วัสดุประกอบแต่งสำหรับทดแทนไม้โดยใช้ระบบสารเติมปริมาณสูงพอลิเบนซอกซาซีน

นางสาวจันจิรา จับศิลป์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2545

ISBN 974-17-1549-8

WOOD-SUBSTITUTED COMPOSITES FROM HIGHLY-FILLED POLYBENZOXAZINE SYSTEM

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A Thesis submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2002
ISBN 974-17-1549-8

Thesis Title WOOD-SUBSTITUTED COMPOSITES FROM HIGHLY-FILLED POLYBENZOXAZINE SYSTEM
By Miss Chanjira Jubsilp
Field of Study Chemical Engineering
Thesis Advisor Sarawut Rimdusit, Ph.D.

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จันจิรา จับศิลป์ : วัสดุประกอบแต่งสำหรับทดแทนไม้โดยใช้ระบบสารเติมปริมาณสูงพอลิเบนซอกซาซีน
(WOOD-SUBSTITUTED COMPOSITES FROM HIGHLY-FILLED
POLYBENZOXAZINE SYSTEM). อาจารย์ที่ปรึกษา : ดร. ศราวุธ ริมดุสิต, 92 หน้า.
ISBN 974-17-1549-8.

พอลิเบนซอกซาซีนเป็นพอลิเมอร์ชนิดเทอร์โมเซต ซึ่งมีคุณสมบัติที่สำคัญหลายอย่างเหมาะสมต่อการนำไปใช้เป็นเมตริกซ์สำหรับวัสดุประกอบแต่ง เช่น มีค่าความหนืดก่อนการขึ้นรูปต่ำ ค่าการดูดซึมน้ำต่ำ ค่าการขยายตัวทางความร้อนใกล้ศูนย์ ค่าเสถียรทางความร้อนสูง (ค่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วและอุณหภูมิการสลายตัวทางความร้อนค่อนข้างสูง) การติดไฟยาก และไม่ปล่อยสารพิษเมื่อถูกเผาไหม้ งานวิจัยนี้เป็นการพัฒนาวัสดุประกอบแต่งสำหรับทดแทนไม้จากพอลิเบนซอกซาซีนซึ่งทำหน้าที่เป็นเมตริกซ์ และใช้ผงไม้ยางพาราเป็นสารเติม ซึ่งวัสดุประกอบแต่งประเภทที่ใช้ผงไม้หรือขี้เลื่อยเป็นสารเติมจะสามารถทำให้ลดต้นทุนในการผลิตและเพิ่มมูลค่าของวัสดุเหลือใช้หรือวัสดุที่ใช้แล้วและนำกลับมาใช้ใหม่ ผลของขนาดอนุภาคและปริมาณของผงไม้ยางพาราต่อสมบัติทางความร้อน สมบัติทางกล และสมบัติทางกายภาพของวัสดุพอลิเมอร์ประกอบแต่งที่ได้ พบว่า คุณสมบัติทางความร้อน คือ ค่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วและอุณหภูมิการสลายตัว (Tg, Td) มีค่าสูงถึง 200 และ 273 องศาเซลเซียส ตามลำดับ ปริมาณของ Char Yield มีค่าเพิ่มขึ้นอยู่ในช่วง 33.7-36.3 เปอร์เซ็นต์ เมื่อเปรียบเทียบกับพอลิเบนซอกซาซีนซึ่งมีค่า 27.7 เปอร์เซ็นต์ สำหรับคุณสมบัติทางกล คือ ค่าสโตเรจมอดูลัสมีค่าค่อนข้างสูง เมื่อเปรียบเทียบกับกรณีที่ไม่ได้เติมผงไม้ในพอลิเบนซอกซาซีน (เช่น ค่าสโตเรจมอดูลัส 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) นอกจากนี้ผลของความสามารถในการยึดเกาะระหว่างผงไม้และพอลิเบนซอกซาซีนเมตริกซ์ รูปจากกล้องจุลทรรศน์แบบส่องกราดแสดงให้เห็นว่าผงไม้และพอลิเบนซอกซาซีนเมตริกซ์สามารถยึดเกาะกันได้ดี ซึ่งส่งผลต่อค่ามอดูลัสและความเสถียรทางความร้อนที่สูงดังกล่าว

ภาควิชา.......วิศวกรรมเคมี....... ลายมือชื่อนิสิต..

สาขาวิชา.......วิศวกรรมเคมี....... ลายมือชื่ออาจารย์ที่ปรึกษา..

ปีการศึกษา.......2545.......

4470245421: MAJOR CHEMICAL ENGINEERING
KEY WORDS: POLYBENZOXAZINE / WOOD COMPOSITE / HIGHLY-FILLED SYSTEM.

CHANJIRA JUBSILP : WOOD-SUBSTITUTED COMPOSITES FROM HIGHLY-FILLED POLYBENZOXAZINE SYSTEM. THESIS ADVISOR: SARAWUT RIMDUSIT, Ph.D., 92 pp. ISBN 974-17-1549-8.

Polybenzoxazine, a thermosetting polymer, shows some outstanding properties which are suitable for the utilization as a matrix of composite materials such as low viscosity, low water absorption, near-zero shrinkage, high thermal stability (high Tg, Td), low flammability and no toxic by-products from burning. Wood-substituted composites which use woodflour or sawdust as a filler can increase the value and the utilization of waste materials. 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 ^{o}C and 273 ^{o}C, respectively. The char yield of woodflour-filled polybenzoxazine composite is up to 33.8-36.3 % which is somewhat 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.

Department....Chemical Engineering..... Student's signature...............................
Field of study..Chemical Engineering..... Advisor's signature...............................
Academic year. 2002.....................

ACKNOWLEDGEMENTS

The present research receives partial financial support from Industry-University Joint Research Project of Center of Excellence in Particle Technology. TRF Senior Scholar Project (W. Tanthapanichakoon). One of the authors, S.R., also gratefully acknowledges the additional financial support from the Development Grants for New Faculty/Researchers, of CU and of Chemical Engineering Department, Chulalongkorn University.

The author would like to express sincere gratitude to my advisor Dr. Sarawut Rimdusit. With his vision, intelligence, guidance, and kindness throughout the course of this research. I wish to thank the thesis committee for their comments. Thanks are also due to everyone who has contributed suggestions and especially helpful in the writing up of thesis work.

Furthermore, thanks are due to the Thai Polycarbonate Co.,Ltd. (TPCC), and Department of Corrections Nakorn Si thammarat Province, Thailand for their raw materials support. Many thanks are extended to all organization that had generously supported testing facilities. They are Mettler-Toledo (Thailand) Limited for the kind support in the use of Thermogravimetric Analysis from Mr. Wutti Techakasembundit, Product Manager Analytical Instruments of the company, Department of Science, Chulalongkorn University for the use of Fourier Transform Infrared Spectroscopy, and Department of Chemical Engineering, Chulalongkorn University for using Scanning Electron Microscopy in this study.

Additionally, thanks to all my friends especially Mr Benjapol Kongsombut for his edit in the writing of my work and everyone in the Particle Technology and Material Processing, and the Polymer Engineering Laboratory, Chulalongkorn University, for their discussion and friendly encouragement.

Finally, I would like to express love and thanks to my family, for helping to make this part of my life which existed around and through this work the most splendid of times.

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CHAPTER 1

INTRODUCTION

1.1 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.

1.2 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.

CHAPTER 2

THEORY

2.1 Composite Material (Reinhart and Clements, 1987)

A composite material can be defined as a macroscopic combination of two or more distinct materials, having a recognizable interface between them, However, because composites are usually used for their structural properties, the definition can be restricted to include only those materials that contain a reinforcement (such as fibers or particles) supported by a binder (matrix) material. Composite materials were developed because no single, homogeneous structural material could be found that had all of the desired attributes for a given application. The advantage of composites is that they usually exhibit the vast qualities of their constituents and often some qualities that neither constituent possessed. The Properties that can be improved by forming a composite material include strength, stiffness, weight, electrical conductivity, and thermal conductivity.

2.2 Classification and Characterization of Composite Materials.

Composites can be divided into classes at various manners. Depend on the types of matrices, composites can be categorized as polymer matrix composites, metal matrix composites, ceramic matrix composites, carbon-carbon composites, intermetallic composites or hybrid composites. One simple classification scheme is to separate them according to reinforcement forms as follow;

2.2.1 Particulate-Reinforced Composites

Particulate composites which are composed of particles in a matrix. A reinforcement is considered to be a “Particle” if all of its dimensions are roughly equal. Thus, particle-reinforced composites include those reinforced by spheres, rods, flaked, and many other shapes of roughly equal axes. There are also materials, usually polymers, that contain particles that extend rather than reinforce the material.

These are generally referred to as “filled” systems. Because filler particles are included for the purpose of cost reduction rather than reinforcement, these composites are not generally considered to be particulate composites. Nonetheless, in some cases the filler will also reinforce the matrix material. The same may be true for particles added for nonstructural purposes such as fire resistance, control of shrinkage, and enhanced thermal conductivity.

2.2.2 Fiber-Reinforced Composites

Fiber-Reinforced materials which consist of fibers in a matrix. They contain reinforcements having lengths much greater than their cross-sectional dimensions. Such a composite is considered to be a discontinuous fiber or short fiber composite if its properties vary with fiber length. On the other hand, when the length of the fiber is such that any further increase in length does not, for example, further increase the elastic modulus of the composite, the composite is considered to be continuous fiber reinforced, Most continuous fiber (or continuous filament) composites, in fact, contain fibers that are comparable in length to the overall dimensions of the composite part.

2.2.3 Laminated Composites

Laminated composites consist of layers of at least two different materials that are bonded together, sandwich and honeycomb components as well as the term high-pressure laminates are included. Lamination is used to combine the best aspects of the constituent layers in order to achieve a more useful material. Complicating the definition of a composite as having both continuous and discontinuous phases is the fact that in a laminar composite, neither of these phases may be regarded as truly continuous in these dimensions. The properties that can be emphasized by lamination are strength, stiffness, light weight, corrosion resistance, wear resistance, beauty or attractiveness, etc.

2.3 Wood Composites

The term wood-plastic composites (WPCs) refers to any composites that contain wood (of any form as shown in Fig. 2.1) and thermosets or thermoplastics. The wood used in WPCs is most often in particulate form (e.g., woodflour sawdust, etc.,) or very short fibers, rather than longer individual wood fibers. Filler particles are often incorporated into a polymer to modify properties to meet performance requirements. For certain applications, high filler content are needed to achieve the desired property modification. Two groups of wood particle composites are commonly recognized, i.e. based on size of wood components and methods of manufacture.

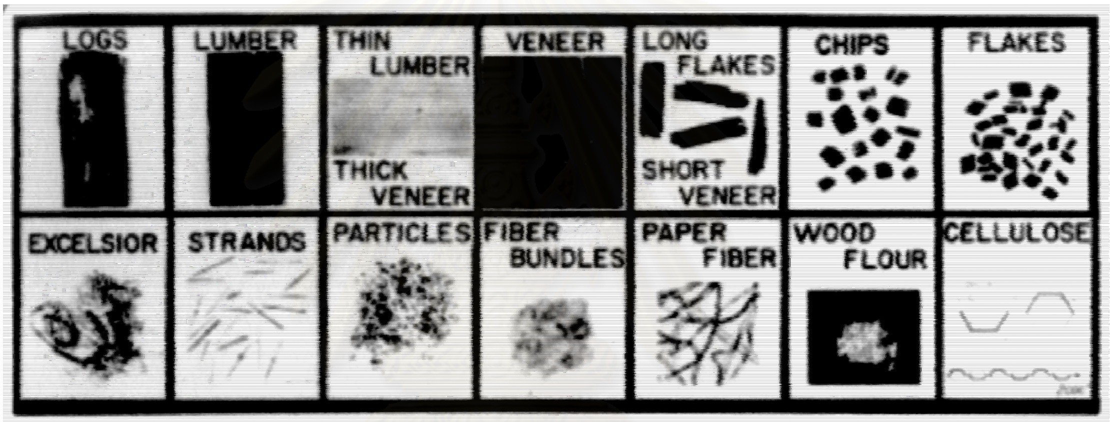


Figure 2.1 Basic wood elements, from largest to smallest (Youngquist, 1999)

The wood particles are mainly produced from residue of other primary wood manufacturing operations or from round wood. Slaps, edgings, trim ends, and whole logs are used to produce the particle. Woodflour has several advantages compared to inorganic filler, including low cost per volume basis, low density, high specific strength, high specific modulus, nonabrasiveness that shows flexibility during the processing with no harm to the equipment, renewable nature and the utilization of waste materials. Polymers with particulate filler or short fiber reinforcements are enjoying a rapid increment in the volume and number of applications because of their good processibility (Liao et al., 1997). A wide variation of mechanical and physical properties can be developed through an appropriate compounding of polymer and fillers. There are, however, some adverse effects for example, addition of high modulus wood fiber to a plastic matrix usually results in increased brittleness

(Xu et al., 2001). In other words, an increment of the stiffness and strength of wood fiber composites are obtained at an expense of their toughness and ultimate elongation (Balasuriya et al., 2001).

2.4 Natural Fibres and Their Chemical Compositions

(Bledzki and Gassan, 1999)

Natural fibers or fillers such as wood, cellulose and jute are renewable materials with very attractive mechanical properties. For instance, cellulose fibers with moduli up to 40 GPa can be separated from wood by a chemical pulping process. A growing awareness of environmental problems and the importance of energy conservation have made such renewable reinforcing materials of great importance.

The components of natural fibres are cellulose, hemicellulose, lignin, pectin, waxes and water-soluble substances, with cellulose, hemicellulose and lignin as the basic components with regard to the physical properties of the fibers.

2.4.1 Cellulose is the essential component of all plant-fibres. In 1838, Anselme Payen suggested that the cell walls of large numbers of plants consist of the same substance, to which he gave the name cellulose. It is generally accepted that cellulose is a linear condensation polymer consisting of D-anhydroglucopyranose units joined together by 1,4-β-D-glucan. The pyranose rings are in the $^4C_1$ conformation, which means that the $-CH_2OH$ and -OH groups, as well as the glycosidic bonds, are equatorial with respect to the mean planes of the rings. One of cellulose’s most characteristic properties is the presence of both crystalline and amorphous regions within its microfibrils. According to the so-called *fringe micellar theory*, a single cellulose chain may run through several crystalline regions as well as through amorphous zones in between. Cellulose, as the skeletal substance, contributes its high tensile strength to the complex of wood structure. The percentage composition of each of these components varies for different fiber. However, hardwoods contain more cellulose than do softwoods. Generally, the fibers contain 60-80 % of cellulose.

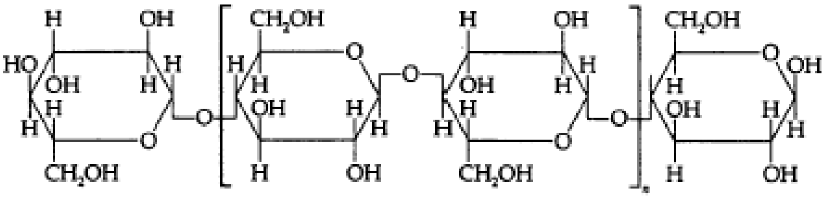


Figure 2.2 Structure of cellulose contains 1,4-β-D-glucan

2.4.2 Hemicellulose is not a form of cellulose at all and the name is an unfortunate one. They comprise a group of polysaccharides (excluding pectin) that remains associated with the cellulose after lignin has been removed. The constituents of hemicellulose differ from plant to plant. The function of hemicellulose is less clear, there are existing some possibility that they serve as a temporary matrix before lignification. The hemicellulose differs from cellulose in three important aspects. In the first place the contain several different sugar units whereas cellulose contains only 1,4-β-D-glucopyranose units. Secondly they exhibit a considerable degree of chain branching, whereas cellulose is a strictly linear polymer. Thirdly, the degree of polymerization of native cellulose is ten to one hundred times higher than that of hemicellulose. Hemicellulose is responsible for the biodegradation, moisture absorption, and thermal degradation of the fiber as it shows least resistance. Wood contain the hemicellulose about of 5 to 20 %

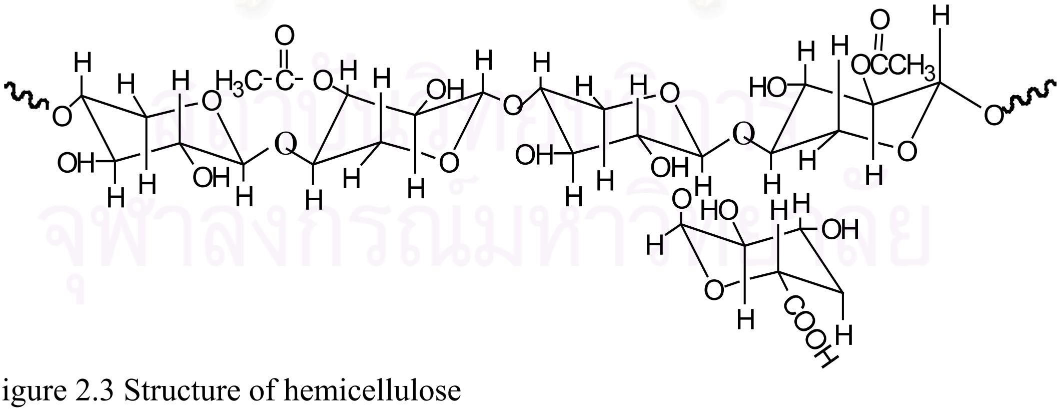


Figure 2.3 Structure of hemicellulose

2.4.3 Lignins are complex hydrocarbon polymers with both aliphatic and aromatic constituents. Their chief monomer units are various ring-substituted phenyl-propanes linked together in ways, linked together by C-O-C and C-C linkages. These are still not fully understood. Structural details differ from one source to another. The mechanical properties are lower than those of cellulose. At the value of 4 GPa, the lignin is thermally stable but is responsible for the UV degradation. Composition of lignin in wood contains about of 2 to 15 %.

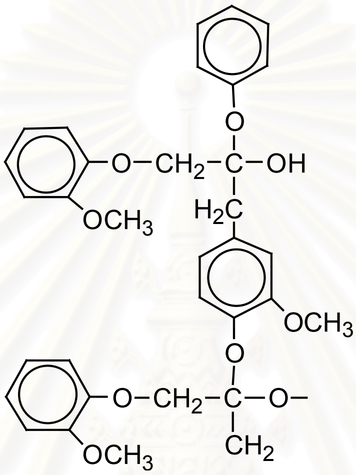


Figure 2.4 Structure of lignins

2.4.4 Pectin is a collective name for heteropolysacharides, which consist essentially of polygalacturon acid. Pectin is soluble in water only after a partial neutralization with alkali or ammonium hydroxide.

2.4.5 Waxes make up the part of the fibres, which can be extracted with organic solutions. These waxy materials consist of different types of alcohols, which are insoluble in water as well as in several acids.

2.5 Matrices

A role of a matrix in a fiber-reinforced composite is (1) to transfer stresses between the fibers, (2) to provide a barrier against an adverse environment, and (3) to protect the surface of the fibers from mechanical abrasion. The matrix plays a minor role in the tensile load-carrying capacity of a composite structure. However, selection of a matrix has a major influence on the interlaminar shear as well as on in-plane shear properties of the composite material. The interlaminar shear strength is an important design consideration for structures under bending loads, whereas the in-plane shear strength is important for structures under torsional loads. The matrix provides lateral support against the possibility of fiber buckling under compression loading, thus influencing to some extent the compressive strength of the composite material. The interaction between fibers and matrix is also essential in designing damage-tolerant structure. Finally, the processability and defects in a composite material depend strongly on the physical and thermal characteristics, such as viscosity, melting point, and curing temperature of the matrix. Additional functions of a matrix are to keep the fibers in place in the structure, to help distribute of transfer load, to protect the filaments, both in the structure and before fabrication, to control the electrical and chemical properties, and to carry interlaminar shear. Other desirable properties of a matrix, depending on the purpose of the structure, are to minimize moisture absorption, wet and bond to fiber, flow to penetrate completely and eliminate voids during the compacting and curing processes, have strength at elevated temperature (depending on the application), have low shrinkage, have dimensional stability, with reasonable strength, modulus, and elongation.

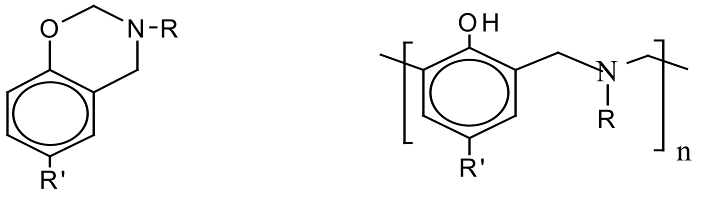
2.5.1 Thermosetting Resins

Thermosetting resins form the most widely used class of matrix materials in polymer-based composite where thermoplastics cannot compete because of either inferior properties or high costs. For example, phenolics constitute a first option when fire resistance is required because they are self-extinguishing and exhibit low smoke emission. Urea-formaldehyde polymers play a major role in wood agglomerates whereas melamine-formaldehydes are for furniture coatings. Unsaturated polyesters are extensively used to produce structural parts with a glass-fiber reinforcement. In addition, epoxies, cyanate esters, and polyimides are employed for aeronautical and electronic applications where their excellent properties cannot be matched by thermoplastics. However, despite well established, they suffer from a number of well-known limitations and it is to address these problems that current research efforts are largely devoted. Reinforced thermosetting plastics are utilized because increased tensile, flexural, torsional, or impact strengths; enhanced modulus of elasticity; improved creep resistance; reduced coefficient of thermal expansion; elevated thermal conductivity; and, in many case, lower costs.

One of the most important parameters characterizing a thermosetting polymer is the location of its glass transition temperature (Tg) with respect to the temperature at which it is used (Tuse). Most thermosetting polymers are formulated and selected so that their Tg is higher than Tuse; therefore, they behave as glasses during their service. Materials exhibiting a Tg lower than Tuse are classified as rubbers, but they can also be regarded as thermosetting polymers operationg in the rubbery state.

2.5.2 Polybenzoxazine

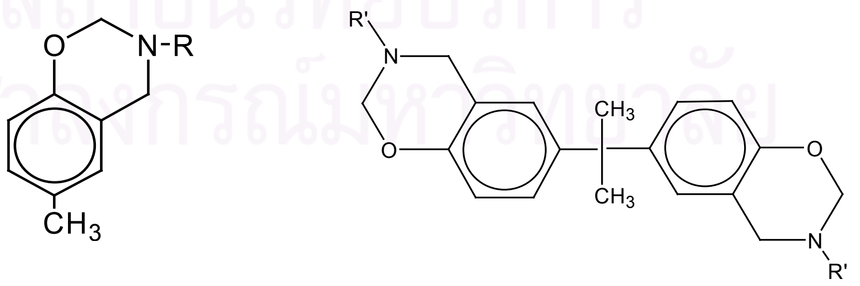
Phenolic resins have been widely used particularly in composite applications. However, their attractiveness is compromised by the problematic nature of their chemistry. Well-known shortcomings of phenolic resins are the production of water during polymerization, poor processibility, short shelf life for resole-types, use of chemically harsh catalysts, and limited molecular design flexibility. Recently introduced benzoxazine resins overcome almost all drawbacks of conventional phenolic resins, Furthermore, the materials exhibit a number of special properties that have been rarely observed in other commonly used polymers. The resin chemistry is based on a ring-opening polymerization of benzoxazine precursors. The material offers superb molecular design flexibility, while performance properties can be tailored and optimized to meet specific application requirements. The benzoxazine resin can be synthesized from phenolic derivatives, primary amine, and aldehyde. The polymerization occurs by a simple ring-opening addition reaction and did not yield any reaction by-product. Benzoxazine resins cure without the aid of any strong acid catalysts required by traditional phenolic materials. Molecular structures of the monomer and the resulting polymer are shown in Fig. 2.5.



(a) (b)

Figure 2.5 Benzoxazine resin (a), and ring-opening polymerization of the resin (b) (R = amine group, R’ = phenol group)

Benzoxazine is a single benzene ring fused to another six-membered heterocycle group containing one oxygen atom and a single nitrogen atom, called an oxazine ring. The oxazine ring is the reactive site for curing of the benzoxazine. There are a number of possible isomers of benzoxazine depending on the relative positions of the two heteroatoms and the degree of oxidation of this oxazine ring system. Benzoxazine may be synthesized as monofunctional or difunctional. The latter can produce crosslinked structures. The polymerization of monofunctional benzoxazine produces only linear oligomeric phenolic structure. However, difunctional benzoxazine monomers are tetrafunctional in terms of reactive sites and can be polymerized to form crosslinked networks, resulting in phenolic materials with substantial mechanical integrity. The two monomeric structures are shown in Fig 2.6.



(a) (b)

Figure 2.6 Chemical structure of benzoxazine resins, monofunctional (a), bifunctional (b)

The polybenzoxazines overcome many of the traditional shortcomings of conventional novolak and resole type phenolic resins, while retaining their benefits. The physical and mechanical properties feature a wide range. The balance material properties of these resins such as good thermal, chemical, electrical, mechanical, and physical properties make the polybenzoxazine family an attractive option in many existing applications (Agag and Takeichi, 2001). In addition, these new materials possess high glass transition temperatures, high char yield, high moduli, low water absorption despite the large amount of hydroxyl groups in the backbone structure, excellent resistance to chemicals and UV light, low melt viscosities compared to conventional phenolics, near-zero volumetric shrinkage or expansion upon polymerization and relatively low coefficients of thermal expansion. The polybenzoxazines are; therefore, suitable for various high-performance adhesives and composites (Rimdusit and Ishida, 2000).

2.6 Polymerization of Benzoxazine Resin

Benzoxazine resins are bicyclic heterocycles generated by a Mannich-like condensation of a phenol, a formaldehyde, and an amine (Ishida: US Patent, 1996). They have long been recognized for their wide range of biological activity with uses as herbicides and agricultural microbiocides, as well as, bactericides, fungicides, and antitumor agents (Wang and Ishida, 2000). On the other hand, polybenzoxazines, one of a series of phenolic-type polymers, which are generated upon thermal polymerization from various types of substituted 3,4 dihydro-2*H*-1,3-benzoxazines, offer excellent mechanical, physical, and thermal properties due to the phenolic groups, Mannich base linkages, and the existence of extensive inter-and intra-molecular hydrogen bonds (Wang and Ishida, 2000).

2.6.1 Polymerization Machanisms

The preferential conformation of a mono-oxazine ring containing benzoxazine is a distorted semichair structure, with the nitrogen and the carbon between the oxygen and nitrogen on the oxazine ring sitting, respectively, above and below the benzene ring plane. The resulting ring strain from this molecular conformation makes it possible for this type of six-membered ring containing molecule to undergo ring-opening polymerization under certain conditions. In addition, from the chemistry point of view, both the oxygen and the nitrogen on the oxazine ring can be potential cationic polymerization initiation sites due to their high basicity by Lewis definition.

2.6.2 Hydrogen-Bonded Network Structure of Polybenzoxazine

According to Kim and Ishida (2002), it has been determined that the network structure of polybenzoxazine is supported by the interaction of polymer chains due to strong hydrogen bonding as well as chemical cross-linking. Therefore, taking into account the low cross-linking density in polybenzoxazines, the role of hydrogen bonding in the polymer system is of great importance in interpreting structure-property relationships. The polybenzoxazine (bisphenol-A/aniline-based polymer; BA-a) has a relatively small amount of intramolecular hydrogen bonding. Instead, the large portion of hydroxyl groups in the BA-a polymer forms either weak –OH•••¶ intramolecular hydrogen bonding or -OH•••O intermolecular hydrogen bonding. Since the intermolecular hydrogen bonding has a significant effect on the packing of polymer chains, the BA-a polymer chain may have a chance to be more extended during the ring opening polymerization and; therefore, shows low volumetric expansion. Although polybenzoxazines are chemically cross-linked by the ring-opening reaction of the benzoxazine rings, the cross-linking density is rather low to explain the very high modulus of the polymers. Therefore, it is believed that the physical interaction of polymer chains due to hydrogen bonding plays an important role in fostering the excellent properties of polybenzoxazines.

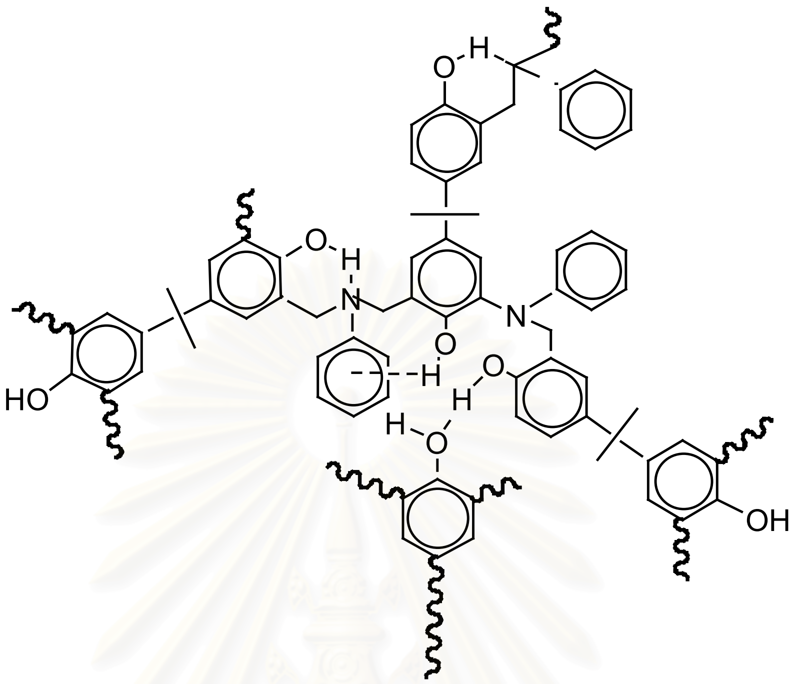


Figure 2.7 Proposed hydrogen-bonded network structure for polybenzoxazine (BA-a)

2.7 Theory of the Action of Fillers and Reinforcements

(Gachter and Muller, 1987)

An interface is a dominant factor in the fracture toughness properties of composite materials and in their responses to aqueous and corrosive environments. Composite materials with weak interfaces have relatively low strength and stiffness but high resistance to fracture whereas materials with strong interfaces have strength and stiffness but are very brittle. In a simple system, bonding at an interface is due to adhesion between a fiber and a matrix. The action of an active filler can be attributed to several mechanisms. Some fillers form chemical bond with the material to be reinforced, such as carbon black produces crosslinking in elastomers by means of radical reaction. Other fillers act mainly through the volume they take up. The chain molecules of the polymer to be reinforced cannot assume all the conformational positions that are basically possible. Moreover, it can be assumed that in certain zones around the filler particles the polymeric phase differs in structures and properties from the polymer matrix. The polymer segments attached to filler surfaces by primary or secondary valence bonds, in turn, cause a certain immobilization of adjacent segments and circumstances permitting an orientation of the polymer matrix. An increase in glass transition temperature observed in filled polymers, resulting from the restricted of mobility in the filler/polymer boundary zone, can be regarded as due to reduced conformation in this theoretical concept.

The zone adjacent to filler surface, whose structure might appear to be ordered, causes a stiffening of the material as a whole. Lower deformability and higher strength are also attributed to this composite nature. Uniform distribution of fillers is especially important, so that maximum polymer chains can be bound to the free filler surface. The free surface energy and the polarity of the bond between the filler and the matrix are, thus, significant factors in this regard.

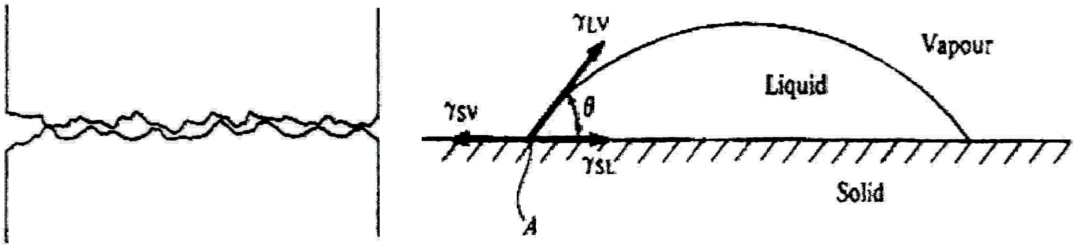
Another mode of action of active fillers arise from the fact that when the polymer molecules are subjected to mechanical stress with energy absorption mechanisms, they can slide off the filler surface. An impact energy can; therefore, be more uniformly distributed and an impact strength increases as, for example, in the unplasticized PVC/calcium carbonate system. In some cases, microcraze, that destroys the impact energy at the filler/polymer interface, is also facilitated

2.7.1 Theories of Adhesion (Hull, 1990)

Adhesion can be attributed to five main mechanisms, which can occur at the interface either in isolation or in combination to produce the bond.

2.7.1.1 Adsorption and Wetting

When two electrically neutral surfaces are brought sufficiently close together there is a physical attraction which is best understood by considering the wetting of solid surfaces by liquids as illustrated in Figure. 2.8 (a). The physical situation of a liquid drops on a solid surface, as Figure. 2.8 (b), by using the Young's equation.



(a) (b)

Figure 2.8 Isolated contact points leading to weak adhesion between two rigid rough surfaces. (a), Surface tensions (γ) for a liquid drop on a solid surface. (b).

Work of adhesion, W_{SL}, as shown by the Yong's equation

$$W_{SL} = \gamma_{LV}(1+\cos\theta) = \gamma_{sv} + \gamma_{LV} - \gamma_{SL} \tag{2.1}$$

Where θ is the contact angle and γ is the surface tensions of solid-vapor (SV), solid-liquid (SL), and liquid-vapor (LV) interfaces, respectively.

2.7.1.2 Mechanical Adhesion

Some bonding may occur purely by the mechanical interlocking of two surfaces as illustrated in Figure 2.9 (a). The strength in shear may be very significant and depends on the degree of roughness.

2.7.1.3 Electrostatic Attraction

Forces of attraction occur between two surfaces when one surface carries a net positive charge and the other surface a net negative charge as tin the case of acid-base interactions and ionic bonding and coupling agents laid down on the surface of the filler, as shown in Figure 2.9 (b).

2.7.1.4 Chemical Bonding

A chemical bond is formed between a chemical grouping on the fiber surface and a compatible chemical group in the matrix as seen in Figure. 2.9 (c) and (d) respectively. The strength of the bond depends on the number and type of bonds and interface failure must involve bond breakage.

2.7.1.5 Interdiffusion

It is possible to form a bond between two polymer surfaces by the diffusion of polymer molecules on one surface into the molecular network of the other surface, as shown in Figure 2.9 (e) and (f) respectively. The bond strength will depend on the amount of molecular entanglement and the number of molecules involved.

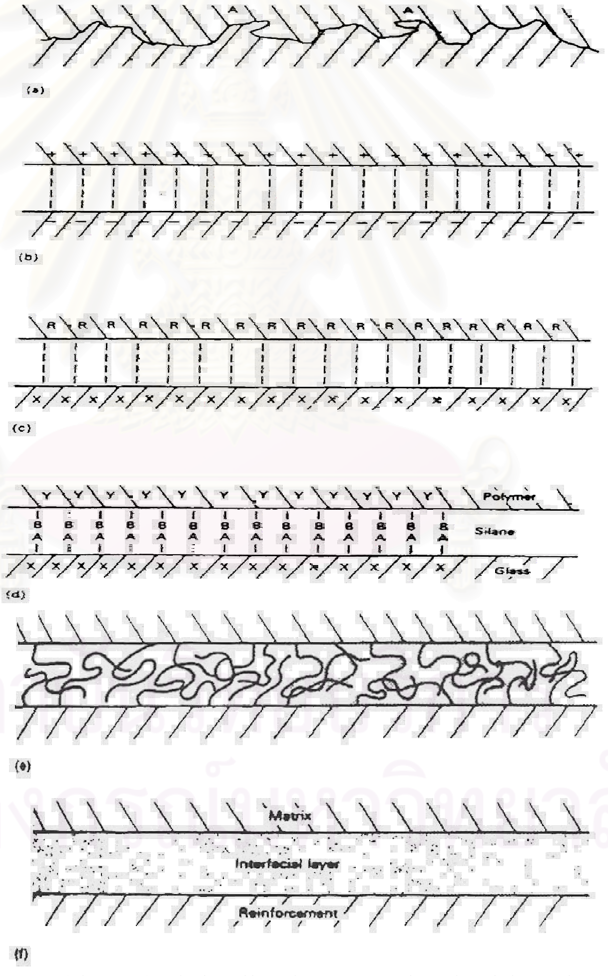


Figure 2.9 Mechanism of interfacial adhesion. Mechanical bond (a), Bond formed by electrostatic attraction (b), Chemical bond (c) and (d), Bond formed by molecular entanglement following interdiffusion (e) and Bond formed by interfacial layer by interdiffusion (f) (Matthew, 1994).

2.8 Particle Packing and the Maximum Packing Fraction

(Rothon, 1995)

The packing behaviour of particles in a polymer matrix is a critical factor in the understanding and design of polymer composites, especially when highly filled systems are involved.

The maximum packing fraction is a particularly useful concept, being the maximum volume fraction of particles that can be incorporated before a continuous network is formed and voids begin to appear in the composite. In addition to indicating the maximum practical loadings obtainable, the maximum packing fraction is also useful in understanding and describing the effect of filler loading on composite properties. Many properties change rapidly as one approaches of the maximum packing fraction and this parameter is now incorporated into many mathematical treatments of property-loading dependence. Indeed, it often goes a long way to explaining why different physical forms of the same material can give markedly differing results at the same loading.

2.8.1 Particle Packing Theory

Much effort has been devoted to studying the effect of particle size and shape on the packing properties of powders. The packing behaviour of particulate materials depends largely on their particle size, shape and surface characteristics. The behaviour of model systems with closely defined size and shape distributions is now well understood. Real particulate materials are much harder to treat, largely due to the difficulty in determining and describing their size and shape distributions accurately.

The aims of particle packing theory are to predict the maximum volume fraction that can be obtained under a given set of circumstances and the structure of the particle assembly at this point. The first point to appreciate is that there are several ways of packing the same collection of particles, each one resulting in a different maximum volume fraction. The circumstances under which the particles are assembled will determine which of these structures is obtained in practice. In the extreme case, considering a three-dimensional jigsaw puzzle, theoretically the jigsaw can be assembled to give perfect packing with no free space. This is known as ordered packing. However, if the pieces are put in a container and shaken, it is extremely unlikely that they will ever discover this perfect packed structure. Nevertheless, providing there are enough particles, a certain packed density can be reproducibly obtained implying that some statistically balanced structure is obtainable. This is known as a random packing situation. More than one ordered and random packing fractions may be observed with many systems.

Appreciation of the nature of ordered and random packing is important in understanding the application of packing theory. Ordered packing results in long-range structure as in a crystal lattice and, although it can sometimes be observed in suspensions of monodispersed spherical particles, is not of great importance in our context. As its name implies, random packing is a statistical process with no long-range structure and it is more relevant to particulate-filled composites whereas some ordered packing configurations can render higher packing densities than random packing. Two classes of random packing are recognized.

2.8.1.1 Loose random packing refers to the sort of packing obtained when particles are randomly assembled under conditions that they can’t easily move past each other. In powder technology terms, loose random packing corresponds with a pour density.

2.8.1.2 Dense random packing are the conditions that particulate movement is still possible. Dense random packing corresponds with a tapped density in powder technology.

The simplest case to consider first is the packing of smooth, regular, mono-size particles. This has been well studied for smooth spherical particles, which can readily move past one another. With these particles, a maximum ordered packing fraction of 0.74 has been established, although other less dense packings are feasible. Random loose packing fraction is difficult to predict accurately but is about 0.60. Random dense packing is more readily predicted and is about 0.64. The theory has been extended quantitatively to a number of regular non-spherical shapes. Many of these such as cubes, rectangles and plates can have ordered packing fractions of unity but most have less dense random packing than spheres, largely due to the difficulty of the particles to move with respect to one another to optimize packing. Cubic particles; however, seem to have a slightly higher random packing density than spheres (about 0.75). Quantification of the packing behaviour of irregular particles is poorly developed at present but the enhanced interparticle friction soon causes the packing fraction to decrease as the particles depart from sphericity. Values of 0.50 are not uncommon for three-dimensional irregular particles. Very low packing fractions (< 0.1) are obtained with high aspect ratio fibres.

A general approach to achieve high packing fraction powders is to use small particles to fill the pores in the packed structure obtained from large particles and then to use even smaller particles to fill in the remaining pores and so on. A simple view of this is presented in Fig. 2.10. The approach is known as multimodal packing, and much effort has been devoted to defining the optimum particle size ratios and quantities of the various modes and the resulting packing fraction obtained.

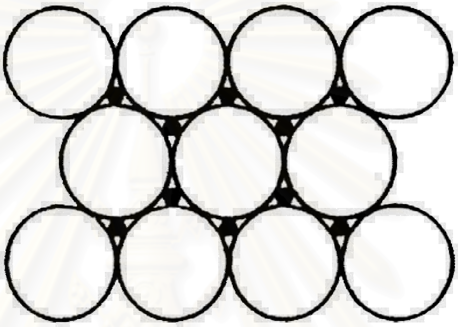


Figure 2.10 Classical bimodal packing effect

2.8.2 Filler Content, Density, and Void Content

Theoretical calculation for strength, modulus, and other properties of a filler-reinforced composite are based on the filler volume fraction in the material. Experimentally, it is easier to determine the filler weight fraction, W_f, from which the filler volume fraction, V_f, and composite density, ρ_c can be calculated: (Piyawan, 1998)

$$V_f = \frac{W_f/\rho_f}{(W_f/\rho_f) + (1 - W_f)/\rho_m} \tag{2.2}$$

$$\rho_c = \frac{1}{(W_f/\rho_f) + (1 - W_f)/\rho_m} \tag{2.3}$$

Where W_f = Filler weight fraction

$(1\text{-}W_f)$ = Matrix weight fraction

ρ_f = Filler density

ρ_c = Matrix density

In term of filler volume fraction, V_f, the composite density, ρ_c, can be written as

$$\rho_c = \rho_f V_f + \rho_m V_m \tag{2.4}$$

During incorporation of filler into the matrix or during manufacturing of laminates, air or other volatiles may be trapped in the materials which may significantly affect some of their mechanical properties.

The void content in a composite can be estimated by comparing the theoretical density with its actual density ;

$$V_v = \frac{\rho_c - \rho}{\rho_c} = 1 - (V_f + V_R) \tag{2.5}$$

Or $V_v = 1 - (W_f/\rho_f + W_R/\rho_R)$ (2.6)

Where V_v = Volume fraction of voids

ρ_c = Theoretical density

ρ = Actual density, measured experimentally on composite specimen

R = Polymer matrix

f = Fiber

W = Weight fraction

2.9 Water in Polymer

The water molecule is relatively small and in the liquid and solid states is strongly associated through hydrogen bond formation. This combination of features distinguishes it from the majority of organic penetrants. Whereas the diffusion coefficient generally increases with concentration for an organic vapour, marked decreases have been observed with water in several polymers. Values for the enthalpy of formation of the hydrogen bond in the range 14.25 to 27.63 kJ/mole have been obtained. As a result, strong localized interactions may develop between water molecule and suitable polar groups of the polymer. On the other hand, in relatively non-polar materials, clustering or association of the sorbed water is more pronounced (Barrie, 1989).

2.9.1 Mass Diffusion in Polymers (Neogi, 1996)

In natural fibers, the water-cellulose system has been well studied. The sorption-desorption technique has been widely used because these materials are most readily available in fibre form. The diffusion of water is “non-Fickian” or “anomalous”; integral sorption curves exhibit a pronounced inflection, and differential (interval) curves show a usual two-stage behaviour observed in such systems shown in Fig. 2.11. For the wool-water system at 20 ^{o}C, the initial stage of a differential curve was completed in few minutes whereas the slow second stage could require several days. In both systems, diffusion in the initial stage was Fickian with reversible sorption and desorption to and from the quasi-equilibrium, Sorption in the second stage was not dependent on the thickness of the sample to any great extent suggesting the process was no longer diffusion controlled.

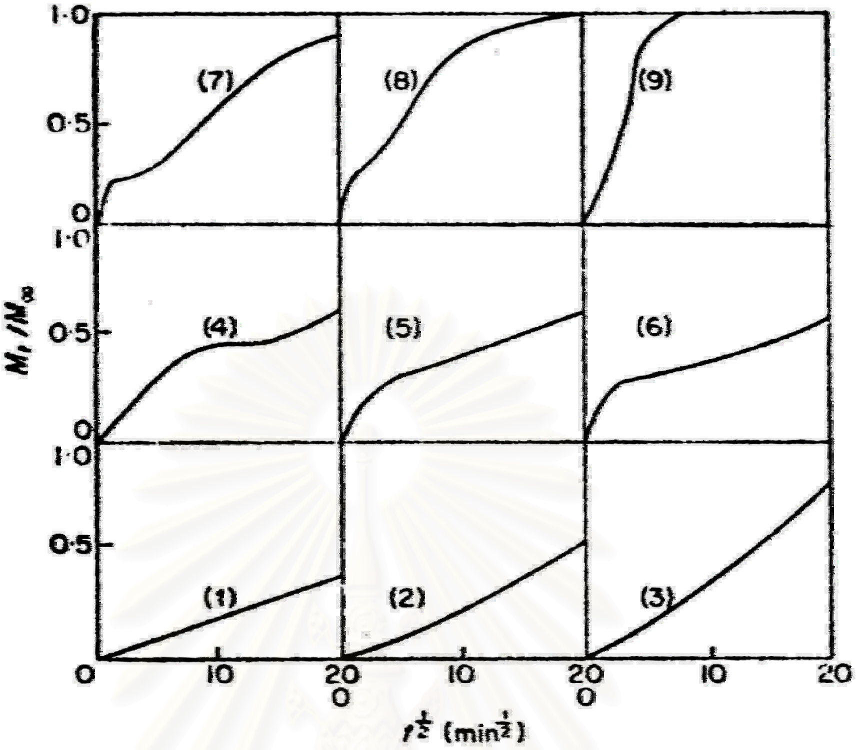


Figure 2.11 Successive sorptions for water-cellulose at 15 ^{o}C. Film thickness 26.2 μm showing a two-stage behavior (data in appendix D-1).

2.9.2 Non-Fickian Diffusion

Some of the basic assumptions made on a medium (particularly a fluid medium) break down in solid polymer. These are conditions of isotropy, homogeneity, and local equilibrium. Glassy polymers are not at equilibrium, but they relax slowly toward it (Rehage and Borchard, 1973). Even crystallites in semicrystalline polymers are not at equilibrium (Hoffman et al., 1975). Stretching beyond the elastic limit gives rise to anisotropy in polymers, which is not restored on heating then cooling, for instance, indicating nonequilibrium configuration. Besides semicrystlline polymers, glassy polymers are also inhomogeneous although overmuch smaller length scales as determined from solubility studies (Hopfenberg and Stannett, 1973). The net result is that the Boltzmann scaling in sorption is no longer satisfied. There are two basic type of non-Fickain sorption. The first of these was identified by Alfrey (1965); the mass uptake in the glassy polymer studies was found to be proportional to time instead of to the expected square foot of time.

The generalized equation to explain the diffusion in the materials can be expressed as:

$$M_t / M_\alpha = k_n t^n \tag{2.7}$$

Where M_t = the mass of sample at time t

M_α = the mass of sample at saturation or infinite time

The diffusion behaviors can be classified as : supercase II (n>1), case II (n=1), anomalous (1/2<n<1), classical/Fickian (n=1/2), or pseuso-Fickian (n<1/2).

The second kind of non-Fickian behavior was reported by Bagley and Long (1955) and by Long and Richman (1960). The fractional mass uptake curve was observed to be sigmoidal but with somewhat classical scaling. Fig. 2.12 explains the different types of responses including one called a two-step response. The physical mechanisms behind the non-Fickian behavior are only now beginning to emerge and are not complete. One mechanism is that of coupled mass and momentum transport, or coupled through swelling. The other explanation, with much less success, is based on the fact that glassy polymers are inhomogeneous.

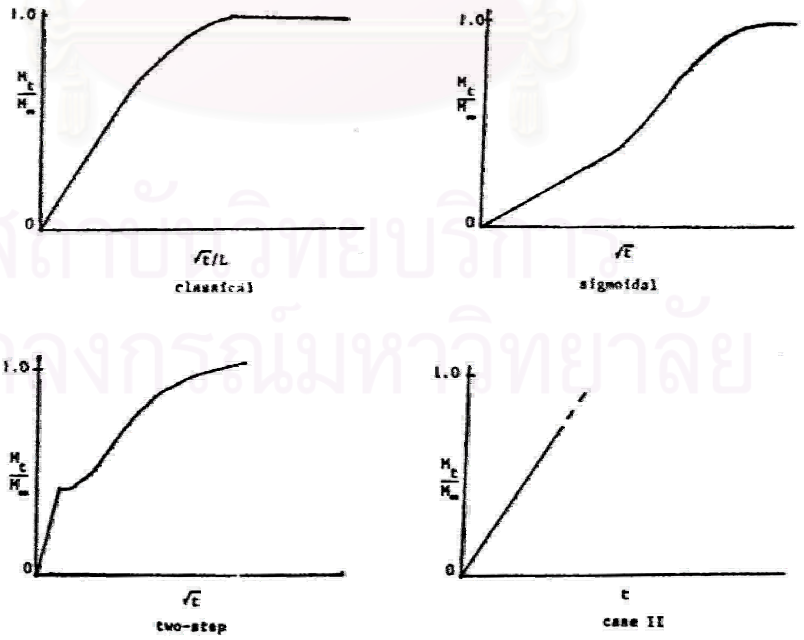


Figure 2.12 The different classes of non-Fickian sorption

2.10 Differential Scanning Calorimetry (Hunt and James, 1993)

Classical adiabatic calorimetry, in which precise quanta of heat are applied and the temperature rise of the sample is noted under shielded conditions, is an extremely slow and laborious technique. By referring the temperature of a sample to that of an inert sample experiencing a closely similar heating profile, equivalent information can be obtained in a rapid scanning experiment. This has many advantages in that structures in the polymer are not annealed and changed during fast thermal scans.

In order to qualify for use as a differential scanning calorimetry (DSC) , rather than just a differential thermal analysis (DTA), the difference in temperature between sample and reference must be capable calibration, such that:

$$\Delta T = K\Delta(mC_p)R \qquad (2.8)$$

Where ΔT = Temperature difference between a sample and a reference

$\Delta(mC_p)$ = Difference in total heat capacity between sample and reference

R = Heating rate (^{o}C/min)

It is a common practice to use closely similar sample and reference crucibles and if the empty crucible is use as a reference, then

$$\Delta T = KmC_pR \qquad (2.9)$$

and this is the usual working equation. All DSC instruments must be calibrated (i.e. K determined) either by measurement of a known specific heat-capacity sample (usually sapphire) or by using samples with known heat of fusion. As K is a slow-moving function of temperature, calibration can be performed from a melting curve such as that shown for indium in Fig. 2.13. In this case:

$$\text{Area under melting curve} = K\, m\Delta HR$$

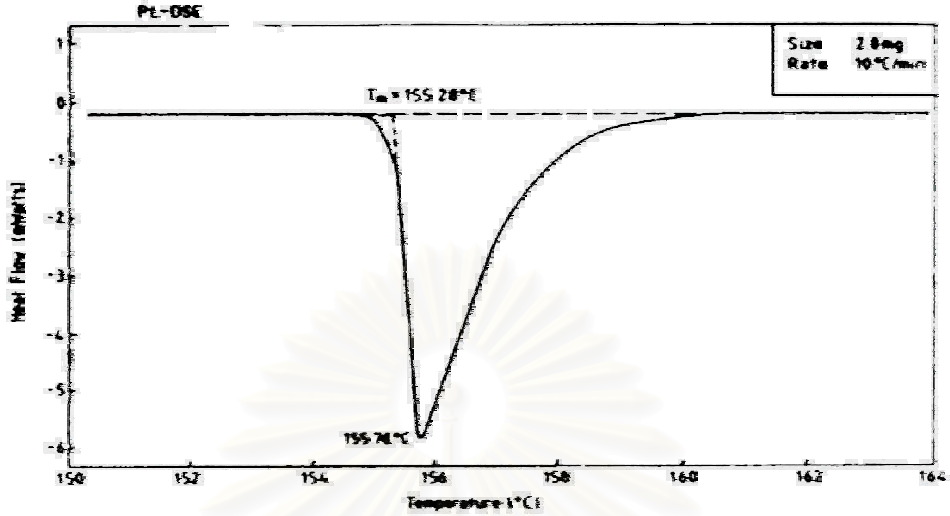


Figure 2.13 DSC trace for sharp melting-point material (indium). Onset construction for Tm is valid in this case

2.11 Dynamic Mechanical Measurements

Dynamic mechanical measurements describe both the liquid and solid states. A freely oscillating torsion pendulum can be used to provide shear moduli data of solid specimens versus temperature or time. A composite specimen made by impregnating a glass-fiber braid with liquid thermoset precursors was used to study liquid systems that change to solids.

Dynamic measurement is very important in the case of polymeric material due to its well-known sensitivity to the speed of loading. The dynamic measurement is often applied when a polymeric test specimen is subjected to repeated (cyclic) load that is not designed to cause failure. For dynamic mechanical measurements, the polymer specimen is deformed cyclically under small amplitude sinusoidal loads while the temperature is raised simultaneously. The deformation induced by the small amplitude sinusoidal load allows the determination of two basic quantities through the theory of linear viscoelasticity. They are the storage modulus that tends to show the elastic response of the material, and the loss modulus or tan δ that is related to the viscous response. Dynamic methods lead to an identification of a glass transition temperature (Tg), an important parameter characterizing all polymers. Thermosetting polymers are usually amorphous because there is almost no possibility of ordering portions of the network structure due to the restrictions imposed by the presence of crosslinks. Exceptions are networks obtained from rigid monomers exhibiting a nematic-isotropic transition. Above the Tg, the molecules have more energy and hence the movement of molecular segments becomes feasible. In the glass transition region, polymer is soften considerably. The Tg was estimated at the peak of loss modulus curve obtained from a dynamic mechanical measurement.

2.12 Morpholigical Investigation

Microscopy is the study of the fine structure and morphology of objects with the use of a microscope. Microscopes range from optical microscopes, which resolve details on the micrometer level. The size and visibility of the polymer structure to be characterized generally determines which instrument is to be used. The essential feature of a scanning microscope is that the image is formed point by point, by scanning a probe across the specimen. The specimen chamber in the millimeters to several inches in diameter can be accommodated. Specimen preparation is generally quite simple. Samples must be fixed to a specimen stub. Nonconductive materials, such as most polymers, require conductive coating or the use of low accelerating voltages. SEM images are easy to interpret. They appear as though the specimen is viewed from the source of the scanning beam, and illuminated by a light at the detector position. The image can reveal fine detail on the specimen a range of useful magnifications from 20❹ to 60000❹. The typical resolution is 10 nm and the best resolution is 4 nm (Sawyer and Grubb, 1987).

2.12.1 Composite Characterization

SEM is the techniques usually employed to evaluate the structure of composite materials. The hardness of composites generally precludes microtomy, so polishing is used to provide thin sections for transmitted light microscopy or thick sections for reflected light study. Fiber and particulate fillers can be obtained prior to compounding. It is important to know the morphology of the fillers before studying their composites. This aids in understanding the complex morphologies. Important information that can be obtained relates to the fiber-resin filler face, which is known to be critical to composite properties, and is often adversely affected by environmental conditions.

CHAPTER 3

LITERATURE REVIEWS

Ning and Ishida (1994a, 1994b) investigated the synthesis of bifunctional benzoxazine precursors. These polyfunctional benzoxazine were found to exhibit excellent mechanical and thermal properties with good handling capability for resin processing and composite 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 terms of molecular design. They do not release by-products during curing reactions and there is no solvent needed in the resin production.

Ishida and Allen (1996b) studied the properties of polybenzoxazine thermosetting resins based on the ring-opening polymerization of benzoxazine precursors (B-a, B-m). They can be synthesized from inexpensive raw materials and polymerize by a ring opening addition reaction to yield no reaction by-product. Benzoxazine resins cure without the aid of the strong acid catalysts normally required by phenolic materials. Dynamic mechanical analysis revealed high moduli and high glass transition temperature with low crosslink densities, i.e., flexural modulus ca. 4.5 GPa, flexural strength ca. 126 MPa, and Tg up to 350 ^{o}C. Polybenzoxazines have significantly higher tensile moduli than both phenolics and epoxies yet maintain adequate tensile strength and impact resistance. In addition, low water absorption and good dielectric properties allow these materials to perform well in electronic applications. Ishida (1996) demonstrated that benzoxazine-based resins are expected to yield significant advantages over many other thermosetting materials. The molecular structure of polybenzoxazine offers superb design flexibility and allows properties of the cured materials to be controlled for specific requirements of a wide variety of individual applications. Polybenzoxazines can be synthesized from a wide selection of raw materials consisting of phenolic derivatives and primary amines. Polybenzoxazines can find applications in areas where polyesters, vinyl esters, epoxies, phenolics, bis-maleimides, cyanate esters, and polyimides are currently used.

Ishida and Krus (1998) examined the synthesis and characterization of structurally uniform model oligomers of benzoxazine resin. The synthesis was made possible by modifying many of the synthetic methods used for similar phenol-formaldehyde model oligomers. With the developed procedures, many different structurally uniform compounds may be synthesized to aid the characterization and deeper understanding of this new class of resin. A synthetic strategy is developed in which bromine is used as an ortho position-blocking group allowing a stepwise synthesis of structurally uniform compounds. Debromination and subsequent hydrogenation is achieved in high yield by using activated Raney nickel catalyst in a methanol/aqueous medium. Benzoxazine oligomers as large as the model tetramer had been synthesized.

Ishida and Rimdusit (1998) developed highly thermally conductive molding compounds for electronic packing application based on polybenzoxazine system. The authors 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. 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 has low melt viscosity and good adhesion to the filler. In addition, a large particle size with multimodal particle size distribution was used. Boron nitride and polybenzoxazine have properties that meet all those requirements and thus exhibit a very high thermal conductivity value. Water absorption at room temperature of this composite is also very low, i.e. at 85 % by weight of boron nitride having 0.02 % at 24 hr (ASTM D570).

Hon and Xing (1992) showed thermoplasticizaton of wood. The thermal behaviors of untreated and esterified wood were evaluated by means of differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). In this work; esterification of wood was demonstrated by using maleic and succinic anhydrides.

The results indicated that wood can be converted into a thermoplastic material by esterification with maleic and succinic anhydride. A DMTA study revealed that the untreated earlywood showed the glass transition temperature of 250 ^{o}C. The untreated latewood provided a relatively higher glass transition temperature of about 280 ^{o}C. The wood-MA and wood-SA exhibited four relaxations between -150 and 200 ^{o}C (α, β, γ, and δ relaxations). A DSC was used to study esterified woods that were decarboxylated between 200 and 300 ^{o}C. TGA also revealed that esterified woods started their weight loss at about. 180 ^{o}C and 210 ^{o}C, which is 65-95 ^{o}C lower than untreated wood.

Shaeb and Jog (1999) explained the growing use of natural fiber to reinforce polymeric materials. Natural fibers are low cost fibers with low density and high specific properties as well as biodegradable and non-abrasive. Fiber-reinforced polymers offer advantages over other conventional materials when specific properties were compared. These composites are finding applications in diverse fields from appliances to space crafts. The use of proper processing techniques, fiber treatments, and compatibilizers/coupling agents can lead to composites with optimum properties for a particular application. The key issues in the development of natural reinforced composites were (i) thermal stability of the fiber, (ii) surface adhesion characteristics of the fibers, and (iii) dispersion of the fibers in the matrix. There has been increasing interest in commercialization of natural fiber composites and their use, especially for interior paneling in the automobile industry. These composites with density around 0.9 g/cm^3, stiffness around 3.0 MPa, impact strength of 25 kJ/m^2, and good sound absorption characteristics are being used by a number of leading companies.

Marcovich et al. (2001) studied the effect of surface treated woodflour which was chemically modified by maleic anhydride as well as the effect of filler content on the mechanical properties of woodflour filled-unsaturated polyester/styrene. The most important effect of the chemical treatment on filler is the improved particle dispersion observed in the esterified particles. This allows greater concentration of woodflour presented in the composites. Composites made from non-treated woodflour showed the maximum achievable packing density of up to 50 % by weight while this value is of only 40 % by weight for the alkaline treated woodflour composites and can reach 75 % by weight for the MAN-treated woodflour. The flexural and compressive properties of the composite fabricated from woodflour at different degree of esterification did not show any major difference. In addition, the authors examined an influence of moisture content and the woodflour chemical modification on the physical and mechanical properties of the resulting composites (Marcovich et al., 1998). From the results, mechanical properties (compression and bending tests) were found to be severely affected by moisture and chemical modifications. In wet conditions, the composites made from treated woodflour had the lowest flexural modulus and ultimate stress because of the humidity of the environment increased. It was also found that the phenomenon was a reversible effect since the original values of the compression properties were recovered after drying. Moisture sorption is known to reduce the glass transition temperature (Tg) of the neat resin and composites. Wet samples at 60 RH were tested. In the first case, a reduction in the temperature of the main transition peak of the UPE matrix was detected in the composites. Anyway, re-dried specimens showed incomplete recovery of the Tg value of the original dry samples.

Simonsen et al. (1996) investigated the use of recycled plastics as a component in composite building materials. Willamette Valley rye grass straw filled in polyethylene or polystyrene with an aid of a compatibilizer were the systems to be examined. It was found that the modulus increased with increasing filler content up to 40 %. The 60 % by weight filled system did not show a significant increase over the 40 % by weight level. As the filler level increased, it reached a point where there was insufficient plastic to thoroughly wet the filler surface. At that point, load transfer from the matrix to the filler became less efficient, resulting in a drop in mechanical properties. Current plastic lumber products exhibit a modulus and strength (ASTM D 790) of 1.2 GPa and 10 MPa, respectively. The composites were compared with those values and indicated that improvements in filled thermoplastic composites for the building products industry are possible.

Mishra and Naik (1998) investigated swelling behavior of fiber-reinforced polymer composites prepared separately from untreated banana, hemp, and agave fibers with novolac resin. The results of absorption of steam and water were showed.

From the experiment, absorption of water was much lower than steam's because water cannot penetrate the resin matrix as effectively as steam. The absorption of water by different fiber-based composites was largely dependent on the availability of free -OH groups on the surface of the reinforcing fiber. The agave fiber composites showed the least absorption of steam and water at ambient temperature with respect to banana and hemp fiber composites.

CHAPTER 4

EXPERIMENT

4.1 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) were purchased from Merck Company, and aniline (AR grade) were purchased from APS Finechem Company. All chemicals were used without further purification.

4.2 Instruments and Equipment

4.2.1 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.

4.2.2 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 each filler content.

4.2.3 Bending Tests

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).

4.2.4 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 composites.

4.2.5 Scanning Electron Microscopy (SEM)

The fracture surface of the composite samples were 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.

4.2.6 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.

4.2.7 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 ^{o}C/min from room temperature to 300 ^{o}C. The experiment was performed under nitrogen purging.

4.2.8 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).

4.2.9 Compression Molding Machine

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.

4.3 Methodology

4.3.1 Monomer Preparation

The chemical structure of benzoxazine resin used in this work are 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).

4.3.1.1 Benzoxazine monomer

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.

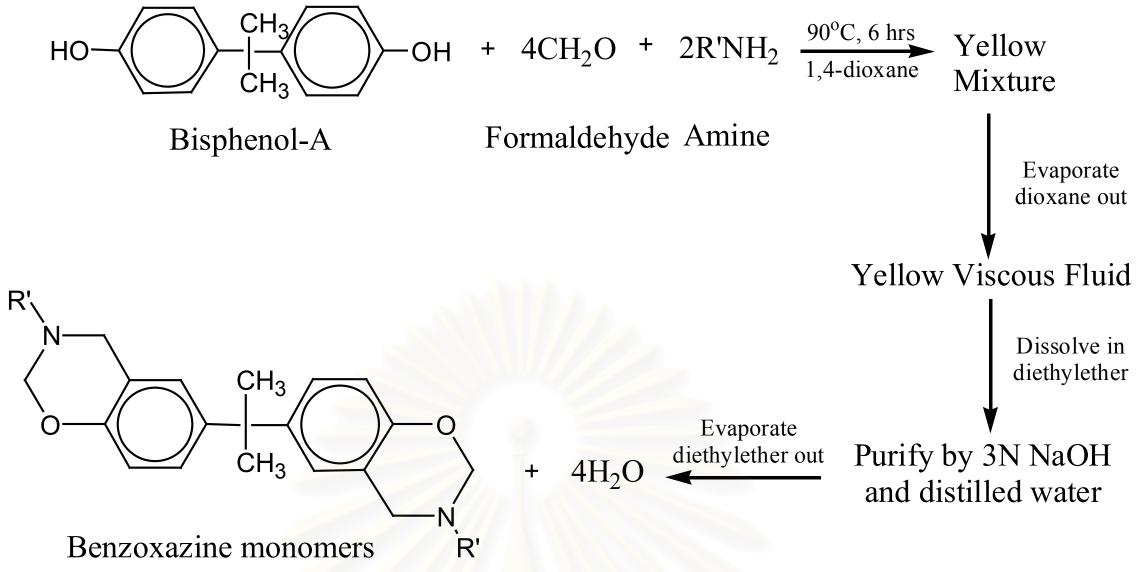


Figure 4.1 Preparation of Benzoxazine-Based Bisphenol-A (BA-a)

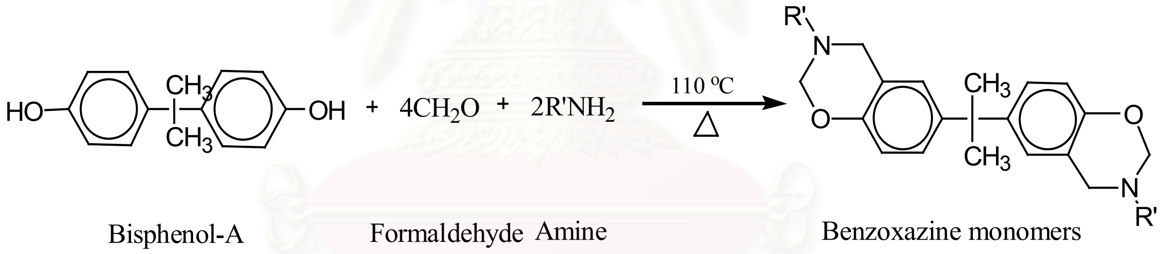


Figure 4.2 Preparation of Benzoxazine-Based Bisphenol-A (BA-a) by using solventless technology

4.3.2 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 °C for 24 hr in a vacuum oven and was kept in the desiccator.

4.3.3 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 3.5 hr. Finally, the specimens was left to cool down at room temperature in the open mold before testing.

4.4 Physical Characterization

4.4.1 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:

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

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 (This value depends on the temperature, see in appendix E-1)

The average value from three specimens was calculated.

4.4.2 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.

$$\%\ \text{filler content}\quad (\text{wt/wt}) = \left(\frac{M_{\text{filler}}}{M_{\text{composite}}}\right) \times 100 \qquad (4.2)$$

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

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

4.4.3 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

$$\text{Water absorbion } (\%) = \frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100 \qquad (4.3)$$

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

4.5 Mechanical Characterization

4.5.1 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.

$$E_B = \frac{L^3 m}{4bd^3} \tag{4.4}$$

$$\sigma_B = \frac{3PL}{2bd^2} \tag{4.5}$$

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

4.5.2 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.

4.5.3 Interfacial Characterization

The fractured specimen was secured on a stub, 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

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Characterization of Materials

5.1.1 Monomer Characterization

The FT-IR spectra of as-synthesized BA-a is shown in Fig. 5.1. 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).

5.1.2 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. 5.1 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).

5.1.3 Woodflour Characterization

According to the FT-IR spectra of woodflour were observed in Fig. 5.1, 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. 5.2. 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. 5.1 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.

5.2 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).

5.3 Properties of Molding Compounds

5.3.1 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. 5.3. 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 are 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. 5.2. 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. 5.4 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 °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. 5.3 and Fig. 5.4 can be used as a database for choosing the suitable processing condition of the molding compounds i.e. curing temperature below 200 °C to avoid thermal degradation of wood . As a general rule, curing or melting temperature should be kept below 200 °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).

5.3.2 Processing Conditions of the Molding Compounds

Fig. 5.5 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 °C. The figures suggested the time suitable for the complete cure of benzoxazine molding compounds to be 2 hr at 180 °C as indicated by the disappearance of the exothermic peak between 160 °C and 225 °C. The reason for selecting curing temperature of 180 °C is shown in Fig. 5.6. 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°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 °C for 2 hours was chosen as an optimum curing condition of these benzoxazine molding compounds

5.4 Physical Characterization

5.4.1 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 in corporated 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. 5.7. 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.

5.4.2 Water Absorption

Fig. 5.8 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 absorptivity 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. 5.8 also shows the effect of woodflour composition on water absorption rate and amount of water absorbed when the steady state is reached. Fig. 5.9 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. 5.10 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 pseuso-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.

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5.4.3 Degradation Temperature of Woodflour-filled Polybenzoxazine Composite

Fig. 5.11 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. 5.12. 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. 5.13 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. 5.13 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.

5.5 Mechanical Characterization

5.5.1 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. 5.14 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). In the contrary, 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 effected by a change in the filler content. As shown in Fig. 5.14, 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. 5.15. A large increase of ca. 20 - 40 ^{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. 5.16 is the DSC thermograms of the fully cured polybenzoxazine wood showing the glass transition temperature of the same systems examined in Fig. 5.15. 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. 5.17 shows effect of filler contents on the glass transition temperature of woodflour-filled polybenzoxazine composites. As seen in Fig. 5.17, 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. 5.18 is the plots of tan δ versus temperature of woodflour-filled polybenzoxazine composites, which show the increase in the peak maxima of tan δ 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.

5.5.2 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 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.

5.5.2.1 Flexural Modulus

Fig.5.19 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 of higher than 75 % by weight, the load transfer from the matrix to the filler becomes less efficient, resulting in a drop in 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).

5.5.2.2 Flexural Strength

The flexural strength or the modulus of rupture is shown in Fig. 5.20. 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).

5.6 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 have 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. 5.21 shows morphology of the fracture surface of the woodflour-filled polybenzoxazine composite. Fig. 5.21 (a) shows morphology of untreated woodflour surface area which is rather smooth and even. Fig. 5.21 (b) and 5.21 (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 transfer to yield high modulus values of the composite materials. Fig. 5.21 (b) and 5.21 (c) also show good miscibility of the two phases which enhance mechanical mixing leading to the improved dispersion of the woodflour in the polybenzoxazine matrix. As explained in Chapter 2, 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.

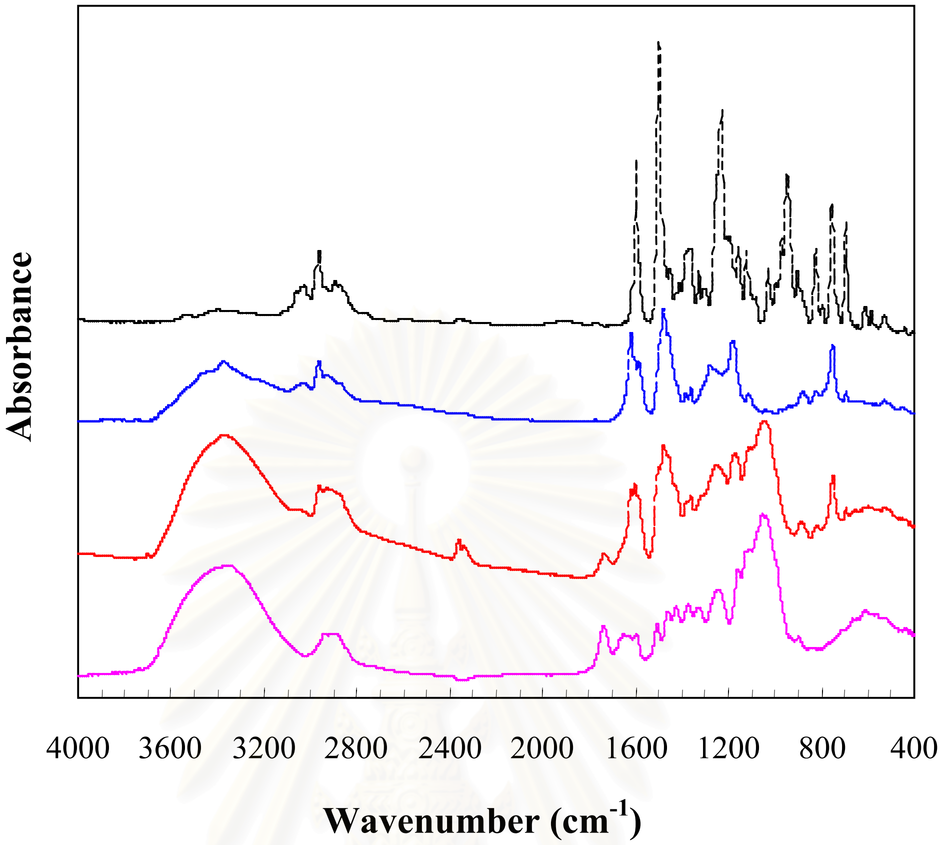

Figure 5.1: IR spectra of benzoxazine monomer, polybenzoxazine, woodflour, and woodflour-filled polybenzoxazine composite. (------) BA-a monomer, (------) polybenzoxazine, (------) 40 wt% WF, (------) woodflour

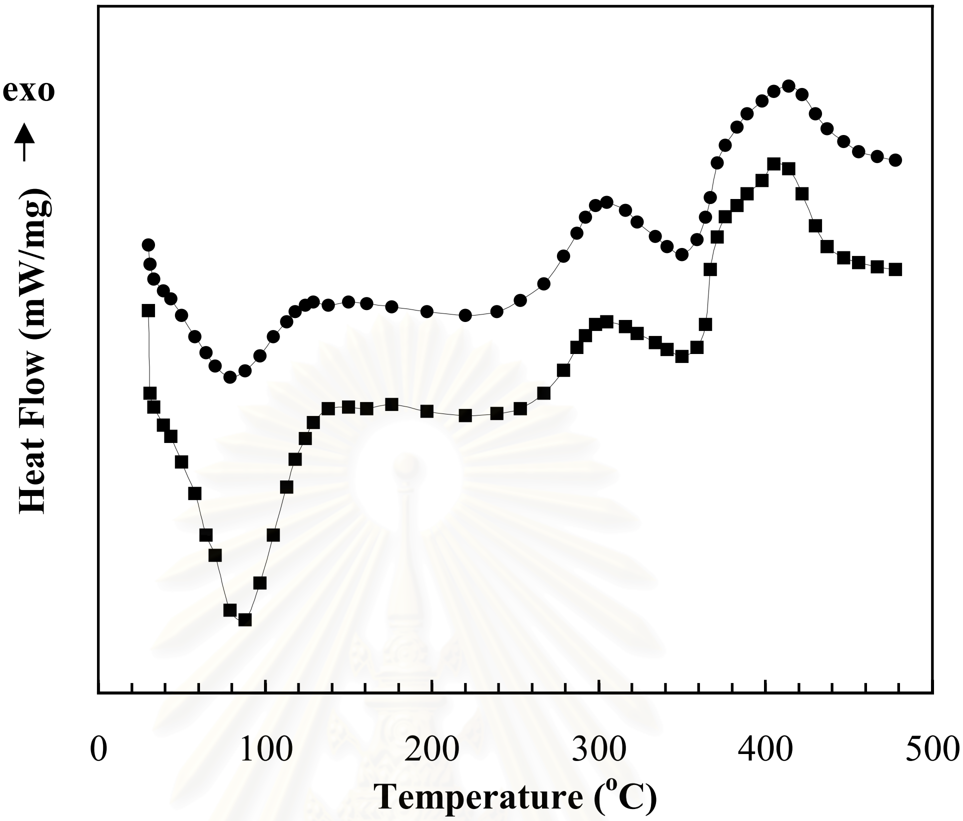

Figure 5.2: DSC thermograms of woodflour (*hevea brasiliensis*) as a function of temperature at particle size < 149 μm. (■) untreated, (▫)heat treated.

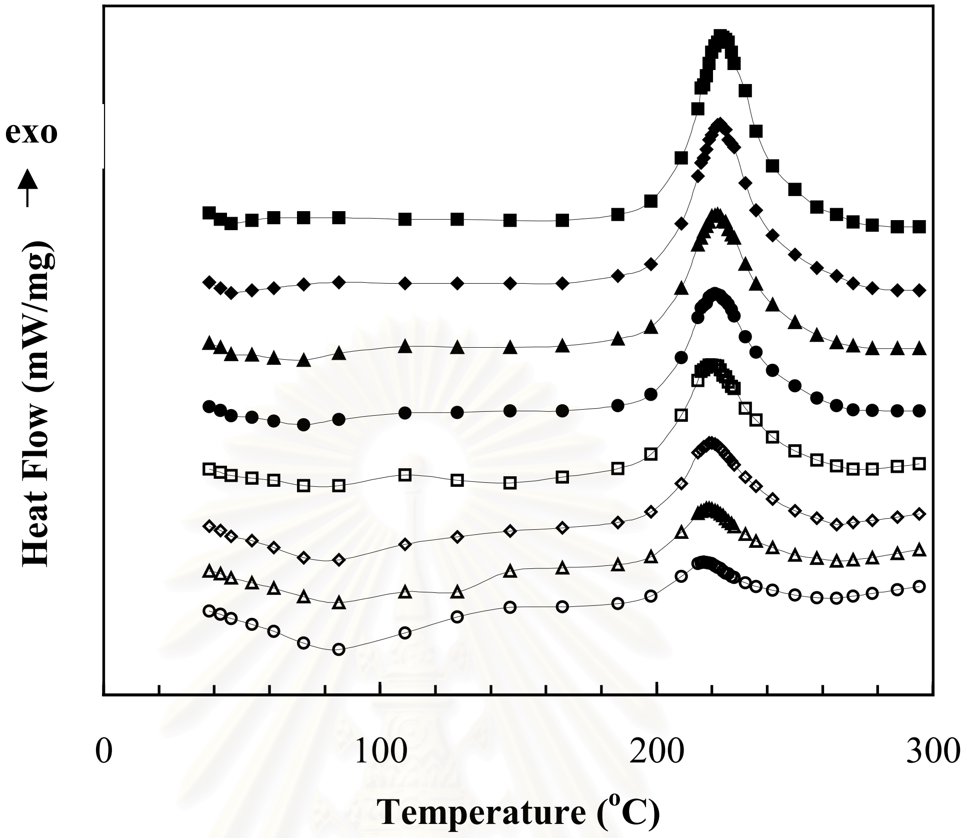

Figure 5.3: DSC thermograms of woodflour-filled polybenzoxazine composite at different filler content. (■) neat resin, (◆) 10 wt% WF, (⁂) 20 wt% WF, (●) 30 wt% WF, (□) 40 wt% WF, (❋) 50 wt% WF, (△) 60 wt% WF, (○) 70 wt% WF.

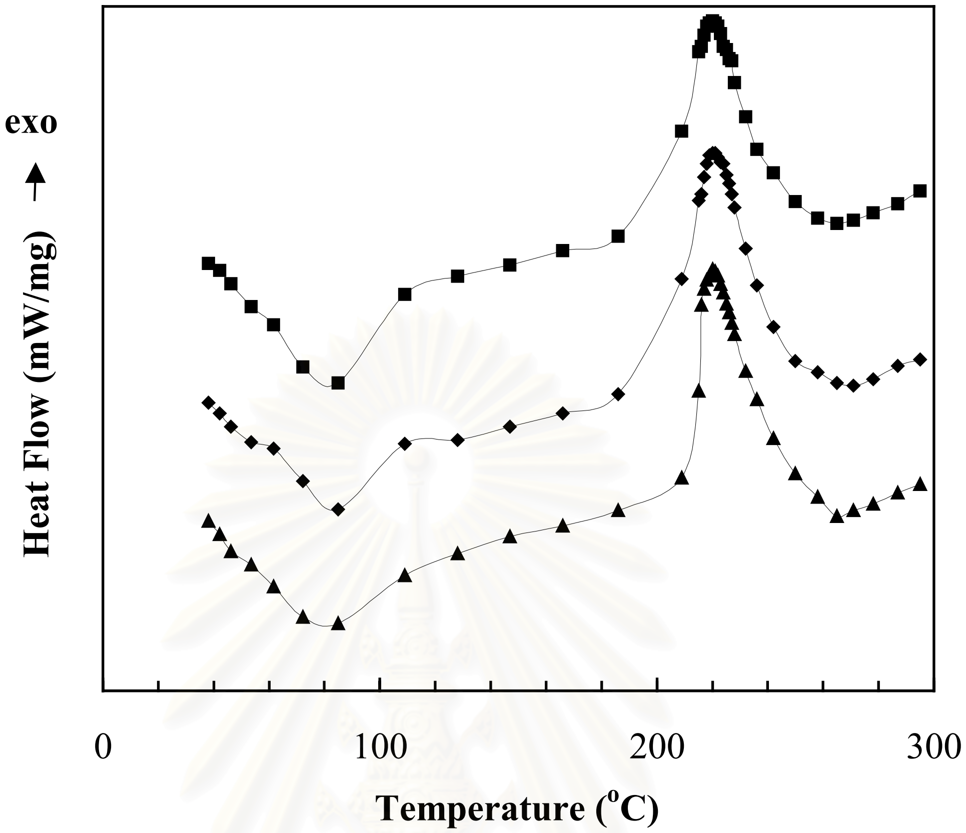

Figure 5.4: Effect of the particle size of woodflour (*hevea brasiliensis*) on curing temperature. (■) 420-595 μm, (◆) 250-297 μm, (▲) < 149μm.

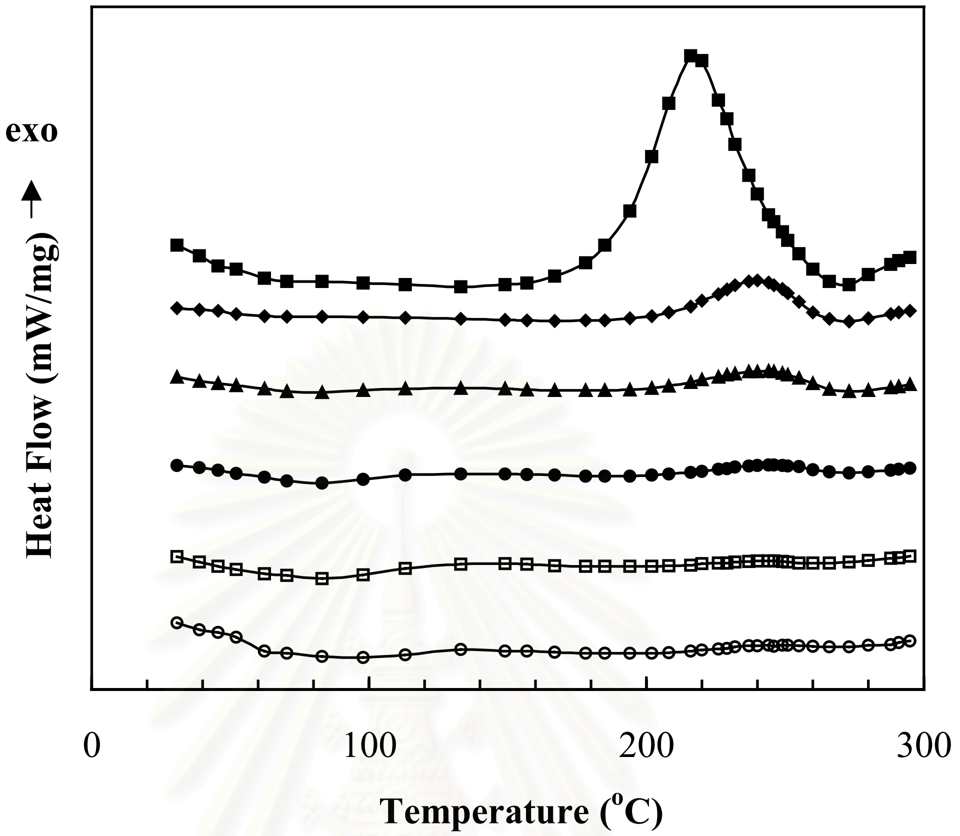

Figure 5.5: Effect of curing time on woodflour-filled polybenzoxazine composite at 40 wt% woodflour content. The condition of curing temperature at 180 ^oC., (■) 0 min, (◆) 30 min, (□) 60 min, (●) 90 min, (□) 120 min, (○) 150 min.

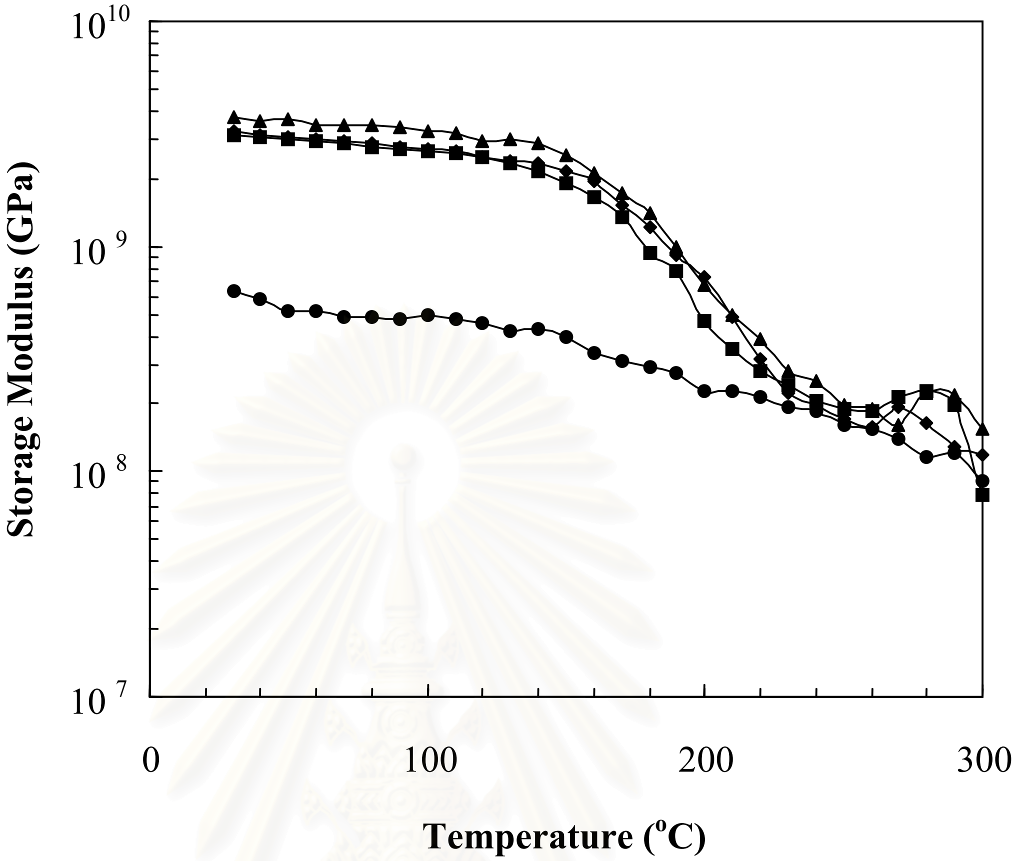

Figure 5.6: Storage modulus of woodflour-filled polybenzoxazine composite as a function of temperature at different curing temperature at 75 wt% of woodflour. (■) 160 °C, (◆) 170 °C, (▲) 180 °C, (●) 200 °C.

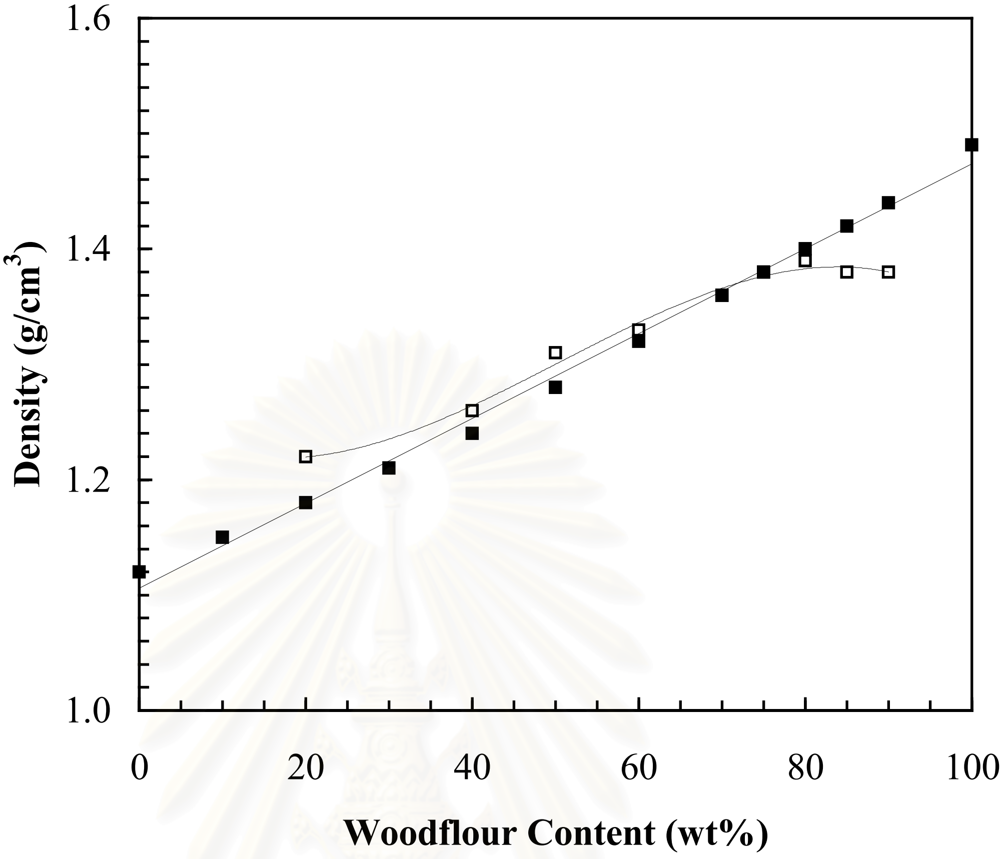

Figure 5.7: The maximum packing density of woodflour-filled polybenzoxazine composite using *hevea brasiliensis* woodflour particle size < 149 µm. (■) theoretical density, (□) experimental density.

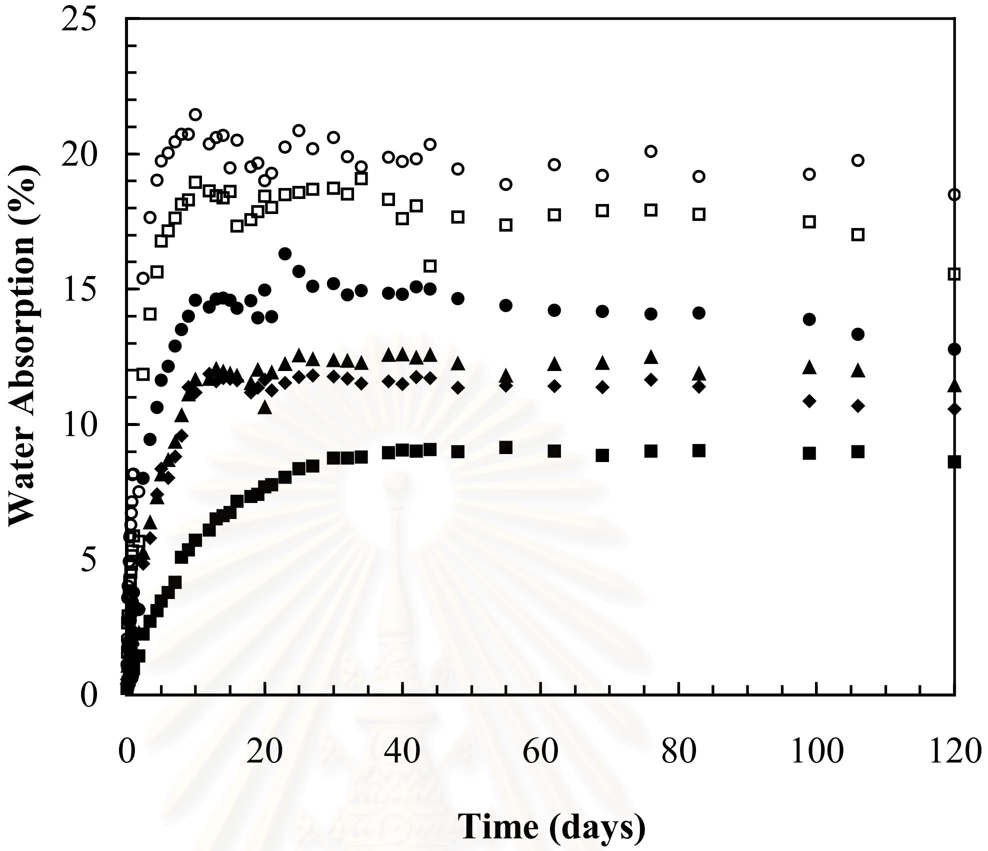

Figure 5.8: Water absorption of woodflour-filled polybenzoxazine composite at different filler content. (■) 40 wt% WF, (◆) 50 wt% WF, (▲) 60 wt% WF, (●) 70 wt% WF, (□) 75 wt% WF, (○) 80 wt% WF.

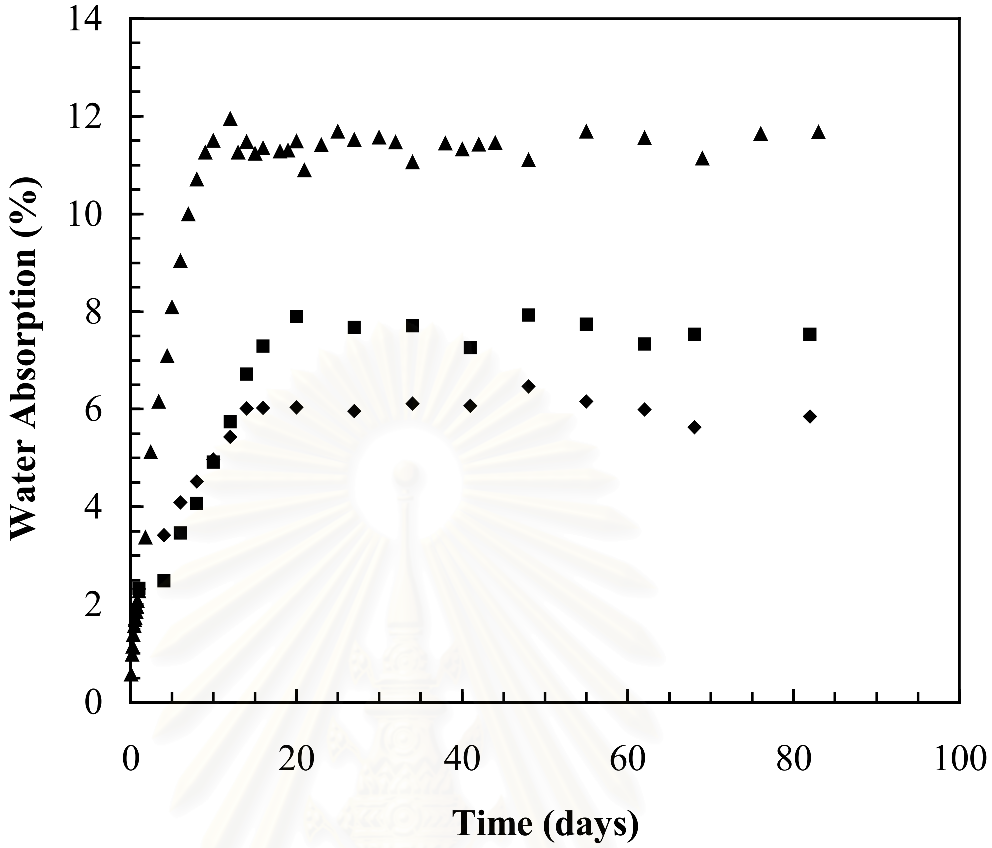

Figure 5.9: Water absorption of woodflour-filled polybenzoxazine composite at 50 wt% of woodflour with different particle size. (■) 420-595 μm., (◆) 250-297 μm, (▲) < 149 μm.

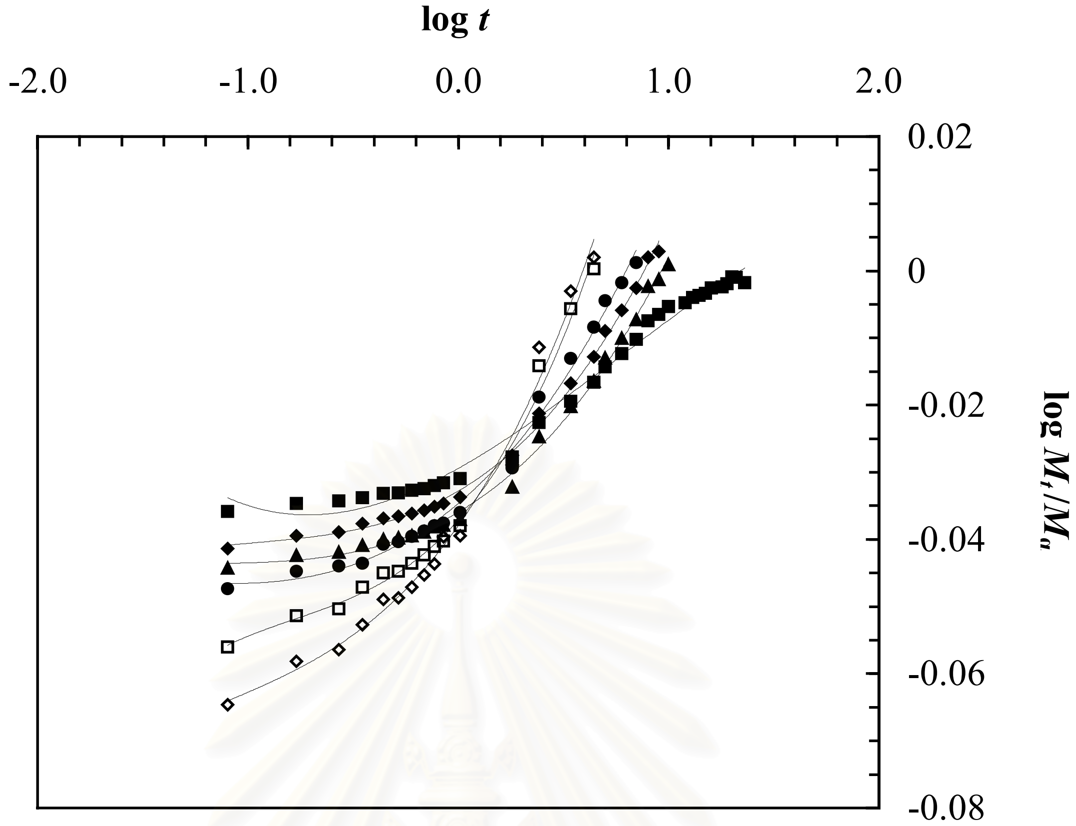

Figure 5.10: Plots between log M_t/M_α and time to determine the diffusion exponents in Eq.(2.7) of woodflour-filled polybenzoxazine composite at different filler content. (■) 40 wt% WF, (◆) 50 wt% WF, (▲) 60 wt% WF, (●) 70 wt% WF, (□) 75 wt% WF, (○) 80 wt% WF.

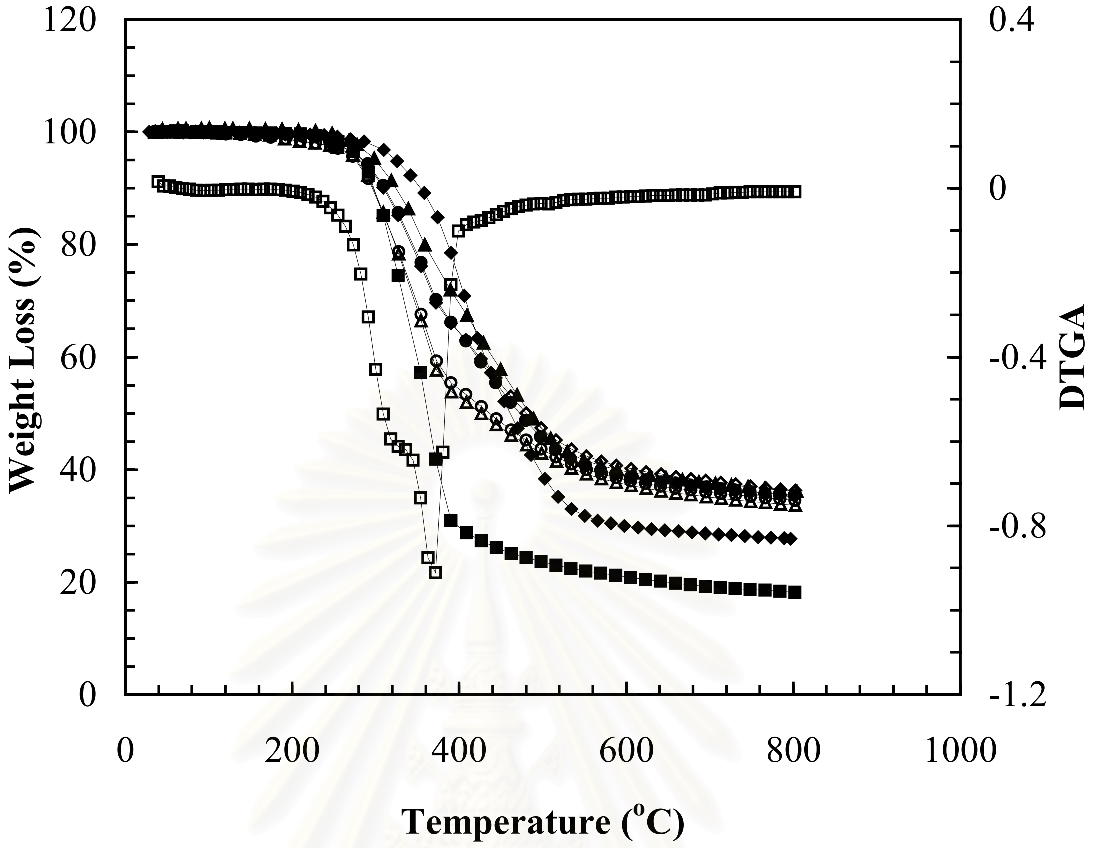

Figure 5.11: TGA experiment for composition determination of woodflour-filled polybenzoxazine composite samples. (■) woodflour, (⊙) DTGA of woodflour, (◆) neat resin, (⁂) 40 wt% WF, (●) 50 wt% WF, (✱) 60 wt% WF, (∆) 70 wt% WF, (○) 80 wt% WF.

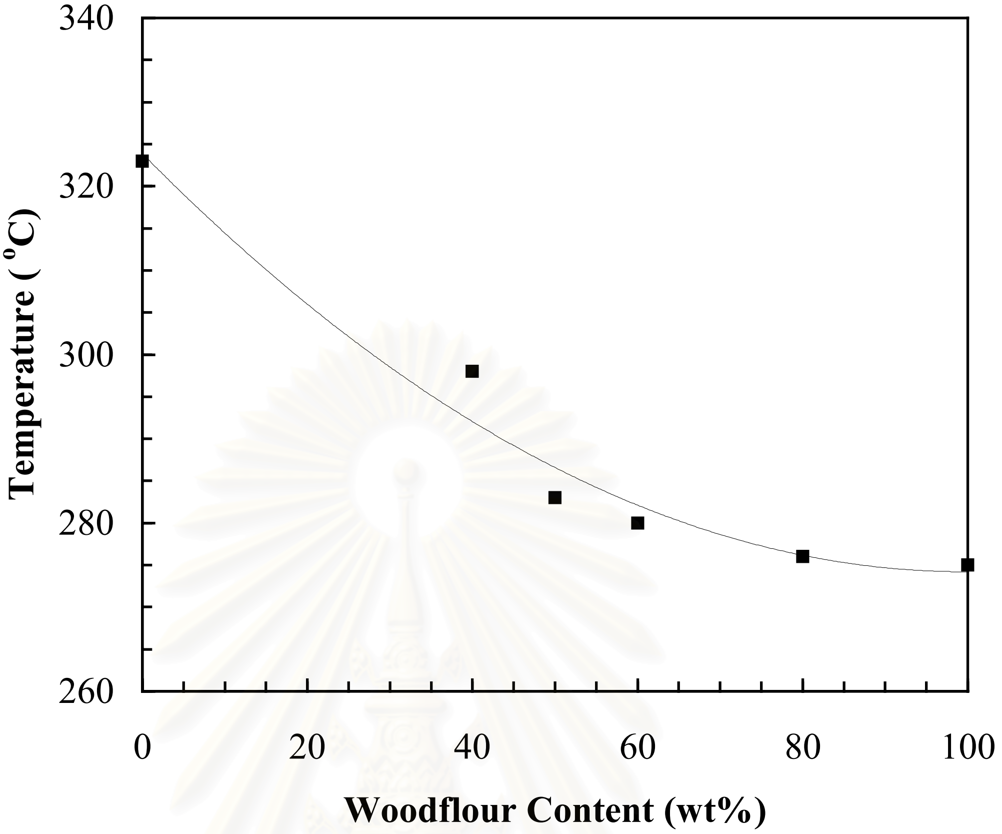

Figure 5.12: Effect of woodflour content on the degradation temperature of the woodflour-filled polybenzoxazine composite (800 ^{o}C under nitrogen atmosphere).

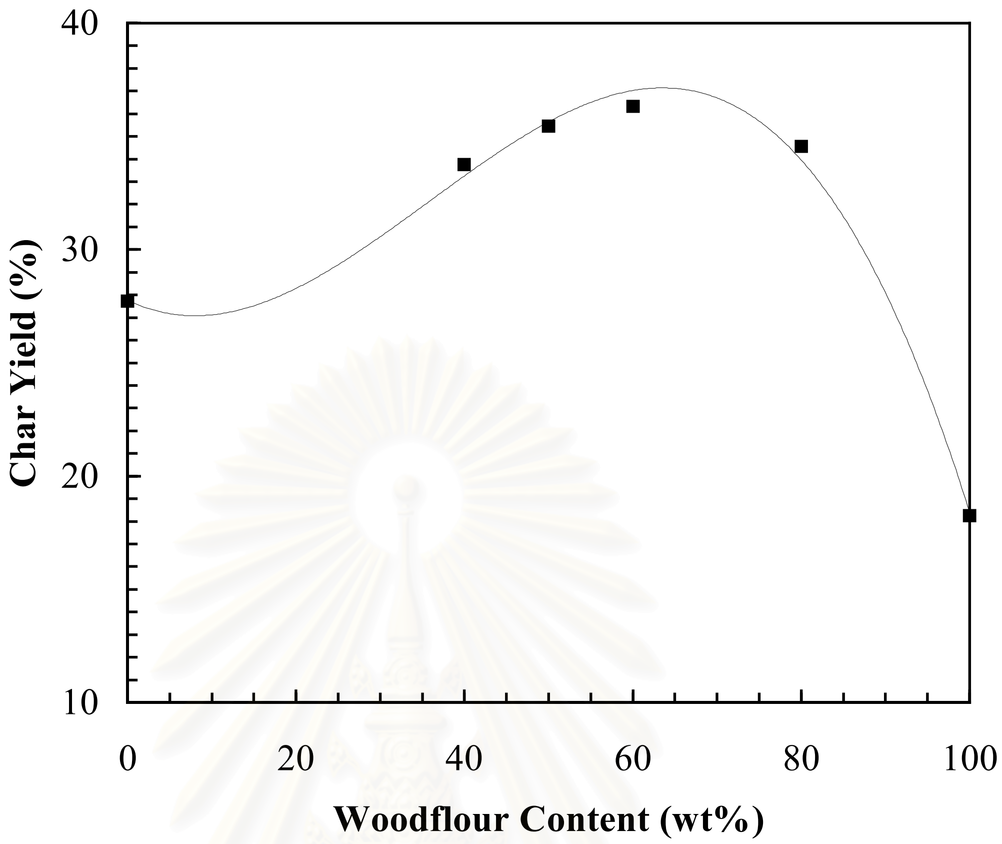

Figure 5.13: Effect of woodflour content on the char yield of the woodflour-filled polybenzoxazine composite (800 °C under nitrogen atmosphere).

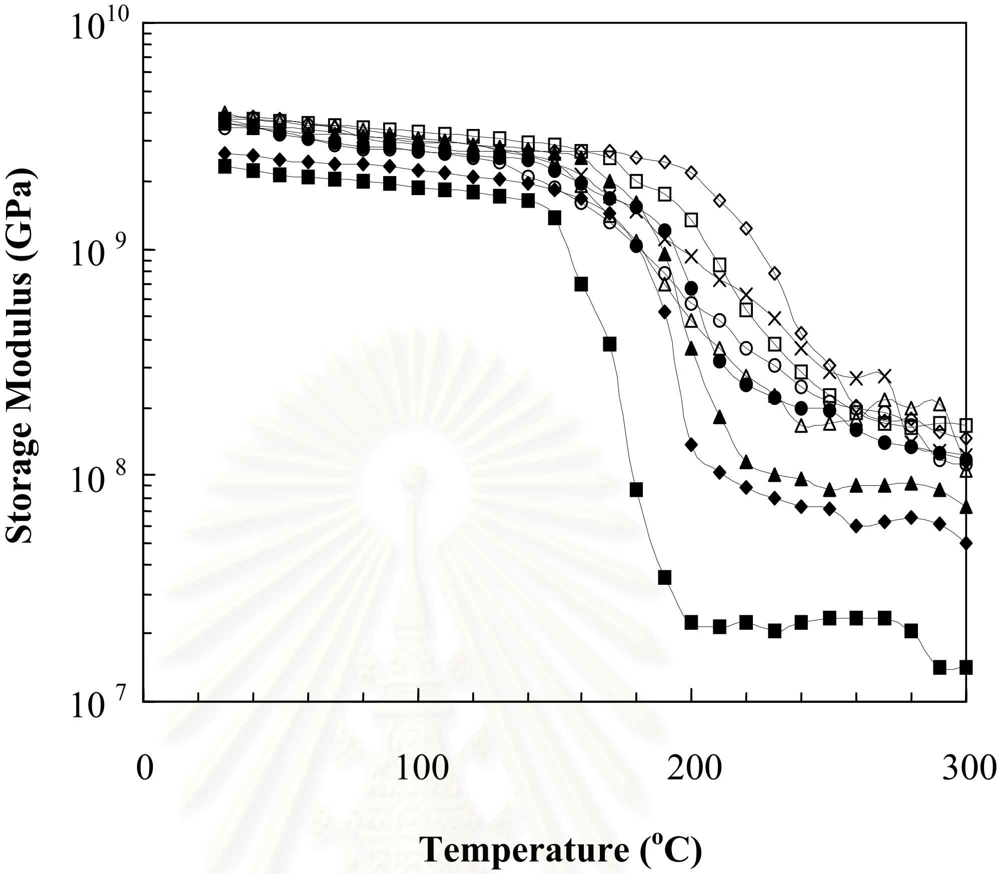

Figure 5.14: Storage modulus of woodflour-filled polybenzoxazine composite as a function of temperature at different filler content. (■) neat resin, (◆) 40 wt% WF, (⁂) 50 wt% WF, (●) 60 wt% WF, (□) 70 wt% WF, (❋) 75 wt% WF, (Δ) 80 wt% WF, (○) 85 wt% WF, (×) 90 wt% WF.

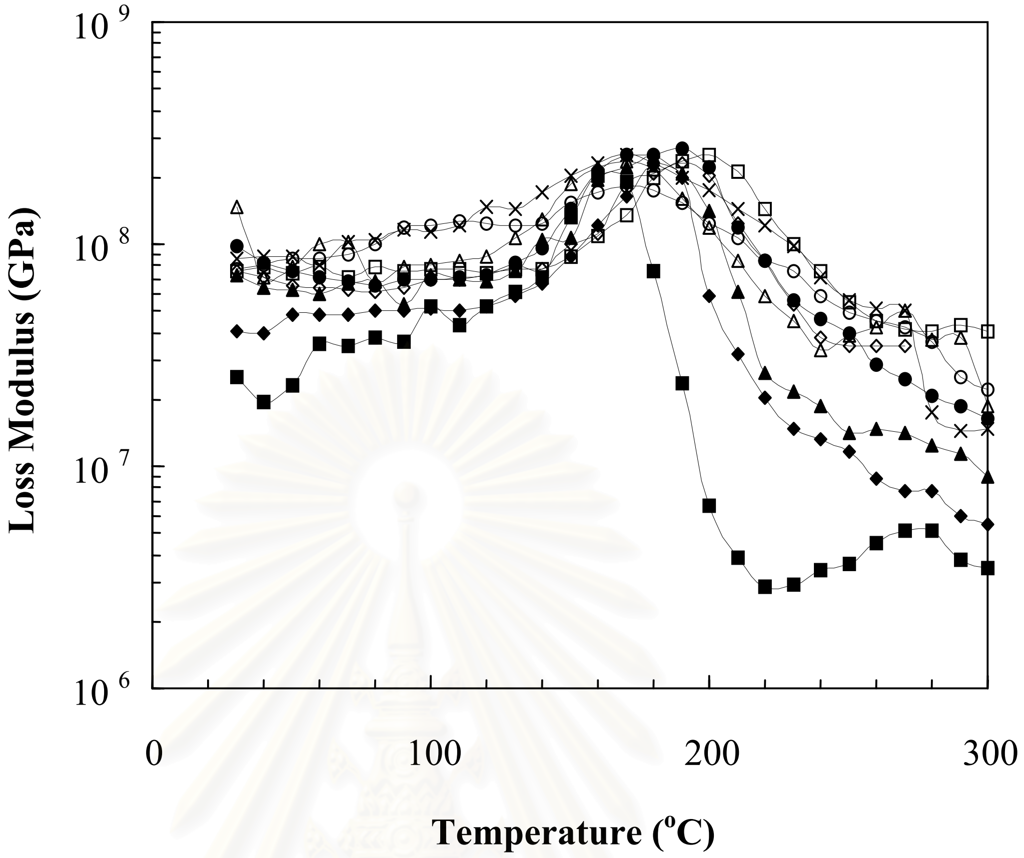

Figure 5.15: Loss modulus of woodflour-filled polybenzoxazine composite as a function of temperature at different filler content. (■) neat resin, (◆) 40 wt% WF, (⁂) 50 wt% WF, (●) 60 wt% WF, (□) 70 wt% WF, (✱) 75 wt% WF, (△) 80 wt% WF, (○) 85 wt% WF, (×) 90 wt% WF.

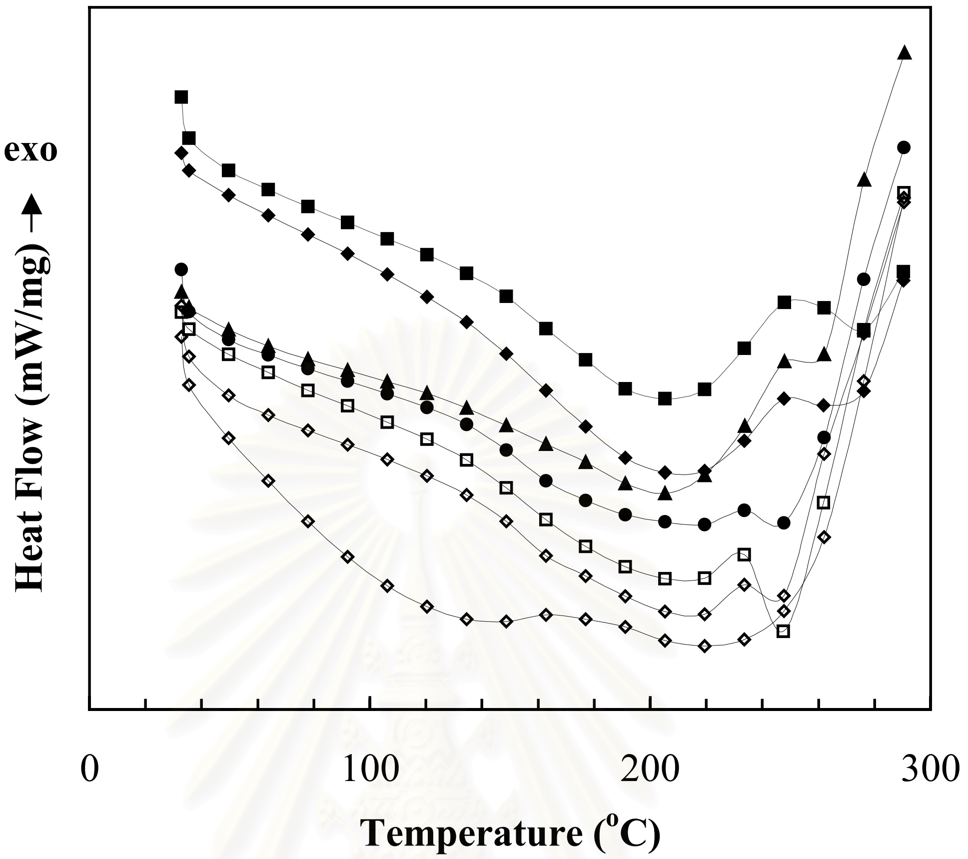

Figure 5.16: DSC thermograms of woodflour-filled polybenzoxazine composite as a function of temperature at different filler content. (■) 40 wt% WF, (◆) 50 wt% WF, (⁂) 60 wt% WF, (●) 70 wt% WF, (□) 75 wt% WF, (❋) 80 wt% WF, (△) 90 wt% WF.

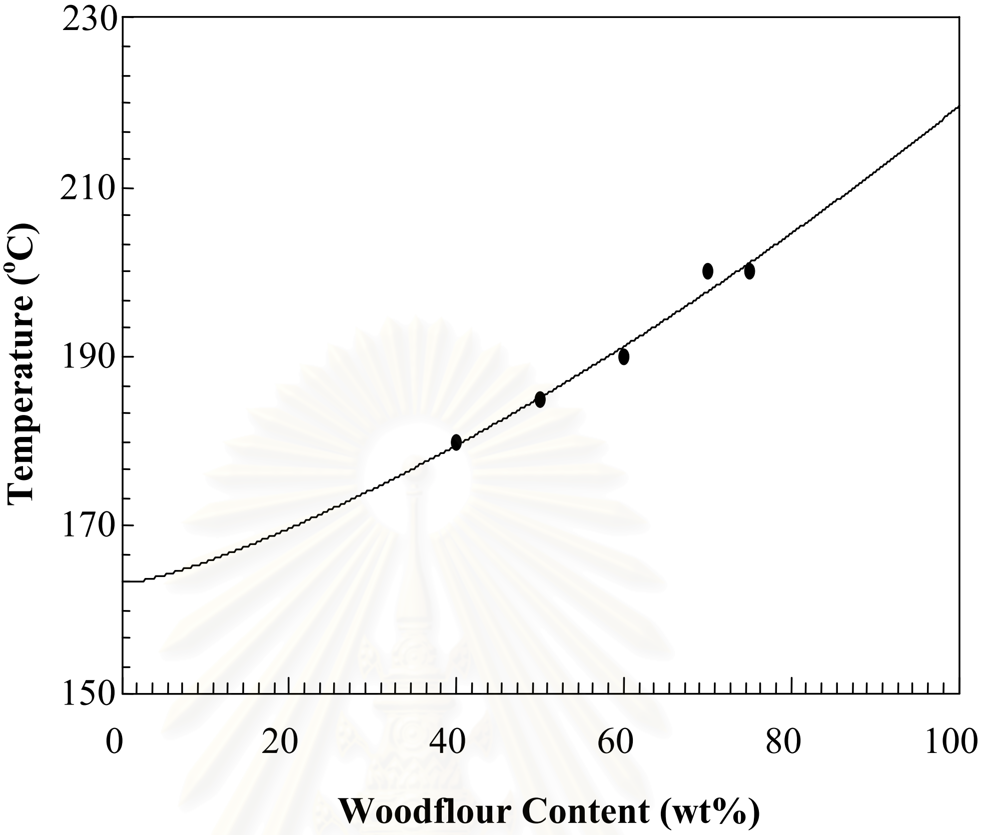

Figure 5.17: The effect of filler content on glass-transition temperature of woodflour-filled polybenzoxazine composite.

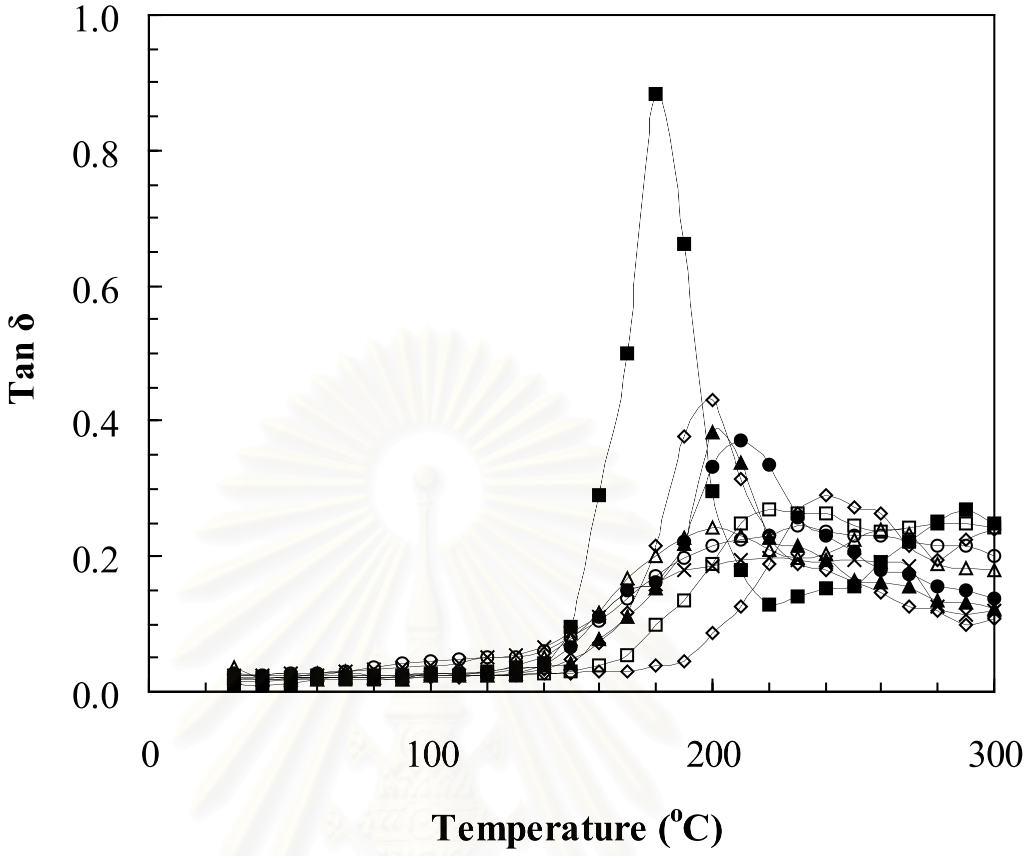

Figure 5.18: Tan δ of woodflour-filled polybenzoxazine composite as a function of temperature at different filler content. (■) neat resin, (◆) 40 wt% WF, (⁂) 50 wt% WF, (●) 60 wt% WF, (□) 70 wt% WF, (✱) 75 wt% WF, (△) 80 wt% WF, (○) 85 wt% WF, (×) 90 wt% WF.

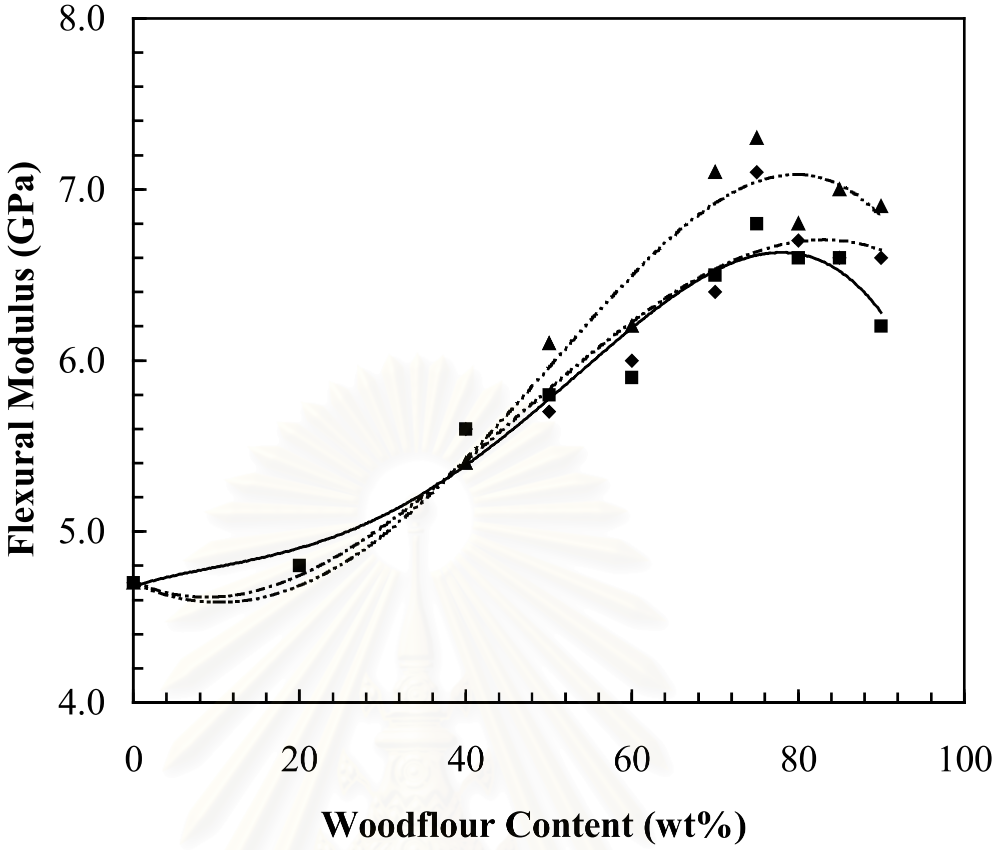

Figure 5.19: Flexural modulus of woodflour-filled polybenzoxazine composite at different filler content. (- - -▲- - -) 420-595 μm, (- - -◆- - -) 250-297 μm, (— ■ —) < 149 μm.

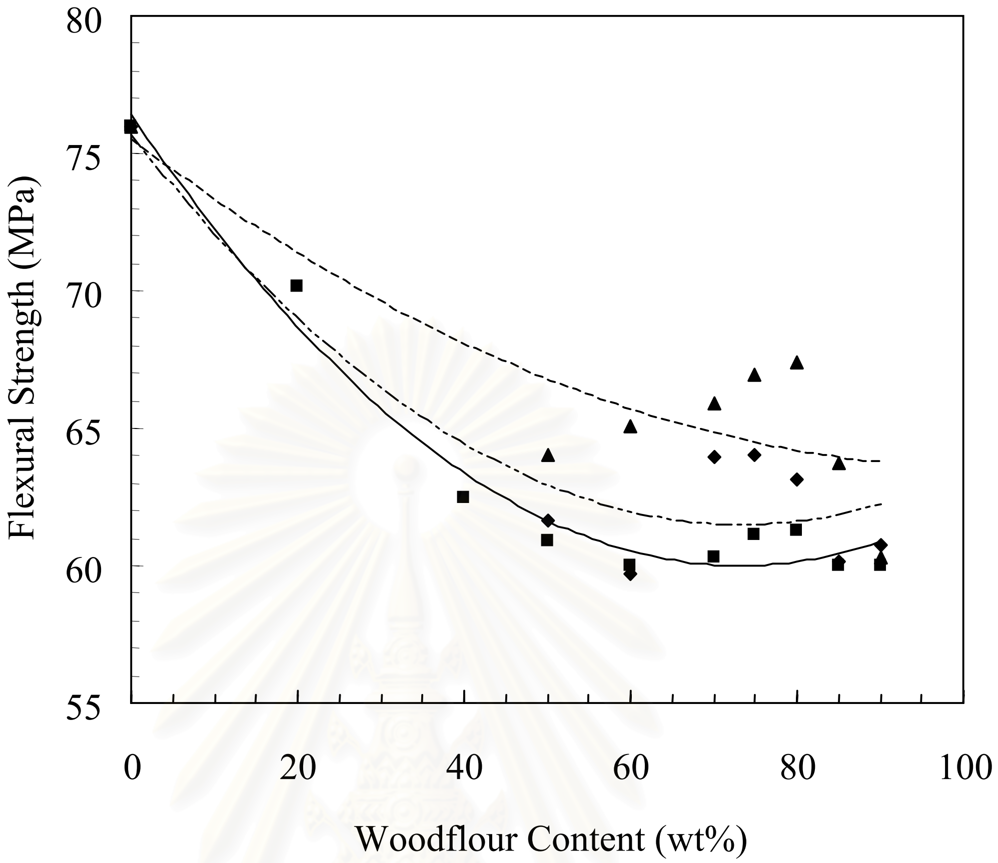

Figure 5.20: Flexural strength of woodflour-filled polybenzoxazine composite at different filler content. (- - -▲- - -) 420-595 μm, (– –◆– –) 250-297 μm, (—■—) < 149 μm.

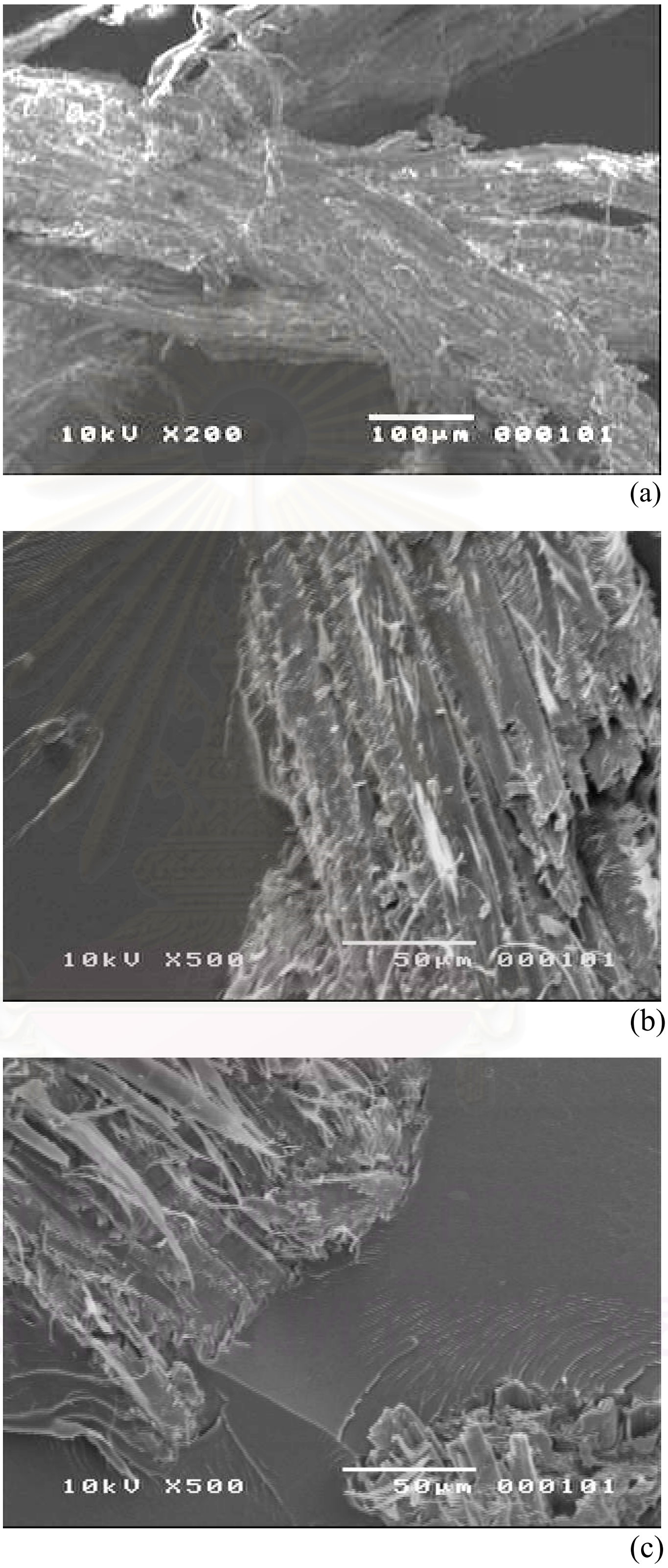

Figure 5.21: SEM micrograph of the fracture surface (a) non-treated of woodflour, (b) and (c) 10 wt% of woodflour in polybenzoxazine matrix.

CHAPTER 6

CONCLUSIONS

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 °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. This 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 our wood composite is higher than the woodflour-filled unsaturated polyester/styrene when compared at the same filler content. The peaks of loss modulus (G″) and tan δ were used to define the glass transition temperature of the specimens. The glass transition temperature of the composite was found to increase with woodflour content i.e. from 160 °C in the case of the unfilled system to 200 °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 shows the value of modulus to be 6.8-7.3 GPa. Therefore, the flexural modulus of our wood composite is in the vicinity of the natural wood (*Hevea brasiliensis* 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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APPENDICES

APPENDIX A

Condition of Process Method of Woodflour-filled Polybenzoxazine Composite

Appendix A-1 using the storage modulus to estimate the condition of processing by compression molding at time 2 hr.

Temperature (^{o}C)	Storage Modulus (Pa)
160	3.11×10^{9}
170	3.24×10^{9}
180	3.72×10^{9}
200	6.37×10^{8}

APPENDIX B

Physical Characterization

Appendix B-1 The maximum packing density of woodflour-filled polybenzoxazine composite using *hevea brasiliensis* woodflour at different particle size.

Woodflour Content (wt%)	Theoretical Density (g/cm^3)	Real Density of particle size < 149 μm.	Real Density of particle size 250-297 μm.	Real Density of particle size 420-595 μm.
0	1.12	-	-	-
10	1.15	-	-	-
20	1.18	1.22	-	-
30	1.21	-	-	-
40	1.24	1.26	1.28	1.26
50	1.28	1.31	1.31	1.29
60	1.32	1.33	1.34	1.34
70	1.36	1.36	1.35	1.37
75	1.38	1.38	1.37	1.38
80	1.40	1.39	1.36	1.37
85	1.42	1.38	1.36	1.37
90	1.44	1.38	1.36	1.35
100	1.49*	0.64**	0.67	0.67

* Density of woodflour

** Density of wood at 16 % Moisture Content

Appendix B-2 Water Absorption of woodflour-filled polybenzoxazine composite, particle size < 149 μm.

Woodflour Content (wt%)	24 hr (%)	7 days (%)	Saturation (%)
0	0.11	0.28	1.9
40	0.97	4.17	8.94
50	2.37	8.81	11.76
60	2.32	9.34	12.57
70	3.79	12.88	14.95
75	5.88	17.63	18.49
80	8.16	20.44	19.71

Appendix B-3 The glass transition and the degradation temperature of woodflour-filled polybenzoxazine composite.

Woodflour Content (wt%)	Glass Transition Temperature (^oC)	Degradation Temperature (^oC)	Char Yield (%)
0	160	323	27.72
40	180	298	33.76
50	185	283	35.45
60	190	280	36.32
70	200	-	-
75	200	-	-
80	-	276	34.56
100	240	275	18.24

APPENDIX C

Mechanical Characterization

Dynamic Mechanical Measurement

Appendix C-1 The storage modulus of woodflour-filled polybenzoxazine composite, particle size < 149 μm.

Woodflour Content (wt%)	Storage Modulus (GPa)
0	2.33
40	2.65
50	3.58
60	3.78
70	3.78
75	3.85
80	4.03
85	3.47
90	3.61
100	5.62

Flexural Properties

Appendix C-2 Flexural modulus and flexural strength of woodflour-filled polybenzoxazine composite by using *heavea brasiliensis* woodflour.

Woodflour Content (wt%)	Flexural Modulus (GPa)			Flexural Strength (MPa)		
	< 149 µm.	250-297 µm.	420-595 µm.	< 149 µm.	250-297 µm.	420-595 µm.
0	4.7	4.7	4.7	76.00	76	76.00
20	4.8	-	-	70.13	-	-
40	5.6	5.6	5.4	-		-
50	5.8	5.7	6.1	60.91	61.65	64.60
60	5.9	6.0	6.2	60.00	63.18	65.04
70	6.5	6.4	7.1	60.27	67.73	69.11
75	6.8	7.1	7.3	61.10	72.80	70.15
80	6.6	6.7	6.8	61.29	63.13	67.39
85	6.6	6.6	7.0	60.00	60.17	63.72
90	6.2	6.6	6.9	60.00	65.65	60.72
100	9.7*	9.7	9.7	66.00**	66.00	66

* Flexural Modulus of wood at 12 % Moisture Content

** Flexural Strength of wood at 12 % Moisture Content

APPENDIX D

Data of Figure 2.11

Appendic D-1 Successive sorptions for water-cellulose at 15 ^{o}C.

Film thickness 26.2 μm.

Curve No.	Vapour Pressure Increment (mm Hg)	Concentration Increment (g/g)
1	0.00-0.55	0.000-0.029
2	0.55-1.29	0.029-0.045
3	1.29-2.74	0.045-0.072
4	2.74-3.89	0.072-0.089
5	3.89-5.12	0.089-0.108
6	5.12-6.50	0.108-0.134
7	7.73-9.03	0.155-0.187
8	9.03-10.17	0.187-0.226
9	10.17-11.45	0.226-0.283

VITAE

Miss Chanjira Jubsilp was born in Nakorn Si thammarat, Thailand, on October 24th, 1977. She graduated at high school level in 1995 from Benchamarachutist (Nakorn Si thammarat) school. She received the Bachelor Degree of Engineering with a major in Chemical Engineering from the Faculty of Engineering, King Mongkut's University of Technology Thonburi in 2000. After graduation, she entered study for a Master Degree of Chemical Engineering at the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.