacuum oven and was kept in the desiccator.

2.3.3 Processing Method

Woodflour and benzoxazine resin molding compounds were prepared by measuring desirable mass fraction of both components. The mixture was mixed by hand in an aluminum container at 80 ^{o}C for at least 15 min to ensure particle wet out by the resin. The compression-molded compound was shaped using a metal spacer of various dimensions and a curing temperature of 180 ^{o}C. The reaction was carried out under hydraulic pressure of 35 MPa for 2.0 hr. Finally, the specimens were left to cool down at room temperature in the open mold before testing.

2.4 Physical Characterization

2.4.1 Composition and Density Measurement

The density of the woodflour reinforced benzoxazine composites were measured by water displacement method according to the ASTM D792-91 (Method A). The density of benzoxazine (BA-a) was also determined as a reference. The specimens were disk-

shape with a 51 mm diameter and a 2.0 mm thickness. All specimens were weighed both in air and in water.

The density was; therefore, calculated from the following equation:

$$\rho = \left(\frac{A}{A - B} \right) \times \rho_0 \qquad (2.1)$$

Where ρ = Density of the specimen

A = Weight of the specimen in air

B = Weight of the specimen in the auxiliary liquid

ρ_0 = Density of the auxiliary liquid at the given temperature

The average value from three specimens was calculated.

2.4.2 Filler Content (weight/weight) Calculation

The percent filler (woodflour) content was calculated from the completely cured woodflour-filed polybenzoxazine composite with known weight of woodflour and polybenzoxazine composites, according to the following equation.

$$\%\ \text{filler content}\quad (\text{wt/wt}) = \left(\frac{M_{filler}}{M_{composite}} \right) \times 100 \qquad (2.2)$$

Where M_{filler} = Mass of the woodflour in the composite

$M_{composite}$ = Mass of the composite ($M_{filler} + M_{resin}$)

2.4.3 Water Absorption Measurement

Water absorption measurements were conducted following ASTM D570-95 using three disk-shaped specimens having a 51 mm. diameter and a 3.2 mm thickness. All specimens were conditioned in an oven at 50^{o}C for 24 hr. Then cooled in a desiccator and were weighed again to the accuracy of the analytical balance to 4 decimals. The specimens were then immediately immersed in distilled water, and were weighed periodically.

The amount of water absorbed was calculated based on the initial conditioned mass of each specimen from the following equation

$$\text{Water absorbion (\%)} = \frac{\text{wet weight - conditione d weight}}{\text{conditione d weight}} \times 100 \qquad (2.3)$$

Where Wet weight = The weight of woodflour-filled polybenzoxazine composite

Conditioned weight = The weight of woodflour-filled polybenzoxazine composite after water immersion at a certain period of time

2.5 Mechanical Characterization

2.5.1 Bending test

Three point bending tests were used to investigate flexural properties of woodflour-filled polybenzoxazine composites. The specimens were measured according to ASTM D790-92 (Method I). Five specimens with dimensions of 60 mm × 25 mm ×2.4 mm were tested. The modulus of elasticity in bending (E_B) or modulus of elasticity (MOE) and flexural strength (σ_B) or modulus of rupture (MOR) were calculated from the following equations.

$$E_B = \frac{L^3 m}{4bd^3} \qquad (2.4)$$

$$\sigma_B = \frac{3PL}{2bd^2} \qquad (2.5)$$

Where L = Support span

b = Width of beam tested

d = Depth of beam tested

m = Slope of the tangent to the initial straight-line portion of the load deflection curve

P = Load at break on the load-deflection curve of specimen

2.5.2 Dynamic Mechanical Measurement

The dimensions of the specimen were ca. 25 mm × 5.0 mm × 2.0 mm and were tested in temperature sweep mode. The strain was applied sinusoidally with a frequency of 1 Hz. The data were collected at 16^{o}C intervals from 30^{o}C to a temperature above the glass transition temperature of the sample.

The storage modulus (G′), loss modulus (G″), and damping curve (tanδ) were determined. The glass transition temperature was taken as the maximum point on the loss modulus curve in the temperature sweep tests.

2.5.3 Interfacial Characterization

The fractured specimen was secured on a stub, and then coated with gold for 4 min to obtain a thickness of approximately 300 A^{o}. The woodflour/polybenzoxazine interface was then observed in a cross sectional view perpendicular to the fracture surface

RESULTS AND DISCUSSION

3.1 Characterization of Materials

3.1.1 Monomer Characterization

The FT-IR spectra of as-synthesized BA-a are shown in Fig.3.1. The C-H stretching of benzene ring can be detected at 3029 cm^{-1}. The symmetric methylene wagging and twisting bands are shown by weak band at 1370-1250 cm^{-1}. The region from 1490-1460 cm^{-1} is assigned to the methylene antisymmetric deformation. The C-H out-of-plane deformation of the 1, 2, 4-tri-substituted benzene ring can be found in the band centered near 949 cm^{-1}.The band around 1495-1497 cm^{-1} attributes to the tri-substituted benzene ring mode in the oxazine ring structure. The antisymmetric and symmetric C-N-C stretching modes can be found at 1159 cm^{-1} and in the region from 830 cm^{-1} to 740 cm^{-1} respectively. The region of 1240-1210 cm^{-1} is due to the aromatic ether C-O-C antisymmetric stretching, while the symmetric stretching mode appears around 1040-1020 cm^{-1}. For BA-a monomer, the methyl group vibration occurs at 2968 cm^{-1} and 2872 cm^{-1} whereas that of hydroxyl group of the phenolic structure appears at 3421 cm^{-1} (Agag and Takeiche, 2001).

3.1.2 Polybenzoxazine Characterization

The polymerized structure of benzoxazine resin can also be analyzed more thoroughly by FT-IR to determine the nature of the polymerization reactions. Fig.3.1 shows the region from 940-920 cm^{-1} associated with the oxazine ring which almost completely disappeared, indicating a nearly complete loss of the oxazine ring in the benzoxazine monomers. This band agrees well with the frequency predicted for the out-of-plane, out-of-phase hydrogen-wagging mode for 1, 2, 3, 5-tatrasubstituted aromatic ring. This ring substitution is expected if the reaction takes place ortho to the phenolic moiety. The regions associated with the aromatic C-O and aromatic ether C-O-C stretches are nearly absent as well. A new characteristic band of a phenolic C-O species was arise as seen at 1285 cm^{-1} (Ishida and Sanders, 2000).

3.1.3 Woodflour Characterization

According to the FT-IR spectra of woodflour were observed in Fig.3.1, the bands associated with the aromatic and aliphatic C-H stretching are presented at 2900 cm^{-1}. The C-O stretching and the hydroxyl peaks are observed from 1000-1100 cm^{-1} (Hon and Xing, 1992). The bands centered near 1725-1750 cm^{-1} associated with the carboxylic and ester groups were detected. The presence of carboxylic groups in wood leads to its ability to absorb a certain amount of moisture. In addition, the aromatic stretching is shown from 1600-1700 cm^{-1}. Liu and Rials (1998) presented the FT-IR spectra of woodflour after heat treatment. The spectra changed considerably from that of untreated woodflour. The aromatic and aliphatic C-H stretching peak at 2900 cm^{-1} of woodflour decreases after heat treatment when compared to untreated woodflour. This result indicates the loss of some hydrocarbon compounds as volatile. Broad absorption peaks at 3400 cm^{-1} were also detected. This implies that the residual hydroxyl groups still present in the wood. The carbonyl peak at 1725-1750 cm^{-1} was reduced in comparison to both the 3400 cm^{-1} and 1000-1100 cm^{-1} peaks as well as the aromatic stretching around 1600-1700 cm^{-1}, indicates a loss of this functionality from the surface due to the decomposition of lignin (Hon and Xing, 1992). The peak at 730 cm^{-1} was also greatly reduced after heat treatment. This phenomenon is due to the reaction of the alkene functionality presenting in the untreated woodflour during heat treatment.

The DSC thermograms of woodflour are shown in Fig.3.2. In the past investigation (Marcovich et al, 2001), the endothermic peak at temperature between 80^{o}C and 120^{o}C on a thermogram was assigned to the vaporization of water in woodflour. Since wood is a hygroscopic material, it always contains a certain amount of water. All the hydroxyl and carboxylic groups in the wood are capable of absorbing moisture. This phenomenon is also observed in the FT-IR spectra of Fig.3.1 as a broad absorption peak at 3400 cm^{-1} due to the presence of abundant hydroxyl groups. The endothermic peak of woodflour after heat treatment was reduced when compared with untreated one confirming the water evaporation thermal event of the peak. An exothermal peak at about 315^{o}C was observed and was assigned to the primary thermal decomposition of hemicellulose and the cleavage of the glycosidic linkages of cellulose as well as the decomposition of lignin. The depolymerization may be accompanied by dehydration of sugar units in cellulose, which gives unsaturated compounds and a variety of furan derivatives. The rearrangement and condensation reactions, which occurred during thermal depolymerization, contribute to the exothermic reactions (Hon and Xing, 1992),

and the reaction at relatively high temperature between 350°C and 450°C was assigned to a predominant thermal decomposition of lignin.

3.2 Properties of Benzoxazine Resin

Benzoxazine-based phenolic resins are expected to yield significant advantages over many other plastics materials. Synthesized from inexpensive raw materials, the polymerization occurs by a simple ring-opening addition reaction and does not yield any reaction by-products. Benzoxazines cure without the aid of the strong acid catalysts required by other phenolic materials. The purified monomer compound is then heated to open the ring. The ring-opening thermal polymerization is typically achieved in a temperatures range between 150°C and 220°C. At this temperature range, gelation of multifunctional benzoxazine resins takes place at a time interval ranging from a few minutes (using initiators) to ten minutes and more if no initiators are employed (Ishida, 1998).

3.3 Properties of Molding Compounds

3.3.1 Effect of Filler Content and Particle Size on Curing Temperature

DSC thermograms in the temperature range of 35-300°C at the heating rate of 10°C/min of woodflour-filled benzoxazine resin at different filler content are shown in Fig. 3.3. The thermograms at all filler content show the curing exotherms with the same peak maxima of 225°C, which is a characteristic of the thermal curing of this type of benzoxazine resin (Ishida, 1998). This implies that the woodflour content has no effect on the curing process of the benzoxazine monomers. In addition, the filler content affect the curing thermograms in such a way to decrease the area under the exothermic peaks. Moreover, the step change of the thermograms at the temperature about 45°C at different filler content is the glass transition temperature of the benzoxazine monomer, Tgo. The endothermic peaks at the temperature between 50°C and 120°C were likely due to the vaporization of water in woodflour as explained in Fig.3.2. The positions of all peaks shifted to higher temperature with increasing woodflour content in the molding compounds. The presence of a less hydrophilic benzoxazine monomer on the wood surface seems to be able repel the adsorbed water in woodflour; therefore, water can be

released from the molding compounds more readily with increasing benzoxazine monomers.

Fig.3.4 shows the curing exotherms of the mixtures between benzoxazine resin and woodflour at 50 % by weight with different particle sizes. The thermograms at every particle size show the curing exotherms with the same peak maxima at 225^{o}C. Consequently, we can conclude that woodflour particle size shows no effect on the curing behaviors of its benzoxazine molding compounds. However, fillers as well as modifying agents are known to have varying degrees of catalytic or retarding effects on thermosetting curing. Among these, alumina trihydrate strongly inhibited the cure of polyester resins while zirconium silicate inhibited the cure only slightly. The curing temperature of benzoxazine-epoxy copolymers shows an increase in the degree of retardation with increasing amount of epoxy resin (Rimdusit and Ishida, 2000). However, Kharade et al., (1998) had shown that the curing characteristics of novolac resins were relatively unaffected by the presence of agro-based biomass similar to our systems. The results obtained from Fig.3.3 and Fig.3.4 can be used as a database for choosing the suitable processing condition of the molding compounds i.e. curing temperature below 200^{o}C to avoid thermal degradation of wood. As a general rule, curing or melting temperature should be kept below 200^{o}C at the presence of woodflour, except for only short periods. Higher temperature can result in the release of volatile or odor, discoloration, and embrittlement of the wood component (Youngquist, 1999).

3.3.2 Processing Conditions of the Molding Compounds

Fig.3.5 exhibits the DSC thermograms of the mixtures of benzoxazine resin and 40 % by weight of woodflour using particle size of less than 149 μm at various curing time. All specimens were cured isothermally at 180^{o}C. The figures suggested the time suitable for the complete cure of benzoxazine molding compounds to be 2 hr at 180^{o}C as indicated by the disappearance of the exothermic peak between 160^{o}C and 225^{o}C. The reason for selecting curing temperature of 180^{o}C is shown in Fig.3.6. This figure indicated the dynamic mechanical spectra of woodfour-filled polybenzoxazine composites using constant curing time of 2 hr at different curing temperature. The curing temperature at 180^{o}C was found to yield the highest storage modulus indicating a completely cured specimen without or with minimum degradation. As a consequence, the

curing temperature at 180^{o}C for 2 hours was chosen as an optimum curing condition of these benzoxazine molding compounds

3.4 Physical Characterization

3.4.1 Density Measurement

The general problem in using wood and cellulose fibers/particle together with a thermoplastic polymer is the occurrence of agglomeration due to insufficient dispersion because of its high viscosity when it melts. Therefore, wood and cellulose fibers/particle can be incorporated into a thermoplastic polymer of less than 50-60 % by weight. Recently, Takeyasu, (1999) reported woodflour-filled polyvinyl chloride composites at 55 % woodflour content and woodflour-filled polyethylene composites or polypropylene composites shown 60 % woodflour. In some cases; the filler content of woodflour in composites can be increased by doing surface treatment with either chemical or physical methods. However, these will likely result in a higher production cost of the composites (Bledzki at el., 1998).

One outstanding property of polybenzoxazine is its low melt viscosity in which the highly-filled composite can easily be obtained. The density of the composites at room temperature was calculated using equation 2.2. The density of woodflour-filled polybenzoxazine composites as a function of filler content is shown in Fig.3.7. The theoretical densities of the composites were calculated from the mixing rule based on the woodflour density of 1.49 g/cm^3 (measured by gas pycnometer) and the polybenzoxazine density of 1.12 g/cm^3 (a published value). The maximum packing density of the filler was defined by the maximum value of density observed, corresponding to its theoretical density. If the woodflour was filled over its maximum packing, density, it will lead to the reduction of the real density to be lower than the theoretical density due to the presence of void in the specimens. Air gap will be the third phase in the specimen and will lower the density of the specimen. The woodflour particles having a size of less than 149 μm is used in this investigation. From the experiment, we were able to make a specimen with a maximum packing density up to about 75 % by weight of woodflour. The attempt to add woodflour beyond 75 % by weight tended to decrease the observed composite packing density to a value lower than the theoretical density. For example, the theoretical density of 80 % by weight of woodflour filled polybenzoxazine should equal 1.40 g/cm^3; however, the real density was measured to be 1.37 g/cm^3 etc.

3.4.2 Water Absorption

Fig.3.8 shows the water absorption of the woodflour-filled polybenzoxazine at different woodflour contents ranging from 40 to 80 % by weight for up to 120 days. As the woodflour content increases, the water absorption increases as expected. Typically, the water absorption of woodflour based composites largely depends on the availability of the hydrophilic groups, the free-OH and -COOH groups, on the surface of reinforcing woodflour. It is clear that an increase in water absorption should obtain from an increase in the amount of woodflour. Fig.3.8 also shows the effect of woodflour composition on water absorption rate and amount of water absorbed when the steady state is reached. Fig.3.9 examines the variation of water absorption with the particle size of the woodflour content at 50 % by weight. It was observed that water absorption increases in smaller particle size composites. Because a larger surface area of particles should be expected at lower particles sizes consequently, a higher availability of OH groups coming from cellulose which could absorb more water (Ichazo et al.).

The generalized equation for explaining the diffusion in materials can be expressed in equation 2.7. Fig.3.10 illustrates log M_t/M_α versus log t plots which show the slopes ranging from 0.004-0.07. Thus we can conclude that our composite material exhibited a behavior close to pseudo-Fickian type diffusion (Neogi, 1996). The woodflour-filled polybenzoxazine composites of this work are compared with the wood polymer composites of other related works. It is found that, at the same absorption time and filler content, our polybenzoxazine wood composite can absorb water significantly less than those of untreated natural wood-fiber polymer composites, i.e. banana, hemp, and agave fibers in novolac resin. 24-hr water uptake of 50 % by weight of filled specimens, woodflour-filled polybenzoxazine composite has a water absorption value of 2.37 % by weight, while the best result among those three natural wood-fiber novolac composites obtained from the untreated agave-fiber composite has a rather higher water absorption value of 10 % by weight (Mishra, 1998).

In today's wood-polymer composite industry, the content of water absorbed in the wood polymer composite is seriously considered. For example, the tempered hardboard in the range of 2.1 to 9.5 mm in thickness requires the water content of less than 30 to 10 % by weight, or the standard hardboard in the same range thickness requires the water content of less than 40 to 15 % by weight (Youngquist, 1999). According to our

experimental results, at 3.2 mm of thickness (ASTM D570), the water absorption content of our polybenzoxazine wood is in the range of 5 to 25 % by weight which meets the above industrial requirement.

3.4.3 Degradation Temperature of Woodflour-filled Polybenzoxazine Composite

Fig.3.11 exhibits the TGA thermograms of polybenzoxazine and woodflour-filled polybenzoxazine composite at different woodflour contents. From the thermograms, the degradation temperature decreases with increasing the woodflour content due to the degradation temperature of woodflour at 280^{o}C which is lower than that of benzoxazine resin. The degradation temperature as a function of woodflour content is also shown in Fig.3.12. The degradation temperature (reported at 5 % weight loss) of woodflour-filled polybenzoxazine composites in the range of 40 to 80% by weight of woodflour is ranging from 298^{o}C to 275^{o}C under nitrogen atmosphere. The degradation temperature of woodflour-filled polybenzoxazine composite decreased about 25^{o}C to 48^{o}C from the value of 323^{o}C of the neat polybenzoxazine. Another important feature in the thermograms is the percent residue at 800^{o}C or the char yield of the woodflour-filled polybenzoxazine composite.

Fig.3.13 shows the char yield, one of the parameters related to the material flame-resistance, of the neat resin and woodflour-filled polybenzoxazine composite with filler contents ranging from 40 to 80% by weight. The presence of woodflour in the composites is found to enhance the char yield of both the woodflour and the polybenzoxazine. The reason for the observed synergistic behavior in this system is probably due to the substantial interaction between the woodflour and polybenzoxazine matrix via strong chemical bonding. Fig.3.13 indicates that the char yield of the composites increases with increasing the woodflour content up to 60 % by weight and then decreases at higher loading. For example, the char yield of composites of 40 to 60 % by weight of woodflour is 33.8 to 36.3 % and decreases to 33.7 % in the composite at 70 % by weight of woodflour. Exceeding amount of woodflour filler will overcome the effect of strong chemical bonds in char yield enhancement due to much lower inherent char yield value of the woodflour.

3.5 Mechanical Characterization

3.5.1 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis senses any changes in molecular mobility in the sample when temperature is raised or lowered. The dynamic modulus is one of the most important properties of materials for structure applications. Typically, mechanical damping is often the most sensitive indicator in determining all kinds of molecular motions, which are taking place in polymeric materials particularly in the solid state. Fig.3.14 exhibits the dynamic flexural moduli of the woodflour-filled polybenzoxazine composites with filler contents ranging from 40 to 90% by weight with the temperature ranging from 30 to 300^{o}C. The storage moduli (G'), a measure of material elastic properties, of the composites expectedly increase with increasing amount up to 75% by weight of woodflour. Beyond 75% by weight, the modulus value decreases throughout the whole temperature range to a value which is; however, always greater than that of the matrix. At room temperature, the modulus of woodflour-filled polybenzoxazine composite at the filler content of 75% by weight has a value up to 3.85 GPa which is very high compared to that of wood fiber based polyurethane composite i.e. 2.9 GPa, comparing at the same filler content. Moreover, our composite also exhibits a considerably more stable modulus as a function of temperature i.e. glass transition more than 200^{o}C, when compared to woodflour-filled unsaturated polyester/styrene at the same filler content of 75% by weight which has a stable value of only 100^{o}C (Rials and Wolcott, 1998).

Moreover, the moduli of the woodflour-filled polybenzoxazine in the rubbery plateau increase with increasing amount of woodflour. The effect is due to the fact that the load transfer in the composite occurs mainly through the filler particles, in which they are touching each other. Furthermore, the particles introduce an elevated degree of mechanical restraint that reduces the mobility and deformability of the rubber matrix. This behavior is reminiscent of a multiphase copolymer where the plateau modulus increases with increasing volume fraction of a hard component. The transition region between elastic solid and viscous liquid is also affected by a change in the filler content. As shown in Fig.3.14, the curve in transition region is observed to be less steep when the filler content is increased. This may be due to high content of the filler which greatly restricts the motion of the polymer molecules and imparts higher thermal stability to the composites.

The glass transition temperature, Tg, of these unfilled and filled polybenzoxazines can be obtained from the peaks of loss modulus as a function of temperature as shown in Fig.3.15. A large increase of ca. 20 - 60^{o}C in the glass-transition temperature of the neat

resin of 160 ^{o}C was observed with increasing filler content of woodflour from 40 to 75 % by weight. Fig.3.16 is the DSC thermograms of the fully cured polybenzoxazine wood showing the glass transition temperature of the same systems examined in Fig.3.15. From the figure, it confirms the major effect of woodflour filler on the enhancement of glass transition temperature of the resulting composites. The implication of these phenomena is possibly due to the contribution of the good interfacial adhesion between the woodflour filler and the polybenzoxazine matrix mentioned previously. Since the woodflour is known as a high stiffness material, the mobility of the matrix can be highly restricted with this filler when adhering on the filler surface. This can also lead to the large increase in the glass transition temperature of their composites.

Fig.3.17 shows effect of filler contents on the glass transition temperature of woodflour-filled polybenzoxazine composites. As seen in Fig.3.17, the experimental results at the filler contents in range of 40 to 75% by weight show a tendency of linear relationship between the glass transition temperature and the filler content. This linear characteristics is useful for predicting the effect of the filler content on the relevant glass transition temperature. For example, the predicted values of the glass-transition temperatures of the neat resin and the pure wood were extrapolated to be 163^{o}C and 220^{o}C, respectively. These values are relatively close to the values obtained from the experiments in which the glass transition temperatures of the neat resin and the wood were found to be 160^{o}C and 240^{o}C, respectively.

Fig.3.18 is the plots of tanδ versus temperature of woodflour-filled polybenzoxazine composites, which show the increase in the peak maxima of tanδ with increasing filler content of woodflour. These curves become flatter when the filler content is increased due to the introduction of a rigid segment into the polybenzoxazine matrix as mentioned earlier.

3.5.2 Flexural Properties

Generally, the strength of woodflour/fiber-reinforced composites depends on properties of constituents and interfacial interaction between the filler and the matrix. However, when the flexural properties are considered, the homogeneity of the overall composite specimen needs to be taken into account. This homogeneity can be affected by filler distribution and filler wetting. The most important property is viscosity of the matrix that indicates the penetrability into the hollow lumens in woodflour/wood fibers of the

matrix. A property that can indicate the homogeneity of a considering woodflour-filled polybenzoxazine composite is the bending, associated with two sides of the specimen: the "convex" side which is extended, and the "concave" side which is compressed.

3.5.2.1 Flexural Modulus

Fig.3.19 shows a comparative study of the flexural moduli, or modulus of elasticity, of the woodflour-filled polybenzoxazine composites at different filler contents. The flexural modulus increases with increasing filler contents from 40 % by weight to a maximum value at 75 % by weight, and then slightly decreases at higher filler content due to insufficient amount of polymer matrix to wet all the filler particles. Comparing to neat resin, it is found that, at every filler content, the flexural modulus of the woodflour-filled polybenzoxazine composite has a value of which is more than that of the neat resin. At the filler content greater than 75% by weight, the load transfer from the matrix to the filler became less efficient resulting in a drop in the composites' mechanical properties.

Generally, an increase in filler content causes both an increase in the stiffness of the composite and a decrease in the composite strength. A comparison between three different woodflour particle sizes of less than 149 μm, 250-297 μm, and 420-595 μm at the same filler content is made and reveals that the smaller woodflour particles gives lower wettability of the woodflour-filled polybenzoxazine composite. This is due to the corresponding increase in surface area of the particles causing insufficient amount of resin to thoroughly wet the filler surface. At 40 % by weight of filler, our composite has a flexural modulus of 5.60 GPa which is larger than those of wood polymer composites in other related works, i.e. wood-polypropylene composite, aspen-fiber-filled polystyrene, and wood-unsaturated polyester/styrene which have flexural moduli of 3.03, 5.20 and 5.22 GPa respectively. Finally, our woodflour-filled polybenzoxazine gives a flexural modulus value significantly larger than those of commercial products such as particleboard-grade composite, particleboard flooring-product-grade composite, and medium-density fiberboard (MDF) composite which have flexural moduli in range of 0.50-2.75, 1.73-3.10 and 1.40-3.45 GPa (Youngquist, 1999).

3.5.2.2 Flexural Strength

The flexural strength or the modulus of rupture is shown in Fig.3.20. The flexural strength of woodflour-filled polybenzoxazine composite tends to decrease with increasing

the filler content at all three range of particle size. However, as the woodflour content increases the increase in interaction between woodflour i.e. by touching or bridging, resists the uniform distribution of the woodflour filler, resulting in the lower flexural strengths of the composites. In addition, the flexural strength was found to decrease with decreasing the particle size. The lower aspect ratio of the woodflour filler observed in the smaller particle size is probably responsible for the weaker reinforcement compared with that of the fibrous filler (Simonsen at el., 1998). Pinchot (2002) has shown the flexural strength of woodflour-filled polypropylene composite at filler content of 40 % by weight to be 44.2 MPa which is much smaller compared to that of our composite having a flexural strength of 62.8-69.0 MPa at the same filler content. Woodflour-filled polybenzoxazine showed the flexural strength in range 60.0-70.0 MPa which is much stronger than the general property values for particleboard grade requirements 3.0-23.5 MPa, 11.0-19.5 MPa for particleboard flooring product grade requirements, and 14.0-34.5 MPa for the medium-density fiberboard (MDF) property (Youngquist, 1999).

3.6 Interfacial Characterization

The dispersion of woodflour/fibers in polybenzoxazine matrix, the wettability of the matrix on the filler, and the interfacial adhesion between the woodflour/fibers and the matrix has been inspected using Scanning Electron Microscopy (SEM) technique. Typically, the technique revealed the appearance of 3 types of the interfacial adhesion via SEM micrographs, i.e. woodflour/fibers pull-out, woodflour/fibers breakage and fibrillation. The woodflour/fibers pull-out corresponds to poor adhesion. On the other hand, the woodflour/fibers breakage and fibrillation are observed in the fractured surface that implies the existence of some degrees of adhesion between the two components.

These results can be related to the system of this work of the woodflour-filled polybenzoxazine. Fig.3.21 shows morphology of the fracture surface of the woodflour-filled polybenzoxazine composite. Fig.3.21 (a) shows morphology of untreated woodflour surface area which is rather smooth and even. Fig.3.21 (b) and 3.21 (c) show the smooth interfaces between the woodflour filler and the polybenzoxazine matrix. Both woodflour/fiber breakage and fibrillation of woodflour are observed. These effects signify good interfacial adhesion between the woodflour filler and the polybenzoxazine matrix. The property is one of the significant load-transferring to yield high modulus values of

the composite materials. Fig.3.21 (b) and 3.21 (c) also reveal good miscibility of the two phases which helps enhance mechanical mixing leading to the improved dispersion of the woodflour in the polybenzoxazine matrix. As explained in earlier, the woodflour contains cellulose and hemicellulose which have a very strong polar hydroxyl groups and C-O-C links in their structure. This makes the woodflour highly compatible with polar acidic or basic polymers such as the polybenzoxazine.

CONCLUSIONS

The effect of woodflour content and particle size on the thermal, mechanical and some important physical properties can be summarized as follows. From DSC experiment, the fully cured condition of the molding compound is 180^{o}C and 2 hours. Moreover, the exothermic curing peaks were not affected by either the woodflour content or the particle size. The storage modulus (G′) of the composites was found to increase with the woodflour content and reach the maximum value at 75% by weight of woodflour. Beyond woodflour content of 75% by weight, the storage modulus decreases which may be due to the insufficient woodflour wetting in the obtained composites. The behavior may be caused by the formation of tiny void or air gap in the specimens and the results were confirmed by density measurement. The glass transition temperature of the composite was found to increase with woodflour content i.e. from 160^{o}C in the case of the unfilled system to 220^{o}C in the case of 75% by weight of woodflour. This indicates substantial adhesion between the woodflour filler and polybenzoxazine matrix. The flexural modulus at room temperature of the natural rubber wood (*Hevea brasiliensis* wood) is recorded as 9.7 GPa compared to the woodflour-filled polybenzoxazine composite with 75% woodflour content which exhibits the modulus value of 6.8-7.3 GPa. Therefore, the flexural modulus of our wood composite is in the vicinity of that of the natural wood. The highest achievable packing density of the composite having no void in the system is; therefore, 75 %by weight. Scanning electron micrographs show smooth interfaces between the filler and the matrix, which further signifies good interfacial adhesion between the woodflour filler and the polybenzoxazine matrix. In addition, our wood composite shows outstanding properties such as relatively high thermal stability (Tg, Td), high char yield, and low water absorption.

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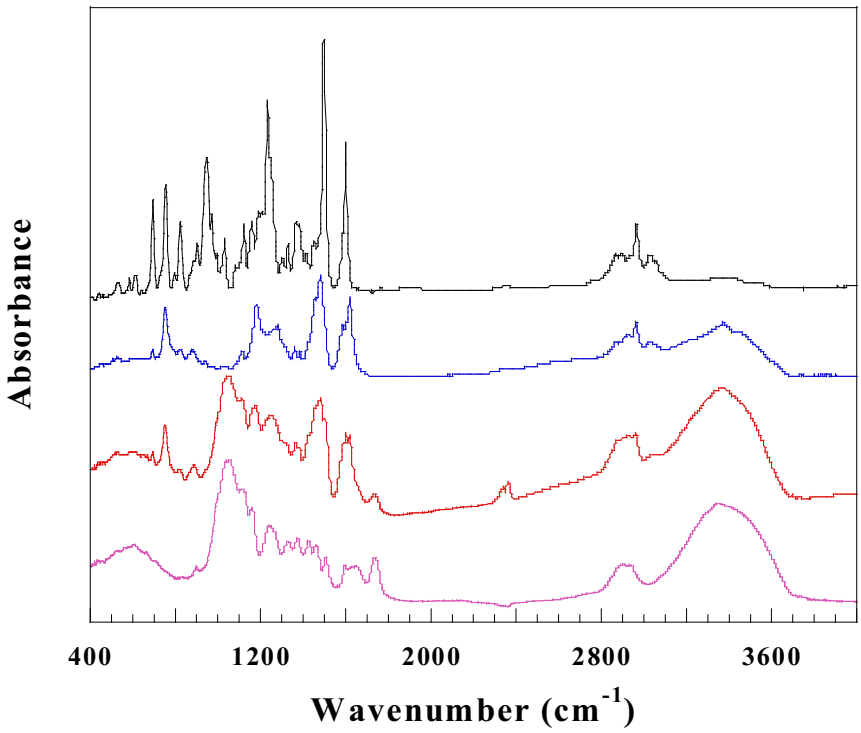

Figure 3.1: IR spectra of benzoxazine monomer, polybenzoxazine, woodflour, and woodflour-filled polybenzoxazine composite. (------) BA-a monomer, (------) polybenzoxazine, (------) 40 wt% WF, (------) woodflour

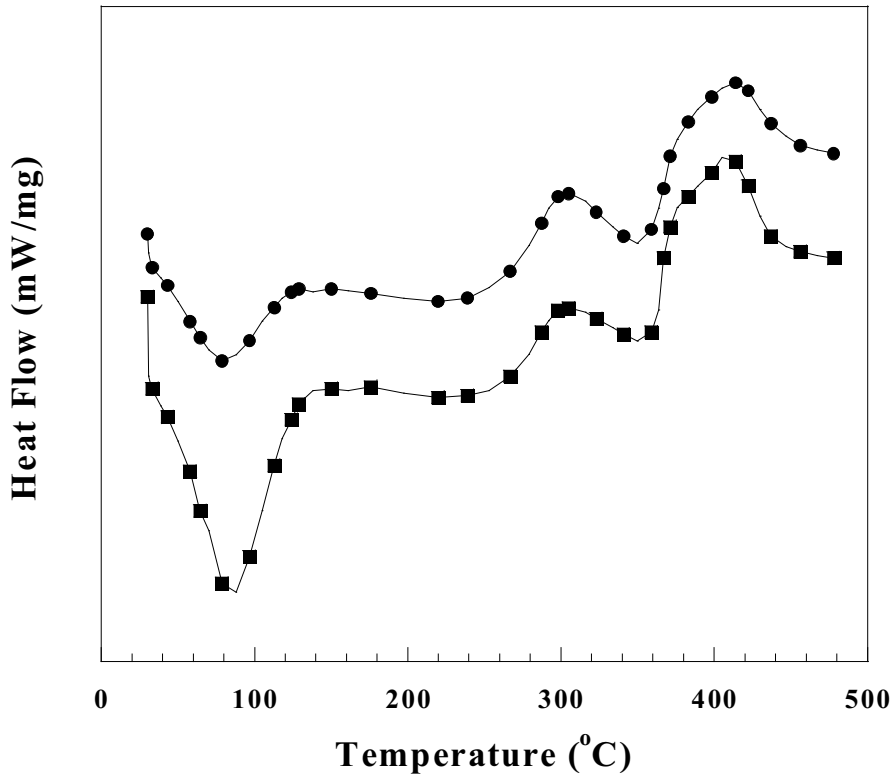

Figure 3.2: DSC thermograms of woodflour (*hevea brasiliensis*) as a function of temperature at particle size < 149 μm. (■) untreated, (□)heat treated.

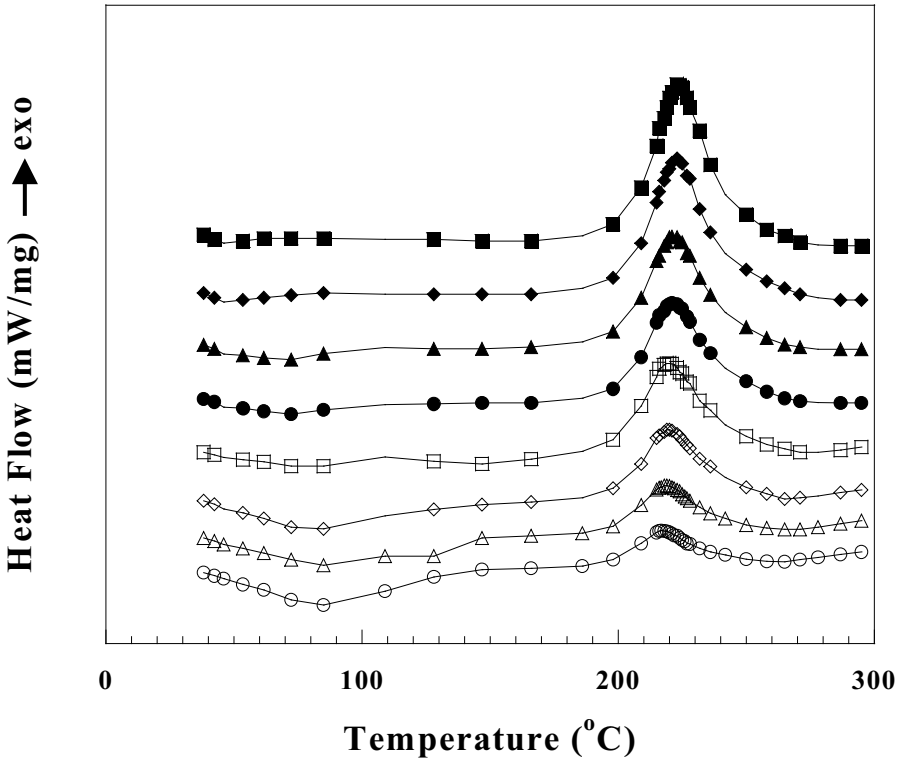

Figure 3.3: DSC thermograms of woodflour-filled polybenzoxazine composite at different filler content. (■) neat resin, (◆) 10 wt% WF, (⁂) 20 wt% WF, (●) 30 wt% WF, (□) 40 wt% WF, (❋) 50 wt% WF, (∆) 60 wt% WF, (○) 70 wt% WF.

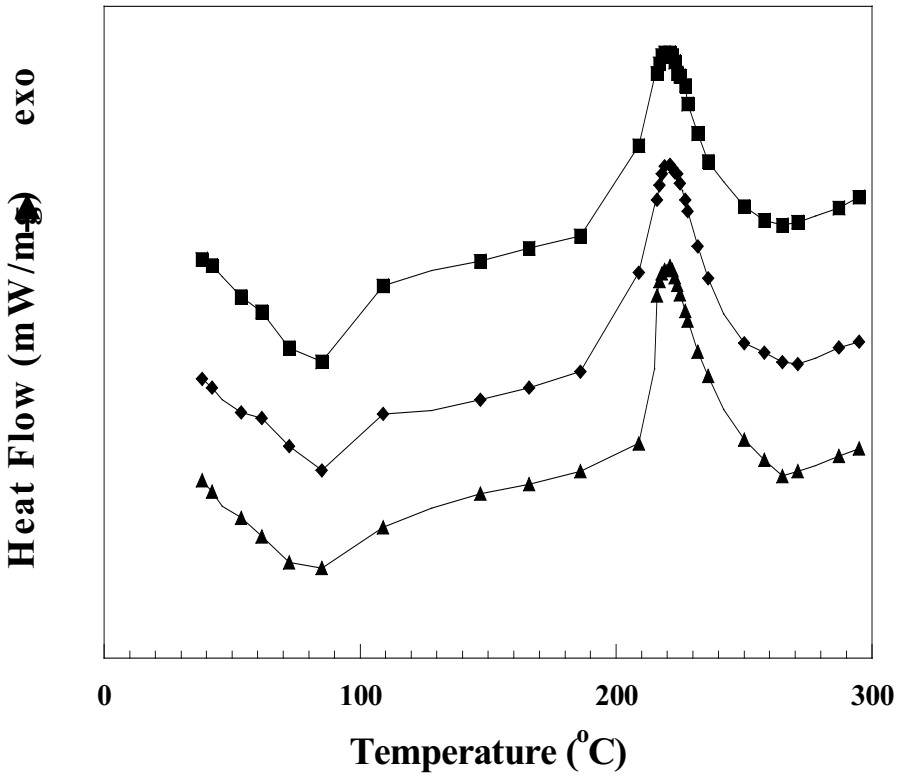

Figure 3.4: Effect of the particle size of woodflour (*hevea brasiliensis*) on curing temperature. (■) 420-595 μm, (◆) 250-297 μm, (▲) < 149μm.

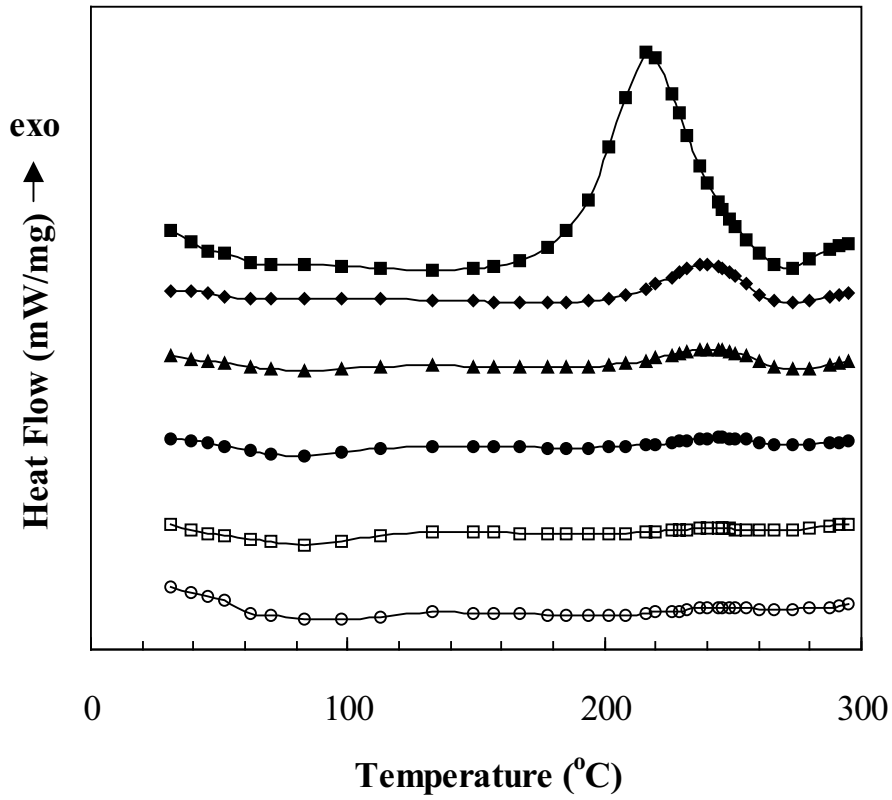

Figure 3.5: Effect of curing time on woodflour-filled polybenzoxazine composite at 40 wt% woodflour content. The condition of curing temperature at 180 °C., (■) 0 min, (◆) 30 min, ( ) 60 min, (●) 90 min, (□) 120 min, (○) 150 min.

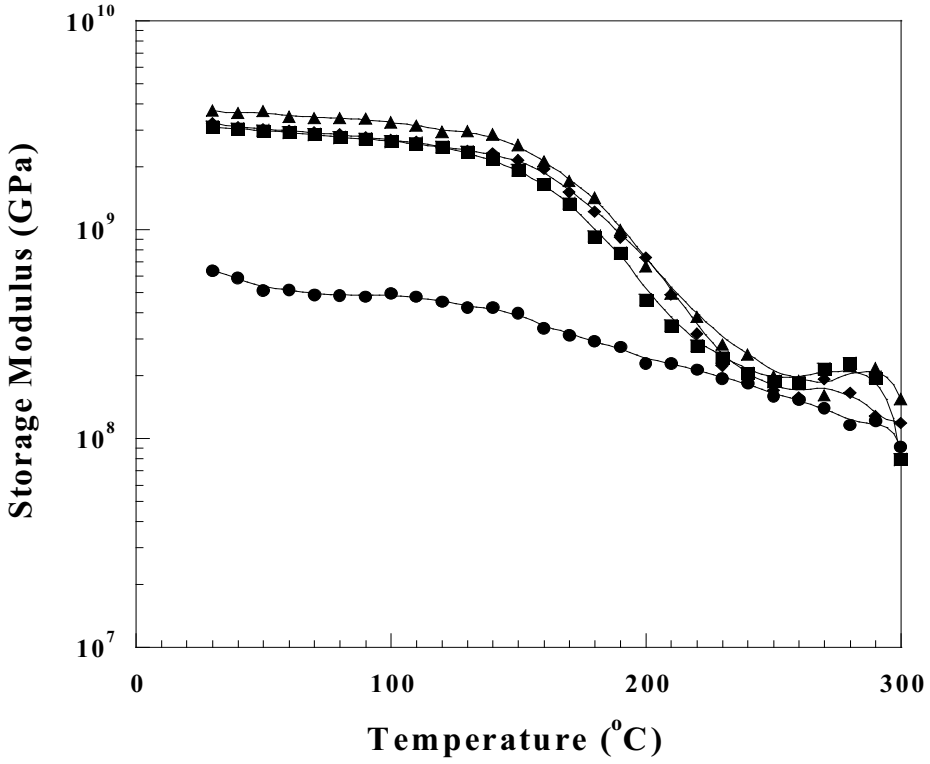

Figure 3.6: Storage modulus of woodflour-filled polybenzoxazine composite as a function of temperature at different curing temperature at 75 wt% of woodflour. (■) 160 °C, (◆) 170 °C, (▲) 180 °C, (●) 200 °C.

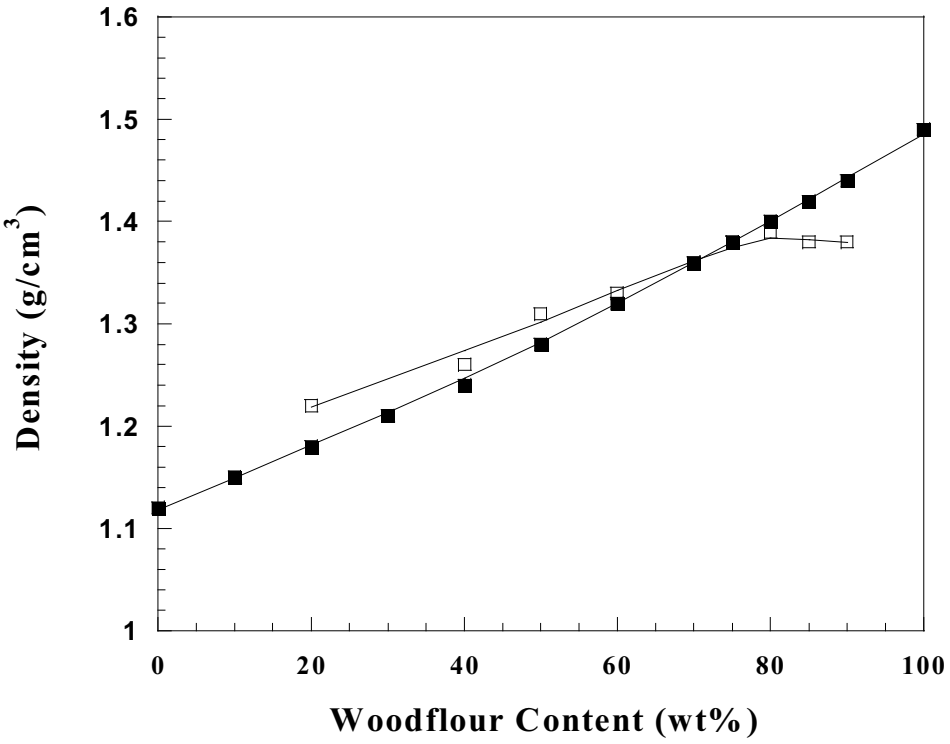

Figure 3.7: The maximum packing density of woodflour-filled polybenzoxazine composite using *hevea brasiliensis* woodflour particle size < 149 μm. (■) theoretical density, (□) experimental density.

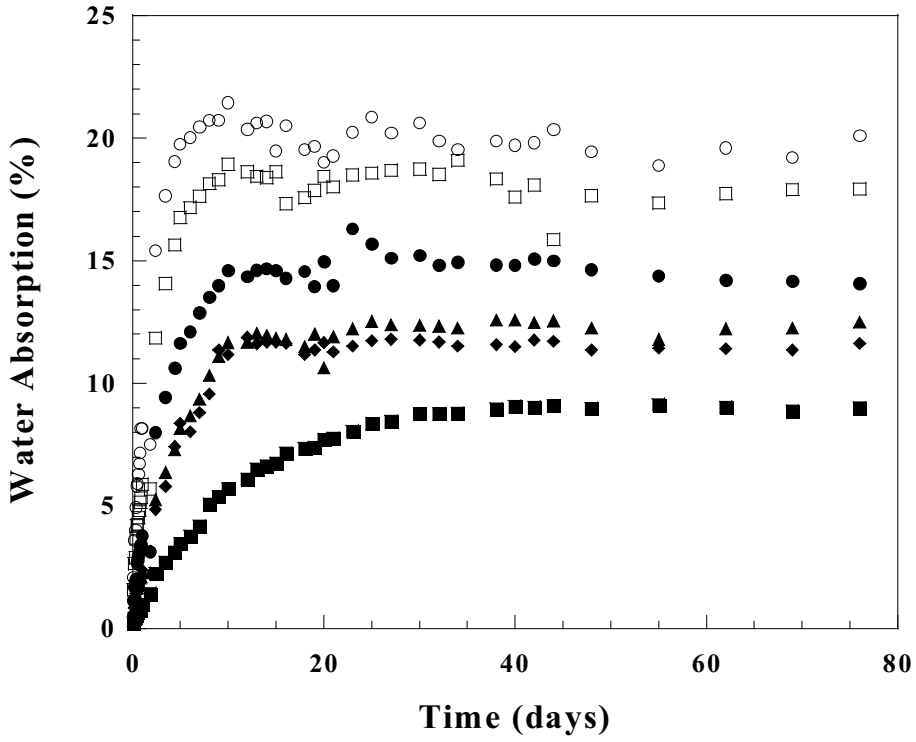

Figure 3.8: Water absorption of woodflour-filled polybenzoxazine composite at different filler content. (■) 40 wt% WF, (◆) 50 wt% WF, (▲) 60 wt% WF, (●) 70 wt% WF, (□) 75 wt% WF, (○) 80 wt% WF.

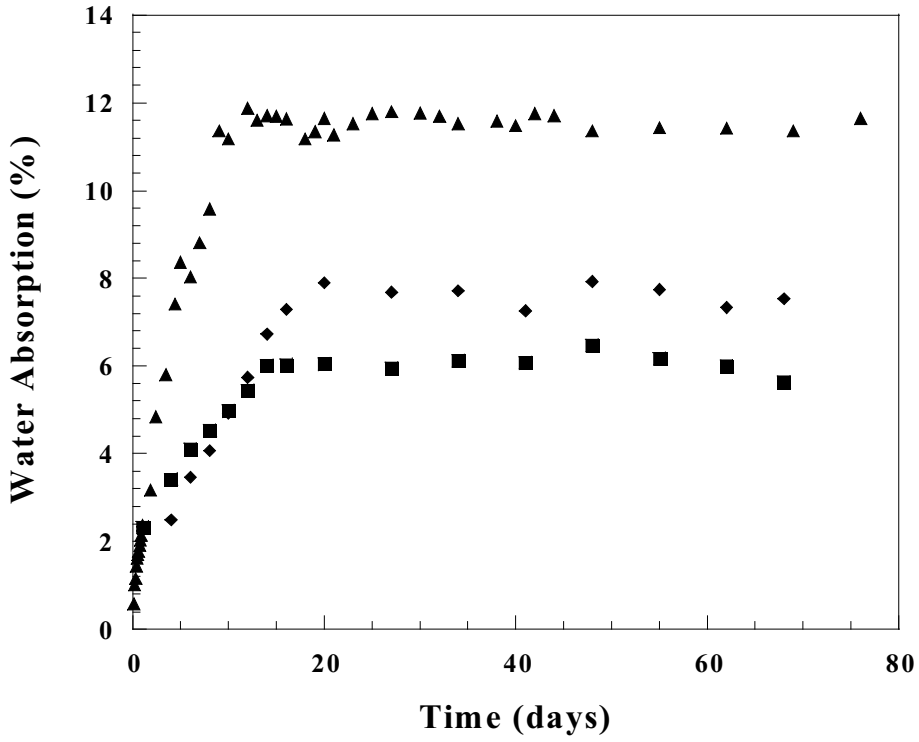

Figure 3.9: Water absorption of woodflour-filled polybenzoxazine composite at 50 wt% of woodflour with different particle size. (■) 420-595 μm., (◆) 250-297 μm, (▲) < 149 μm.