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Development of High Performance PMDA-Modified Polybenzoxazine Composites
Reinforced with Carbon Fiber

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A Thesis Submitted in Partial Fulfillment of the Requirements
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Thesis Title DEVELOPMENT OF HIGH PERFORMANCE
 PMDA-MODIFIED POLYBENZOXAZINE
 COMPOSITES REINFORCED WITH CARBON FIBER

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ชลิตา ปัญญาวานิชกุล : การพัฒนาวัสดุประกอบแต่งสมรรถนะสูงของพอลิเบนซอกซาซีนที่ดัดแปรด้วยสารไพโรเมลลิติก ไดแอนไฮไดรด์ เสริมแรงด้วยเส้นใยคาร์บอน.
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งานวิจัยนี้มีจุดมุ่งหมายเพื่อพัฒนาวัสดุประกอบแต่งสมรรถนะสูงจากพอลิเบนซอกซาซีน (PBA-a) ดัดแปรด้วยสารไพโรเมลลิติก ไดแอนไฮไดรด์ (PMDA) ที่เสริมแรงด้วยเส้นใยคาร์บอน โดยศึกษาผลของเส้นใยคาร์บอนและปริมาณสารไดแอนไฮไดรด์ชนิด PMDA ต่อสมบัติการติดไฟ ทางกล และทางความร้อนของวัสดุประกอบแต่งเส้นใยคาร์บอน เมื่อพิจารณาสมบัติทางกลและทางความร้อนของวัสดุประกอบแต่งเส้นใยคาร์บอนที่ดีที่สุด พบว่า วัสดุประกอบแต่งมีความสามารถในการบรรจุเส้นใยคาร์บอนใน PBA-a:PMDA เมตริกซ์ เท่ากับ 65 เปอร์เซ็นต์โดยน้ำหนัก สำหรับความสามารถในการทนไฟโดยการทดสอบหาค่าปริมาณออกซิเจนที่น้อยที่สุดที่ช่วยในการติดไฟ (Limiting Oxygen Index: LOI) และระดับการทนไฟในแนวตั้งตามมาตรฐานการทดสอบ UL-94 ของวัสดุประกอบแต่งที่ประกอบด้วยเส้นใยคาร์บอนในปริมาณ 65 เปอร์เซ็นต์โดยน้ำหนัก ใน PBA-a:PMDA เมตริกซ์ ซึ่งทำการเปลี่ยนแปลงสัดส่วนโดยโมลของสารไดแอนไฮไดรด์ชนิด PMDA จะได้ว่า วัสดุประกอบแต่งของ PBA-a ที่เสริมแรงด้วยเส้นใยคาร์บอนในปริมาณ 65 เปอร์เซ็นต์โดยน้ำหนัก (65wt% CF/PBA-a) มีค่า LOI เท่ากับ 26.0 ในขณะที่วัสดุประกอบแต่งของ PBA-a:PMDA เมตริกซ์ที่เสริมแรงเส้นใยคาร์บอน ในปริมาณ 65 เปอร์เซ็นต์โดยน้ำหนัก (65wt% CF/PBA-a:PMDA) มีค่า LOI เพิ่มขึ้นเท่ากับ 49.5 นอกจากนี้วัสดุประกอบแต่ง 65wt% CF/PBA-a:PMDA ที่มีความหนาเพียง 1 มิลลิเมตรสามารถทนการติดไฟระดับสูงสุด คือ V-0 สำหรับค่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วและค่าสตอเรจมอดูลัสที่อุณหภูมิ 35 องศาเซลเซียส ของวัสดุประกอบแต่ง 65wt% CF/PBA-a:PMDA มีค่าสูงกว่าเมื่อเปรียบเทียบกับวัสดุประกอบแต่ง 65wt% CF/PBA-a โดยค่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วและค่าสตอเรจมอดูลัสที่อุณหภูมิ 35 องศาเซลเซียส ของวัสดุประกอบแต่ง 65wt% CF/PBA-a:PMDA มีค่าสูงถึง 237 องศาเซลเซียส และ 46 จิกะปาสคาล ตามลำดับ ในขณะที่วัสดุประกอบแต่ง 65wt% CF/PBA-a มีค่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วและค่าสตอเรจมอดูลัสที่อุณหภูมิ 35 องศาเซลเซียสเท่ากับ 183 องศาเซลเซียส และ 41 จิกะปาสคาล ตามลำดับ นอกจากนี้ จากผลการทดสอบด้วยเครื่อง Thermogravimetric analysis (TGA) จะได้ว่า ค่าอุณหภูมิการสลายตัวทางความร้อนและปริมาณเถ้าที่อุณหภูมิ 800 องศาเซลเซียสของวัสดุประกอบแต่ง 65wt% CF/PBA-a (405 องศาเซลเซียส และ 75.7 % ตามลำดับ) มีค่าเพิ่มขึ้นเมื่อมีการเพิ่มสัดส่วนของสารไดแอนไฮไดรด์ชนิด PMDA ใน PBA-a เมตริกซ์ ซึ่งทำให้วัสดุประกอบแต่ง 65wt% CF/PBA-a:PMDA มีค่าอุณหภูมิการสลายตัวทางความร้อนสูงถึง 498 องศาเซลเซียส และปริมาณเถ้าที่อุณหภูมิ 800 องศาเซลเซียส เท่ากับ 82 % ดังนั้นเนื่องด้วยสมบัติการทนการติดไฟ สมบัติทางกลและทางความร้อนที่ดีขึ้น วัสดุประกอบแต่งจากพอลิเบนซอกซาซีน (PBA-a) ดัดแปรด้วยสารไดแอนไฮไดรด์ชนิด PMDA ที่เสริมแรงด้วยเส้นใยคาร์บอนจึงมีศักยภาพในการใช้งานสำหรับวัสดุประกอบแต่งขั้นสูงที่ต้องการสมบัติทางกลที่ดีและเมื่อติดไฟแล้วสามารถดับไฟได้ด้วยตัวเอง

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KEYWORDS: POLYBENZOXAZINE / DIANHYDRIDES / CARBON FIBER /
COMPOSITE / FLAMMABILITY

CHALITA PANYAWANITCHAKUN: DEVELOPMENT OF HIGH
PERFORMANCE PMDA-MODIFIED POLYBENZOXAZINE
COMPOSITES REINFORCED WITH CARBON FIBER. THESIS

ADVISOR: ASSOC. PROF. SARAWUT RIMDUSIT, 'Ph.D., THESIS CO-
ADVISOR: CHANCHIRA JUBSILP, D.Eng., 118 pp.

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

Department : Chemical Engineering Student's Signature

Field of Study : Chemical Engineering Advisor's Signature

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CHAPTER I

INTRODUCTION

1.1 Introduction

Advanced polymer composites have been used in many kinds of high performance industries i.e. automotive, marine, electronic packaging and aerospace industry that require excellent mechanical properties especially in structural utilizations due to their outstanding specific modulus and specific strength [1-4]. Carbon fiber reinforced composites are often used in weight reduction and high specific strength. During production of composites, it is frequently required to form prepregs for easy handling and easy processing. They are supplied in roll or sheet form and are widely used in high performance applications.

Good prepregs characteristics include not only specific end-properties but also processability of the material such as shelf life, pot life of the system at various temperatures, temperature range for completing cure and post-cure conditions etc. [5-10]. There are two general prepregging methods i.e. solution and hot melt impregnation. Each method is depending on the processability of matrix resins to provide the appropriate resin viscosity to coat the reinforcing fiber. Since the composite quality is controlled by resin-fiber interfacial wetting and uniform resin content therefore the low viscosity resins are essentially required [8].

Polybenzoxazine a novel class of phenolic resins have a wide range of interesting properties and potentials to overcome several shortcomings of conventional novolac and resole type phenolic resin, while retaining their benefits like near upon curing, the glass transition temperature (T_g) much higher than cure

temperature, fast mechanical property build-up as a function of degree of polymerization, high char-yield, low CTE, low viscosity, low moisture absorption and excellent electrical properties [11]. The polymer can be synthesized by ring-opening polymerization of the aromatic oxazines, no by-products released upon curing, no catalysts needed, no solvent elimination and no need of monomer purification [12]. The properties of the material good thermal, chemical, electrical, mechanical, and physical properties including high thermal stability, good fire resistant characteristics and fast development of mechanical properties as a function of curing conversion [13]. Therefore this resin was chosen as a candidate for high performance and processability for making composites.

Moreover, the ability of the resin to form alloys with various other resins or polymers often renders a novel class of a resin system with intriguing properties [14]. Ishida and Allen investigated that alloy between benzoxazine resins (BA-a) and bisphenol A-typed epoxy exhibited greatly increase their cross-linked density, raising their glass transition temperature (141°C of neat polybenzoxazine to 155°C at 30% by weight of epoxy), increase flexural stress and flexural strain at break with only a minimal loss of stiffness [15].

Consequently, polybenzoxazines were improved by addition dianhydride like pyromellitic dianhydride (PMDA), 3,3',4,4' -benzophenonetetracarboxylic dianhydride (BTDA), 3,3',4,4' -biphenyltetracarboxylic dianhydride (s-BPDA), which were chosen for using high performance material such as the stiffness property and expectation in enhancement of both the thermal and the mechanical properties of polybenzoxazines as a high performance polymer. Ramsiri and Rimdusit suggested that BA-a/dianhydride could be casted into flexible and strong film. The optimum of mechanical and thermal properties was BA-a/PMDA equals 60/40 percent by mole [16].

Carbon fiber-reinforced composites materials have been used extensively in many engineering fields. The composites used for structural applications require excellent mechanical properties. Jongvisutisan and Rimdusit developed high performance carbon fiber based prepregs based on ternary mixture matrices of benzoxazine, epoxy, and phenolic resin. The resin composition was varied using different resin mass ratio i.e. benzoxazine/epoxy/phenolic (BEP) equals 361, 362, 363, and 364. The optimum composition of the ternary systems for making high processable carbon fiber prepregs is BEP362. The both of flexural modulus and flexural strength of the carbon fiber-reinforced BEP362 high values of about 68 GPa and 1,156 MPa respectively [17].

In this study, we investigated the composition of polybenzoxazine and dianhydride to form carbon fiber prepregs. The characteristics of carbon fiber-reinforced BA-a/dianhydride such as chemical resistant, mechanical and electrical properties, heat insulation properties and fire retardant properties of the material are evaluated.

1.2 Objectives

- 1 To develop high performance composites based on carbon fiber and pyromellitic dianhydride (PMDA) -modified benzoxazine (BA-a) resin systems.
2. To investigate the maximum packing of carbon fiber composite.
3. To evaluate molar ratios of BA-a and PMDA on high performance composites properties, i.e. physical, mechanical, thermal properties and fire resistance.
4. To study interfacial bonding between polybenzoxazine modified with dianhydride and carbon fiber.

1.3 Scopes of the study

1. Synthesis of benzoxazine resin of BA-a type by solventless synthesis technology.
2. Investigating the maximum packing of the carbon fiber composite at various carbon fiber contents ranges from 60-80% by weight at 1.5:1 mole ratio of BA-a:PMDA.
3. Evaluating the physical, thermal, mechanical properties and fire resistance of the carbon fiber composite at various mole ratios of the PBA-a resin and PMDA. i.e., 4:1, 3:1, 2:1, 1.5:1, and 1:1 in dimethylformamide (DMF) as solvent by using the maximum carbon fiber content.
4. Investigating the interfacial bonding between PMDA-modified polybenzoxazine and carbon fiber by analysis fracture surface under flexural test.

CHAPTER II

THEORY

2.1 Advanced Composites Materials [18]

Modern structural composites frequently referred to as advanced composites. The term 'advanced' means the composite materials based on polymer materials with oriented, high-modulus carbon, aramid, glass or ceramic fiber. A composite material can be defined as a microscopic 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 material that contain a reinforcement (such as fiber 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 desired attributes for a given application. The outstanding properties of composite materials include exceptionally high strength and low weight; high impact resistance and dimensional stability under extreme stresses and temperatures; resistance to weathering, rot, water, chemicals, acids, oils and solvent; and low thermal conductivity.



Figure 2.1 Application of advanced composite materials [19]

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 Fiber 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.

2.2.2 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, beauty or attractiveness, etc.

2.2.3 Particulate Composites

Particulate composites which are composed of particles in a matrix, 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, contain particles that extend rather than reinforce the material. There are generally referred to as 'fill' 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.

2.3 Material

2.3.1 Fiber

High-strength fibers used in advanced composites can be the same material or mixed (hybrid combination). The available fibers are not only carbon, glass and aramid, but also high-modulus polyethylene (PE), boron, quartz, ceramic, and newer fiber such as poly p-phenylene-2,6-benzobisoxazole (PBO) [20]. These fibers can be grouped into three broad categories: carbon, organic resin, and inorganic compound. Within each group, several classes of high performance fiber materials have been developed that satisfy the basic criteria of low density, high strength and high stiffness to varying degrees. The mechanical properties of typical fiber reinforcements show in Table 2.1

Table 2.1 Properties of fiber reinforcement [21]

Reinforcement	Specific gravity	Tensile strength MPa	Specific strength 10^4 m	Tensile modulus GPa	Specific modulus 10^6 m
Glass					
E glass	2.54	3.4	13.8	72.4	2.9
S glass	2.48	4.6	18.7	85.5	3.5
Boron on tungsten substrate	2.63	3.1	12.0	400.0	15.5
Graphite					
High strength	1.80	2.7	15.6	262.0	14.8
High modulus	1.94	2.0	10.9	380.0	19.9
Intermediate	1.74	2.5	14.5	186.0	10.9
Organic fiber					
aramid	1.44	2.7	19.5	124.0	8.8

2.3.2 Matrix

There are several matrix choices available. Each type has an impact on the processing technique and the environmental properties of the finished composite. The first key choice is between a thermoplastic and a thermoset composite matrix. Thermoplastic composites are not in general use because high temperature (typically ranges from 300 to 400°C) are required for processing, special autoclaves, processes, ovens, and bagging materials may be needed. A thermosetting matrix is widely used for advanced composites since they provided good processability, mechanical properties, and thermal properties [22]. The following are common thermoset matrices for composites are polyesters, vinyl esters, epoxies, bismaleimides, polyimides and phenolics show in table 2.2

Table 2.2 Relative characteristics of composite resin matrices [23]

Polyesters	Used extensively in commercial applications. Relatively inexpensive with processing flexibility. Used for continuous and discontinuous composites.
Vinyl Esters	Similar to polyesters but are tougher and have better moisture resistance.
Epoxies	High performance matrix systems for primarily continuous fiber composites. Can be used at temperatures up to 250-275°F. Better high temperature performance than polyesters and vinyl esters.
Bismaleimides	High temperature resin matrices for use in the temperature range of 275-350°F with epoxy-like processing. Requires elevated temperature post cure.
Polyimides	Very high temperature resin systems for use at 550-600°F. Very difficult to process.
Phenolics	High temperature resin systems with good smoke and fire resistance. Used extensively for aircraft interiors. Can be difficult to process.

The selection of a matrix material can profoundly affect the processing conditions. The following factors should be considered when selecting a resin matrix:

- Pot-life or working life- This is the time period that a matrix has when the handling characteristics remain suitable for the intended use. Typically, pot-life refers to neat resins (unreinforced) and working life refers to prepregs (reinforced). A long pot-life is desired for processes that use neat resin, such as wet filament winding, resin transfer molding and pultrusion. A short pot-life requires frequent resin bath changes and increased scrapped material. A short pot-life can also negatively affect the quality of the part in a wet process by decreasing fiber wet-out.

- Shelf life- This is the length of time a matrix material can be stored for under certain environmental conditions while meeting all performance and handling requirements. Thermoset prepreg materials are generally stored in a freezer and have a 6-12 month shelf life before re-certification is required. Thermoset materials, whose part A (resin) and part B (curing agent) are supplied in separate containers, generally have longer (~2 years) shelf lives at room temperature. Although not as reactive as a prepreg, viscosity and chemical changes occur over time. Refrigeration slows down the process and extends the shelf life.

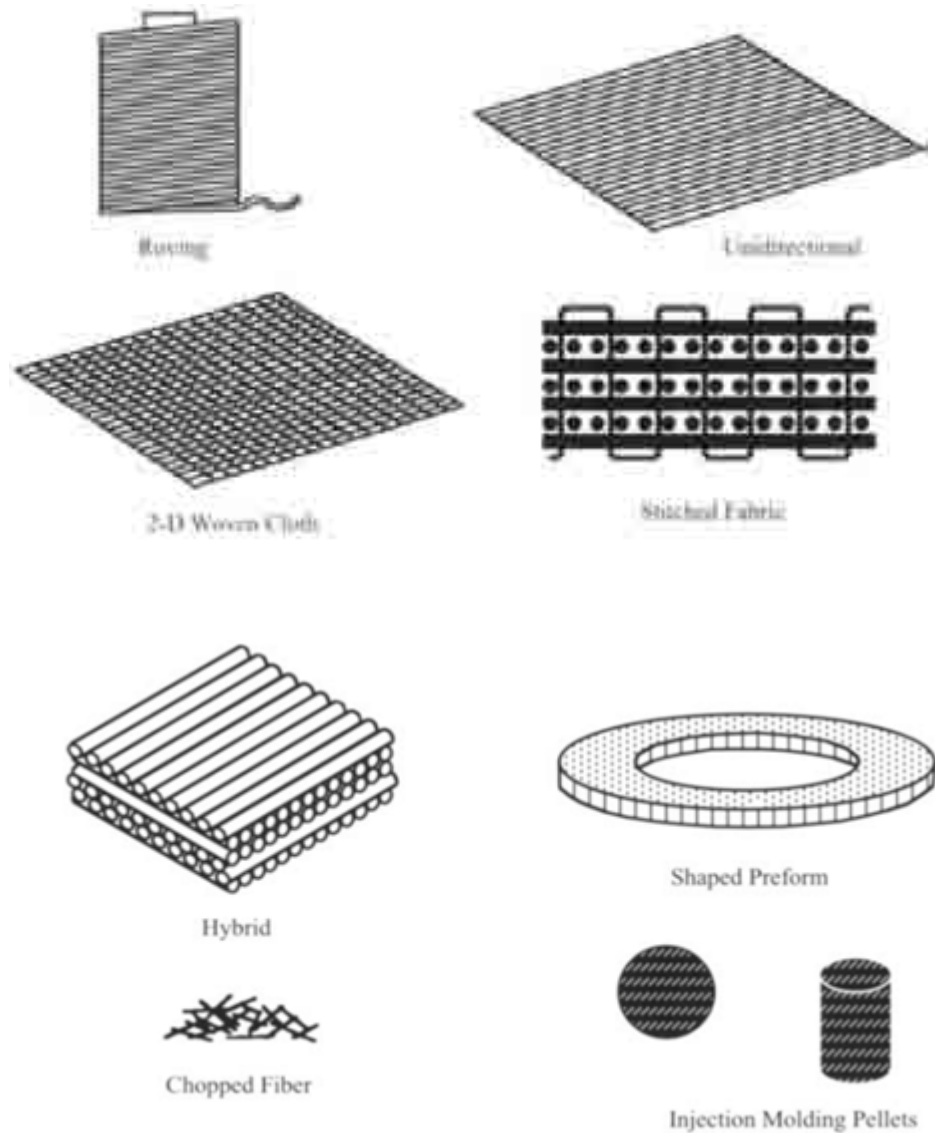
- Viscosity- The viscosity of an uncured resin can be described as its resistance to flow. It is measured in terms of flow, using water as the standard, which has a viscosity of 1 cP (centipoises). Viscosity requirements depend on the process but, typically, the lower the viscosity the easier it is to process and the better the wettability of the matrix to fiber. As a resin is heated, the viscosity initially drops and then rises as the chemical reactions proceed until it sets up or gels. For wet processing of thermosets, typically viscosities of less than 1000 cP are preferred. A thermoset is typically considered gelled when it reaches a viscosity of 100000 cP.

- Cure time- For thermoset resins, the cure time is the time it takes for the cross-linking reactions to take place. Typically, higher-Tg resins require longer cure times. Epoxies generally have cure times of 2-6 h. at elevated temperatures. A post-cure may not be required for some epoxies, polyesters and vinyl esters; therefore, elimination of post-cure requirements should be evaluated as a way to

decrease processing costs. Higher-Tg resins, such as bismaleimides and polyimides, require longer cure cycles and post-cures. Post-curing further develops higher-temperature mechanical properties and improves the Tg of the matrix for some epoxies, bismaleimides and polyimides. Very short cure times are desired for some processes, such as compression molding and pultrusion. Cure temperatures can range from 250°F to 350°F for epoxies. Bismaleimide cure temperatures typically range from 350°F to 475°F (including post-cure). Polyimide cure temperatures range from 600°F to 700°F

2.4 Fiber Matrix Systems [23]

There are a multitude of material product forms used in composite structures, some of which are illustrated in Figure 2.2. The fibers can be continuous or discontinuous. They can be oriented or disoriented (random). They can be furnished as dry fibers or pre-impregnated with resin (prepreg).



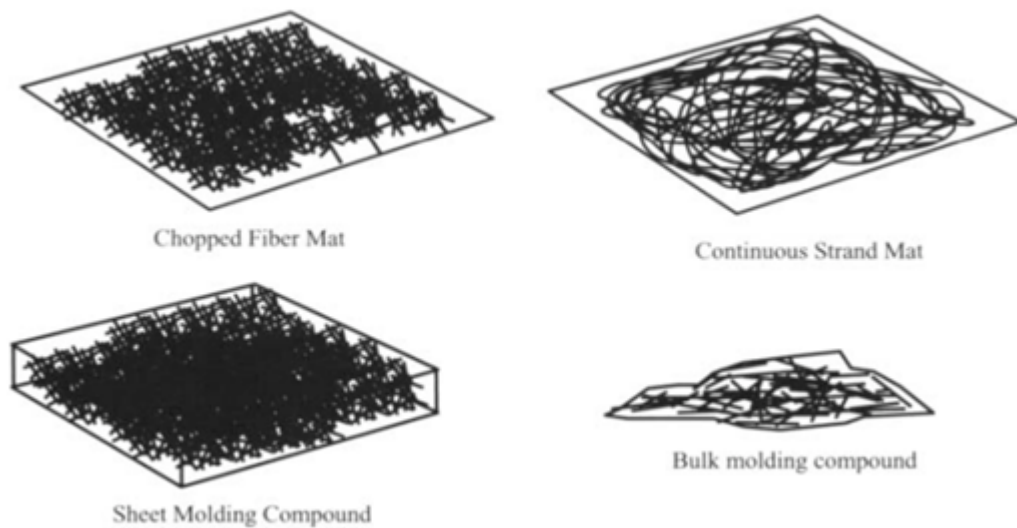


Figure 2.2 Product forms used in composites [23]

- Rovings, tows and yarns are collections of continuous fiber. This is the basic material form that can be chopped, woven, stitched or prepregged into other product forms. It is the least expensive product form and available in all fiber types. Rovings and tows are supplied with no twist, while yarns have a slight twist to improve their handleability. Some processes, such as wet filament winding and pultrusion, use rovings as their primary product form.
- Woven fabric is the most common continuous dry material form. A woven fabric consists of interlace warp and fill yarns. The warp is the 0° direction as the fabric comes off the roll while the fill, or weft, is the 90° fiber.
- A stitched fabric consists of unidirectional fibers oriented in specified directions that are then stitched together to form a fabric. A common stitched design includes 0° , $+45^\circ$, 90° and -45° plies in one multidirectional fabric.
- Hybrids are material forms that make use of two or more fiber types. Common hybrids include glass/carbon, glass/aramid and aramid/carbon fibers. Hybrids are used to take advantage of properties or features of each reinforcement type.

- A preform is a pre-shaped fibrous reinforcement that has been formed into shape, on a mandrel or in a tool, before placing into a mold. The shape of the preform closely resembles the final-part configuration.
- Chopped fiber is made by mechanically chopping rovings, yarns, or tows into short lengths, typically 1/4-2 inches long. Chopped glass fibers are often embedded in thermoplastic or thermoset resins in the form of pellets for injection molding.
- Sheet molding compounds (SMCs) consist of flat sheets of chopped, randomly oriented fibers, typically 1-2 inches in length, with a B-stage matrix, usually consisting of E-glass fiber in either a polyester or vinyl ester resin. The material is available either as rolls or pre-cut sheets.
- Bulk molding compounds (BMCs) are also short randomly oriented pre-impregnated materials; however, the fibers are only 1/8-1-1/4 inches long, and the reinforcement percentage is lower.

2.4.1 Prepregs

Prepregs are material forms consisting of continuous unidirectional or woven fibers pre-coated with a controlled quantity of an uncured catalyzed resin formulation. They are supplied in roll or sheet form, ready for immediate use at a composite manufacturing facility, and are widely used in the aerospace and other industries for high performance structural applications.

Prepregs offer several advantages to the composite parts manufacturer over other product forms (e.g., wet lay-up):

- 1: The resin matrix is formulated by the prepregs supplier to give specific end-properties, such as hot/wet mechanicals, impact resistance, fire retardancy.
- 2: Resin formulation is consistent from batch to batch.
- 3: Prepregs resin content is controlled to set limits, which translates to controlled weight in the finished part.

4: Physical characteristics-resin flow, tack, drapeability, and gel time-of the prepregs can be tailored to meet end-user requirements. Resin flow is a measure of resin movement during the cure process. Flow requirements are determined by the type of process used.

Tack is a measure of the ability of a ply of prepregs to stick to another ply and to the tool surface. This is important in the lay-up process.

Drapeability is a measure of the ability of the prepregs to conform to contoured tool surfaces without fiber damage, also important in the lay-up process.

Gel Time is a measure of the time taken for the resin to reach an immobile state at a given temperature. This is a key parameter associate with the cure process used.

2.4.2 Manufacture of Prepregs

Prepregs are manufactured by taking continuous fibers and impregnating them with a precisely controlled amount of resin. Prepregs can be made from a single strand of fiber called “tow” that consists of 1K to 48K filaments. More commonly, tow is used to make unidirectional prepregs. There are two commonly used methods of manufacturing thermoset prepregs material: solution and hot melt impregnation. The prepregging process for thermoset matrices can be accomplished by feeding the fiber continuous tape, woven fabric, or roving through a resin-rich solvent solution, then removing the solvent by hot tower drying. The excess resin is removed via a doctor blade (a straight piece of material used to spread and control the amount of resin applied to roving, tow, tape, or fabric). Then the product is staged to the cold-stable prepreg form (B stage). The newer technique for prepregs, a hot-melt procedure is gradually replacing the solvent method because of environmental concerns. A film of resin that has been cast hot onto release paper is fed, along with the reinforcement, through a series of heaters and rollers to force the resin into the reinforcement. Two layers of resin are commonly used so that a resin film is on both sides of the reinforcement. One of the release papers is then removed and the prepregs is trimmed, rolled, and frozen [22]. The solution or the melt of the

polymer must have a low viscosity at prepregging stage to wet the whole surface of elementary fiber

2.4.3 Use and Properties

Composite parts are manufactured from preregs by the basic steps of layup, and finishing.

Lay-up. As preregs contains precatalyzed resins, it must be stored under refrigeration to prevent resin advancement. Before use, it is allowed to reach room temperature in the original sealed package to prevent any water condensation on the preregs. Plies of preregs are then cut and stacked in the required fiber orientation on the tool surface. This layup may be done manually or by robotic handling equipment. Depending on the cure process to be used, the tool and ply package is then vacuum bagged appropriately.

Cure. To cure the preregs, heat and pressure must be applied. Standard processes for this are autoclave, press, and vacuum oven. Typical cure temperatures range from 150 to 650 ° F., with pressures ranging from vacuum to 200 p.s.i., depending on the type of resin matrix on the preregs.

Finishing. After removal from the cure took, minimal finishing is needed. Preregs can produce excellent surface finishes on the cured part, which needs no further work. Most of the finishing needed is for edge trimming to the final dimensions.

The properties of the major commercial preregs types are as follows:

Unidirectional Preregs Tape is available in widths ranging from 1 to 60 in., with finished cured ply thickness ranging from 0.002 to 0.012 inch. As the fibers are all in one direction, and not crimped as in the woven fabric preregs, tape gives the best translation of the reinforcing fiber properties. However, the resultant cure part cost is higher, as there is an increased labor cost associated with the layup procedure compared to fabric. Because of this, there is increased use of robotic methods for layup of tape to try to reduce labor.

In the design of composite parts it is quite common to use a combination of unidirectional tape and woven fabric, with the tape used in areas that call for the higher mechanical values.

To eliminate some labor costs associated with unidirectional tape, it is possible to obtain pre-plyed multilayer packages. These are used where the part has a repeat pattern of ply orientation and are combinations of 0 – 90-, and 45 – deg. plies.

Woven Prepregs usually is supplied as broad goods with widths to 72 in. and cured ply thickness of 0.0005 to 0.030 inch. The weave styles can be varied to fit particular end needs. Typical examples are balanced weave, 45 deg., or bias weave and 90% unidirectional. Mechanical properties or fiber strength translation depends on the weave style, e.g., a square weave gives lower translation than an 8-harness section because of the distance between fibers interweaves. Part layup costs are lower as typically less plies are used. However, there is a trade-off as the cost of woven prepregs material is higher than tape.

Prepregs Tow is supplied as individual pre-impregnated fiber bundles on spools in the same type of package as the original dry fibers. They are used for filament winding where they offer the potential for low-cost manufacturing using high-performance matrix resins compared to typical wet wind systems. They also are used as local reinforcements or to fill in layed-up parts such as beams. Properties of the prepregs tow are similar to unidirectional tape material.

2.4.4 Applications

The use of composite materials is extensive and expanding. Applications include aerospace, automotive, marine, sporting goods and, more recently, infrastructure. Examples of aerospace applications include the horizontal and vertical tail planes on the Boeing 777 (see Figure 2.3) that are made of carbon/epoxy to decrease weight and increase fuel performance.



Figure 2.3 Various composite materials are used in structures of the Boeing 777 [24]

Maintenance is a major headache and expense for the marine industry. Composites help minimize these problems, primarily because they do not corrode like metals or rot like wood. Boat hulls ranging from small fishing boats to large racing yachts are routinely made from glass fibers and polyester or vinyl ester resins. Other commercial applications include the recreational industry where prepregs are used in tennis racquets and golf clubs.

2.4.5 Ply Properties

2.4.5.1 Fiber Volume Fraction

Fiber-to-matrix ratio is a determining factor in the ultimate weight and cost of the component and governs the extent to which performance properties inherent in the fiber reinforcement. Fiber-to-resin ratio can range from 20:80 for low cost, nonstructural components to as high as 70:30 in some high-end pultrusion application for structural use. A fiber percentage that is easily achievable and repeatable in a composite for several fibers is 60 percent.

Fiber volume is used to relate the properties of the manufactured composites, the following equations can be used to convert between weight fraction and fiber volume:

$$W_f = \frac{w_f}{w_c} = \frac{\rho_f V_f}{\rho_c} \quad (1)$$

$$V_f = \frac{\rho_c}{\rho_f} W_f = 1 - V_m \quad (2)$$

Where	W_f	=	weight fraction of fiber
	w_f	=	weight of fiber
	w_c	=	weight of composite
	ρ_f	=	density of fiber
	ρ_c	=	density of composite
	ρ_m	=	density of matrix
	V_f	=	volume fraction of fiber
	V_m	=	volume fraction of matrix

In addition the fiber volume fraction can be calculated using the rule of mixtures.

$$V_f = \frac{\rho_c - \rho_m}{\rho_f - \rho_m} \quad (3)$$

Where	ρ_f	=	density of fiber = 1.76 g/cm ³
	ρ_c	=	density of composite
	ρ_m	=	density of matrix
	V_f	=	volume fraction of fiber

2.4.5.2 Fiber Orientation

Three additional factors must be considered when designing with fiber: fiber type, form and orientation. One of the advantages of using a modern composite is the potential to orient the fiber to respond to the load requirements

Unidirectional Properties The properties of unidirectional fiber laminates are listed in Table 2.3 These values are for individual laminate of for a unidirectional composite (0° aligned), and they represent the theoretical maxima (for that fiber volume) for longitudinal in plane properties. Flexural and compression properties will show maxima at different fiber volumes. These values may also be used to calculate the properties of a laminate which has fibers oriented in several directions.

Table 2.3 Unidirectional Composite Properties: 60% Volume Fiber [8]

Material	Epoxy Matrix Resin	Density (g/cm ³)	Properties			
			0° Tension		Flexural	
			Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)
Graphite						
A-S	3501	1.54	1,516	137	1,551	117
HM-S	934	1.63	1,206	220	1,034	193
HT-S	5208	1.55	1,482	172	1,689	158
T-300	5208	-	1,447	137	1,782	137
GY-70	934	1.69	586	275	930	262
Aramid						
49	-	1.38	1,516	82	620	75
S-2 class	002S	1.82	1,241	43	1,172	41

The strength and elasticity properties of composites can be calculated on the basis of the known properties and relation of the component. The rule of mixtures holds for composites. The micromechanics formulas to arrive at Young's modulus for a given composite are [25].

Axial Stiffness (Voigt Model)

$$E_1 = V_f E_f + V_m E_m \quad (4)$$

Since $V_f + V_m = 1$

$$E_1 = V_f E_f + (1 - V_f) E_m \quad (5)$$

Transverse Stiffness (Reuss Model)

$$E_2 = \frac{1}{\left(\frac{V_f}{E_f} + \frac{(1 - V_f)}{E_m} \right)} \quad (6)$$

Where

- E_1 = composite or ply Young's modulus in tension for fiber oriented in direction of applied load
- E_2 = transverse modulus of the lamina
- V = volume fraction of fiber (f) or matrix (m)
- E = Young's modulus of fiber (f) or matrix (m)

Cross Ply Properties [3] Control over the properties of laminated composites is affected using cross lay-up of the layer along the full vertical extent of the material and changing the angle of fiber orientation in the individual layer (Table 2.4). The simplest and most widespread is cross lay-up, wherein the fibers in the material layers are oriented at an angle $\pm\theta$ relative to the principle axes of symmetry, whose special case is represented by the orthogonal lay-up of the layers at

an angle of 0° and 90° when the relation of the layers arranged in the direction of principle axes changes. The increase of the angle between the directions of loading and orientation of the fibers in the adjacent layers is followed by the monotonic decrease of the strength and elasticity characteristics in the direction of axis x, whereas the above characteristic increase along axis y.

Table 2.4 Effect of fiber orientation on elasticity modulus in tension and extent of epoxy boron-fiber composite anisotropy [3]

Relative arrangement of fiber	Angle between direction of fibers in adjacent layer (deg)	Young's Modulus (GPa)			
		E_x	E_y	$E_{\pi/4}$	E_z
Unidirectional					
1:0	0	162	18.6	15.4	18.6
Cross-planer					
1:1 (0:90)	90	86	85.0	16.2	18.7
1:1:1 (0:60)	60	92	93.0	89.3	18.5

The modulus of elasticity and breaking tensile stress of the orthogonally reinforced composites till loss of solidity are calculated by the formulae:

$$E_{x,ult}^+ = E_x^0 t + E_y^0 (1-t) \quad (7)$$

$$\sigma_{x,ult}^+ = E_x^0 t + E_y^0 (1-t) \varepsilon_{x,ult}^+ \quad (8)$$

Where t = fraction of composite unidirectional layers in the loading Direction

E^0 = the Young's moduli of the composite unidirectional layer

On the breakdown of the lateral layer, the elasticity modulus and breaking tensile stress of the orthogonally reinforced composite are determined according to the expression

$$E_{x,ult}^+ = E_x^0 t \quad (9)$$

$$\sigma_{x,ult}^+ = E_x^0 t \varepsilon_x^0 \quad (10)$$

Where σ_x^0 = breaking stress of the composite unidirectional layer

ε_x^0 = relative tensile strain of the composite unidirectional layer

2.5 Carbon Fiber [26]

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



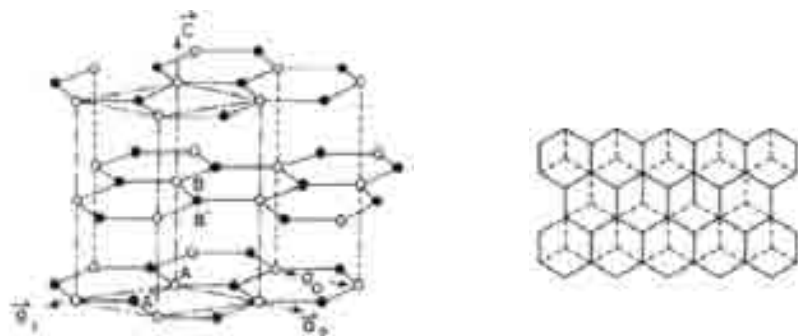
Figure 2.4 Carbon fiber roving (a), Carbon fiber fabric plain weave (b) [27, 28]

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

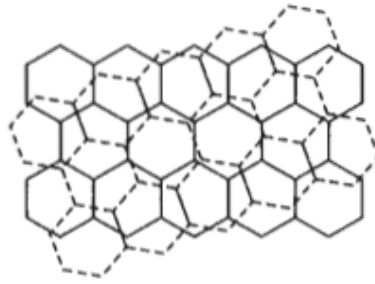
The structure and properties of carbon fiber depend on the raw material used, generally a polymer fiber. Numerous precursors have been tried to produce carbon fiber. The most important type commercially is the fiber made from polyacrylonitrile (PAN), which was initially developed for aircraft applications. It was attractive because of its high strength and modulus, and because it is not subject to creep or fatigue failure. Composites made from PAN-based carbon fiber allowed

for reduction in aircraft weight, and improvement in range, payload and performance. The composites were first adopted in military aircraft, but rapidly spread to commercial aircraft and then to other applications such as sporting goods. Pitch-based general purpose (isotropic) fibers have been used in Japan for large-volume reinforcement of cementitious matrices, especially exterior building panels. Pitch-based high performance (mesophase) fibers were developed for space applications. They are capable of very high Young's modulus (up to that of in-plane graphite) and have a high negative coefficient of thermal expansion along the fiber axis. This makes possible composites with a zero coefficient of thermal expansion, which is important for space applications. When a panel is facing the sun, it may reach 200°C, and when it is facing away from the sun, it may drop to 200°C below zero.

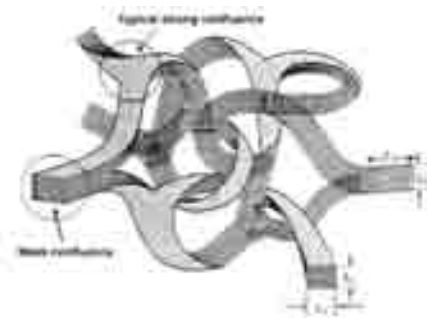
The word 'graphite' is much misused in carbon fiber literature. The word refers to a very specific structure, in which adjacent aromatic sheets overlap with one carbon atom at the center of each hexagon as shown in Figure 2.5a. This structure appears very rarely in carbon fibers, especially in PAN-based fibers, even though they are conventionally called graphite fibers. While high-performance fibers are made up of large aromatic sheets, these are randomly oriented relative to each other, are described as 'turbostratic' (turbulent and stratified) and are shown in Figure 2.5b. Many physical properties depend merely on the large aromatic sheets. The aromatic character of the isotropic carbon is shown in Figure 2.5c.



(a) Graphite



(b) Turbostratic carbon



(c) Isotropic carbon

Figure 2.5 Form of carbon [26]

2.5.1 Properties of Carbon Fiber

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

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

2.5.2 Pan-Based Carbon Fibers

Polyacrylonitrile (PAN) fibers are made by a variety of methods. The polymer is made by free-radical polymerization either in solution or in a solvent-water suspension. The polymer is then dried and re-dissolved in another solvent for spinning, either by wet-spinning or dry-spinning. In the wet-spinning process the spin dope is forced through a spinneret into a coagulating liquid and stretched, while in the dry-spinning process the dope is spun into a hot gas chamber, and stretched. For high-strength carbon fibers, it is important to avoid the formation of voids within the fiber at this step. Dry-spun fibers are characterized by a 'dog-bone' cross-section, formed because the perimeter of the fiber is quenched before much of the solvent is removed. The preferred process for high-strength fiber today is wet-spinning. Processes for melt-spinning PAN plasticized with water or polyethylene glycol have been developed, but are not practiced commercially. A significant improvement in carbon fiber strength was obtained by Moreton and Watt (1974) who spun the PAN precursor under clean room conditions. The strength of fibers spun in this way and subsequently heat treated was found to improve by >80% over conventionally spun fibers. The mechanism is presumed to be removal of small impurities which can act as crack initiators. This technology is believed to be critical for production of high strength fibers such as Toray's T800 and T1000. Initially, commercial PAN-based

carbon fibers were made from the polymers developed for textile applications. However, these fibers were neither very stiff nor strong. Development efforts over the 1960s and 1970s focused on increasing molecular weight, introducing co-monomers to assist processing, and eliminating impurities which limited mechanical strength. The chemistry of conversion of PAN to carbon is quite complex, and the interested reader is referred to an excellent treatment in Peebles (1994). The critical steps are outlined below.

The first critical step in making carbon fiber from PAN fiber is causing the pendant nitrile groups to cyclize, as illustrated in Figure 2.6.

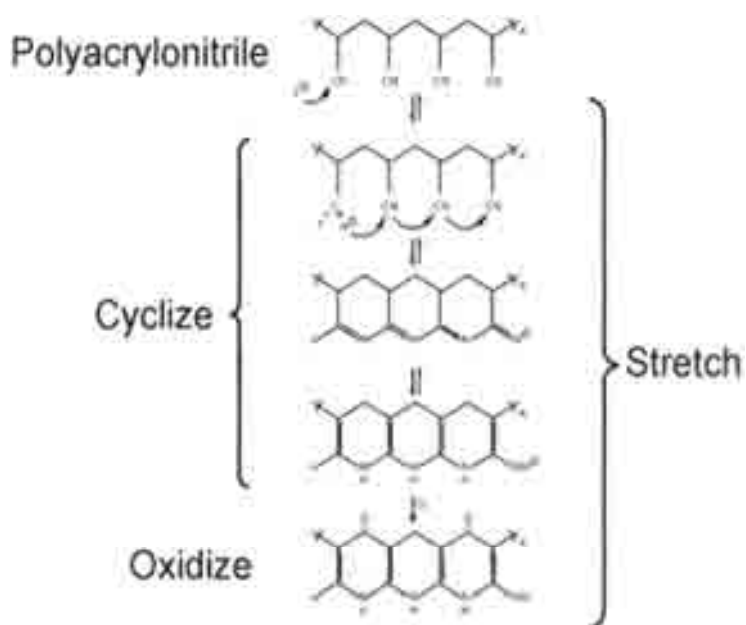


Figure 2.6 PAN-based carbon fiber chemistry: cyclization and oxidation [26]

This process is thermally activated and is highly exothermic. The activation temperature is influenced by the type and amount of co-monomer used. It is also important to keep the fiber under tension in this process, and indeed, during the whole conversion process. The next step is to make the fiber infusible: this is accomplished by adding oxygen atoms to the polymer, again by heating in air. The reaction is diffusion limited, requiring exposure times of tens of minutes. When

about 8% oxygen by weight has been added, the fiber can be heated above 600°C without melting. When the fiber is heated above this temperature, the processes of decyanization and dehydrogenation take place, and above 1000°C large aromatic sheets start to form, as illustrated in Figure 2.7.

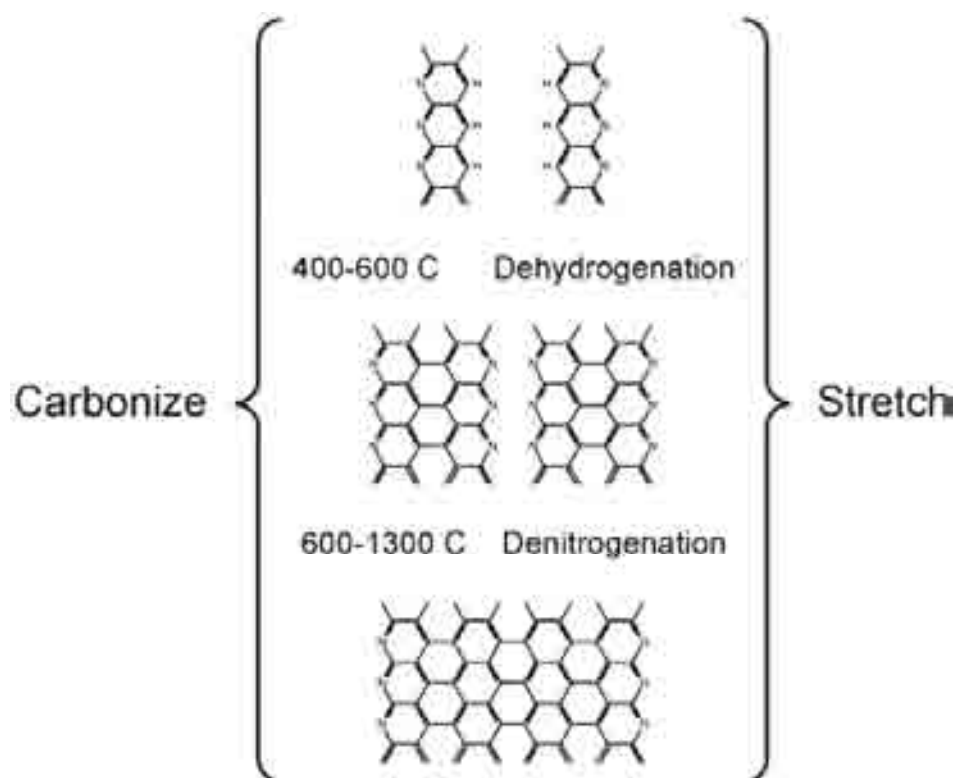


Figure 2.7 PAN-based carbon fiber chemistry: carbonization [26]

2.5.3 Pitch-Based Carbon Fiber

2.5.3.1 General Purpose Pitch-Based Carbon Fiber

These fibers are sometimes referred to as 'isotropic' carbon fibers, since they are made from isotropic pitch. These pitches are prepared from high boiling fractions of petroleum feedstocks, usually heavy slurry oils produced in catalytic cracking of crude oil. A typical commercial pitch is Ashland Aerocarb 70, which has a softening temperature of 208°C and a viscosity of 1 Pa.s at 278°C. Additional

treatments to selectively reduce low molecular weight components are described by Sawran et al. (1985).

General purpose fibers are prepared by two different spinning methods, centrifugal spinning and melt blowing, both of which are high-productivity processes. A more detailed discussion of these processes will be found in Lavin (2001).

2.5.3.2 High-Performance Pitch-Based Carbon Fibers

High-performance fibers are made from mesophase pitch, which is a discotic liquid crystalline material. While mesophase pitches can be made from many starting materials, there are only a few which are of commercial interest. These are dealt with in the sections which follow. These fibers are typically melt spun, and spinning technology is the same for all pitch types.

2.5.4 Applications of Carbon Fiber

Large weight savings are possible when carbon fiber composites are used to replace more conventional materials; they are frequently applied in areas where weight reductions are valuable. Especially, they are used in variety of aerospace components. Typical aerospace-grade tow size range from 1K to 12K PAN- and pitch-based 12K carbon fibers are available with a moderate (33 to 35 Msi), intermediate (40 to 50 Msi), high (50 to 70 Msi), and ultrahigh (70 to 140 Msi) modulus. Heavy tow carbon fibers with filament counts from 48K up to 320K are available at a lower cost than aerospace-grade fibers. They typically have a 33 to 35 Msi modulus and 550-Ksi tensile strength and are used when fast part build-up is required, most commonly in recreational industrial, construction and automotive markets. Carbon fibers and their composites exhibit many characteristics apart from their basic mechanical properties and weight saving. Electrical conductivity is

coupled with excellent mechanical properties in thermoplastics molding compounds for structures in electronic equipment. Corrosion resistance is useful for making pipes, reactions or containers for chemical plants or in marine environment. Examples of sports equipment that contain carbon fiber reinforcement include skis and ski poles, golf clubs tennis racquets, fishing rods, and racing cycles.

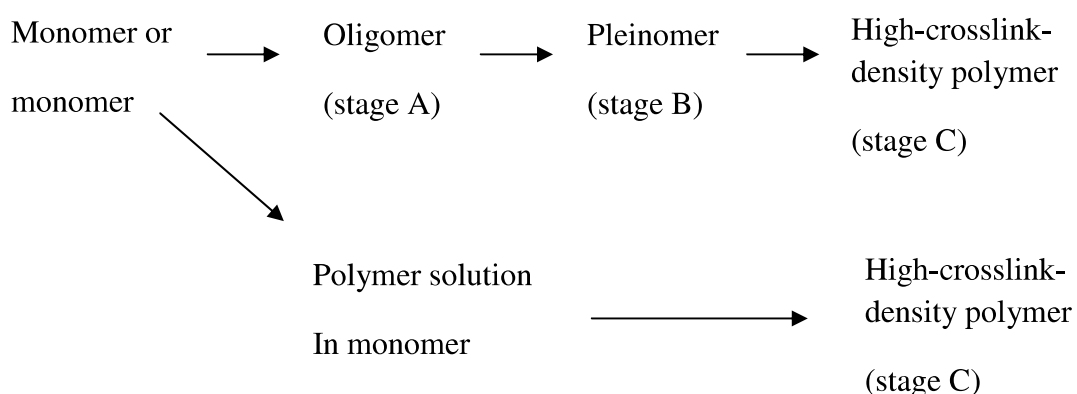


Figure 2.8 Applications of carbon fiber [29-32]

2.6 Thermosetting Resins

Plastic materials can be classified into two main categories based on their response to temperature: thermoplastics and thermosets. Thermosetting polymers differ from thermoplastics in that they become chemically crosslinked during final molding and curing. Thermosets (especially epoxy) have long been used as polymer matrices for carbon fiber composites. A distinctive characteristic of a thermosetting polymer is that one giant macromolecule consisting of covalently bonded repeating units is formed during the polymerization process. The giant macromolecule that percolates throughout the sample is called a gel. This sol-gel critical transition is a distinctive feature value of viscosity. At gelation, viscosity increases to infinite. After gelation an insoluble fraction (the gel fraction) is present in the system. At full conversion of functional groups, in stoichiometric formulation, the sol fraction disappears and the final thermosetting polymer is composed of one giant molecule of a gel [33].

E.B. Trostyanskaya described synthesis of high-crosslink-density polymer are in this stages.



Transition from stage A to stage C, or from the prepolymer stage, is usually called ‘curing’. In the cure process, addition of multifunctional oligomer molecules is accompanied by an increase in the number of branches of different

length. The branches are as a rule in interaction with each other, and lead to ring formation. The curing process can be followed by transmittance, viscosity or elasticity modulus increase, by the increase in the number of functional groups in reaction products.

In addition, the process of impregnation is carried out by immersion of fiber into melt or solution. Therefore the information about melt or solution viscosity and time of attaining on storage (shelf-life) of the resin or prepolymer melt is required.

2.7 Benzoxazine Resin

Benzoxazine resin is a story class of phenolic resin which was developed to defeat almost all shortcomings of the phenolic resins and was expected to replace conventional phenolic, polyesters, vinyl esters, epoxies, BMI, cyanate esters and polyimides in numerous respects. They demonstrate several remarkable properties that have not been regularly observed by other well-known polymers, as follow excellent processability owing to low melt viscosity [11], solvent-less method for benzoxazine resin preparation [12], near-zero shrinkage upon polymerization [15], fast mechanical property build-up as a function of degree of polymerization [11] and benzoxazine resins can be synthesized from low-cost raw materials. The ring opening polymerization is readily achieved by basically heating the purified monomer typically at temperatures in the range between 160°C and 220°C [34-35] and gelation takes place in a metter of minutes to tens of minutes at these temperatures if no initiators are employed [36].

Additionally, the ring opening mechanism occurs by breaking of a C-O bond of the oxazine ring as shown in Figure 2.9 [37] and benzoxazines cure without the support of strong acid catalysis, do not release by-products during the polymerization [38]. The curing behavior of the as-synthesized benzoxazine precursor studied is autocatalytic [39]. The fantastic molecular design flexibility of the polybenzoxazines allow the properties of cured materials to be tailord for the particular requirements of personality applications.

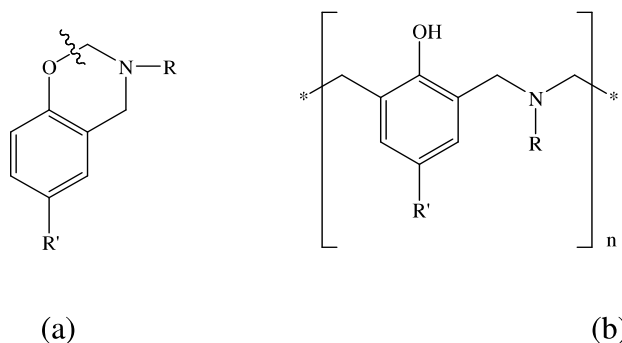


Figure 2.9 Benzoxazine resin (a), and ring-opening polymerization of the resin (b)

(R = amine group, R' = phenol group)

Furthermore, good mechanical properties, such as Tensile Strength = 64 MPa, Tensile Modulus = 5.2 GPa, elongation at break (%) = 1.3, high thermal stability ($T_d = 334^\circ\text{C}$; 5 % wt loss) [13] which is possibly owing to the stabilization of the Mannich bridges by the very strong intramolecular hydrogen bonding between the phenolic OH groups and the nitrogen atom of Mannich bridge [40,41], much higher than cure temperature, the glass transition temperature (T_g) exhibit in the range $160\text{-}340^\circ\text{C}$ depending on the structure, high char-yield due to char formation usually increases with increased content of benzene content and char yield, no dark smoke, self extinguishing, low heat release rate, and low total heat release make them an desirable applicant as non-flammable materials for the transportation industry.

Finally, low dielectric constants ($\epsilon = 3.6$ or lower), long-term immersion studies indicate that these materials have a low rate of water absorption and low water absorption [11, 13, 15, 42] that bisphenol-A and aniline based polybenzoxazine saturated at 1.9% by weight [42], and low coefficient of thermal expansion (CTE), propose an abnormal combination for electronic packaging materials. Their composites are comparable to polyimides and other high performance polymer, but are easily processable [4]. Table.2.5 compares the properties of polybenzoxazine with those of the state-of-the-art matrices [11].

Table 2.5 Comparative properties of various high performance polymers [11].

Property	Epoxy	Phenolics	Toughned BMI	Polybenzoxazine
Density (g/cc)	1.2 - 1.25	1.21 - 1.32	1.2 - 1.3	1.19
Max use temperature (°C)	180	200	~ 200	130 - 280
Tensile strength (MPa)	90 - 120	24 – 45	50 - 90	100 - 125
Tensile modulus (GPa)	3.1 - 3.8	-	3.5 - 4.5	3.8 - 4.5
Elongation (%)	3 - 4.3	0.3	3	2.3 - 2.9
Dielectric constant (1 MHz)	3.8 – 4.5	04/10	3.4 - 3.7	3 - 3.5
Cure temperature (°C)	RT – 180	150 – 190	220 - 300	160 - 220
Cure shrinkage (%)	> 3	0.002	0.007	~ 0
TGA onset (°C)	260 - 340	300 – 360	360 - 400	380 – 400
Tg (°C)	150 - 220	170	230 - 380	170 - 340

Benzoxazine resin can be classified into a monofunctional and a bifunctional type depending on a type of phenol used as shown in figure 10 and 11. The example for the monomer synthesis is

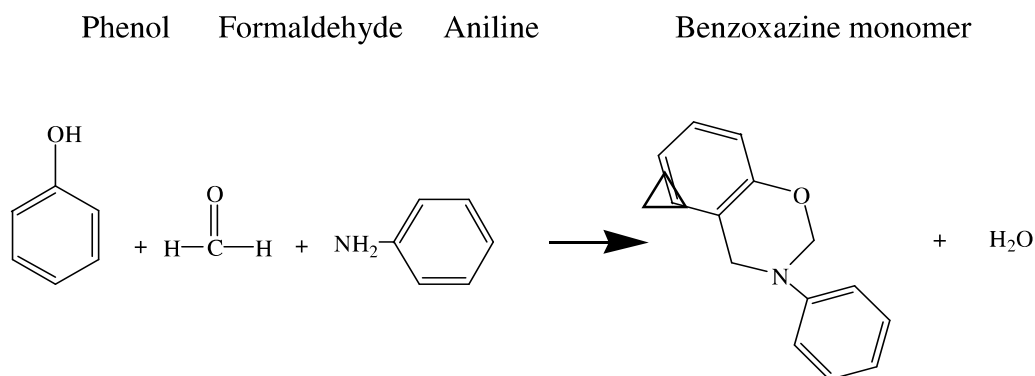


Figure 2.10 Schematic synthesis of monofunctional benzoxazine monomer.

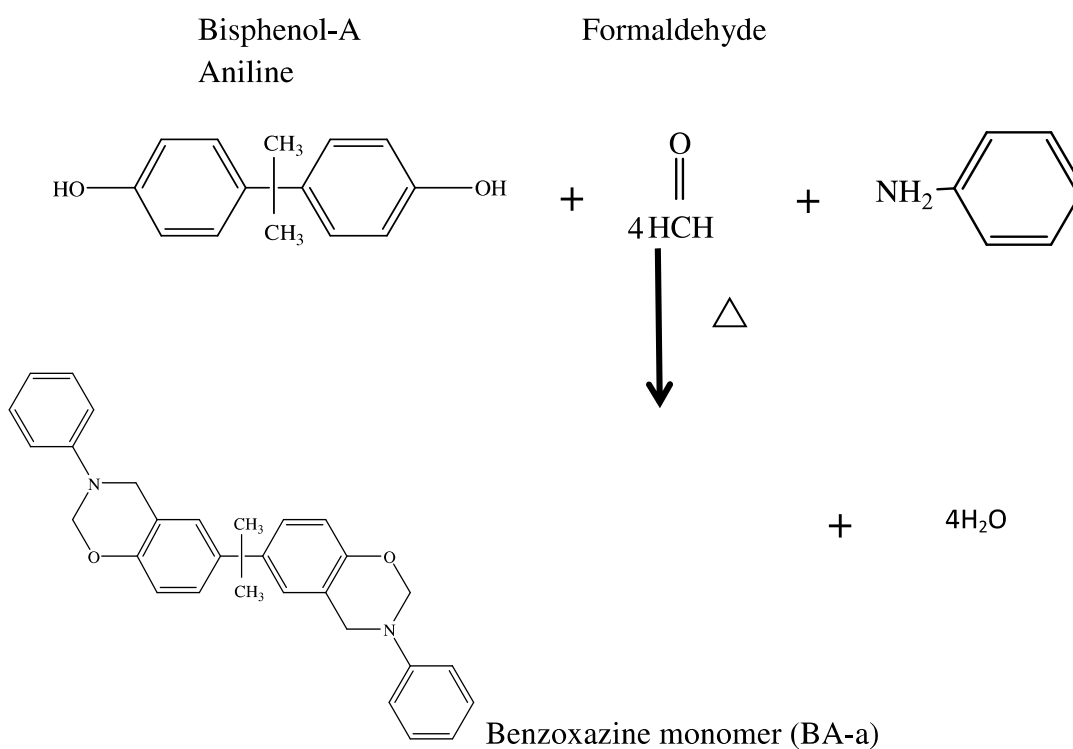


Figure 2.11 Schematic synthesis of bifunctional benzoxazine monomer [43].

2.8 Dianhydrides

Dianhydride have been used to substance in produce polymers such as polyimides [44]. They have vaious types of dianhydride. For example,

- **Pyromellitic dianhydride (PMDA)** is prepared by the vapor phase oxidation of durene, which is 1, 2, 4, 5 tetramethylbenzene, using a supported vanadium oxide catalyst. The synthesis is completely analogous to the synthesis of phthalic anhydride [45, 46].

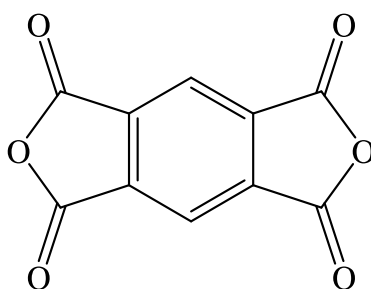


Figure 2.12 Pyromellitic dianhydride (PMDA)

There are two methods of productive phthalic anhydride in industry system. Firstly; about 71% of phthalic anhydride is produced by oxidizing o-xylene. This reaction either conducted in the vapor phase using a fixed or fluidized bed catalyst base on V₂O₅ or a liquid-phase oxidation. The liquid-phase oxidation is conducted 150°C using soluble acetates or naphthenates of cobalt, manganese, or molybdenum in combination with bromine as a promoter [47].

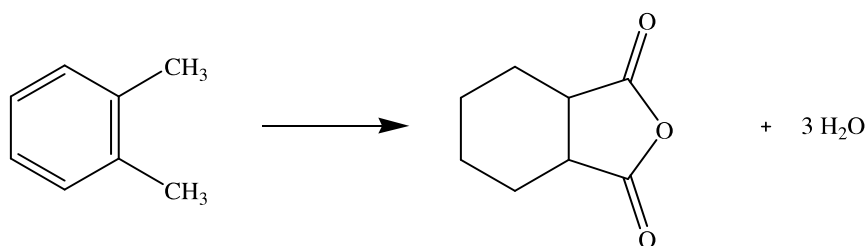


Figure 2.13 The production of phthalic anhydride

Secondly, the air oxidation of naphthalene derived from petrochemical sources or coal is still being used to produce phthalic anhydride. The processes and catalysts are similar [40].

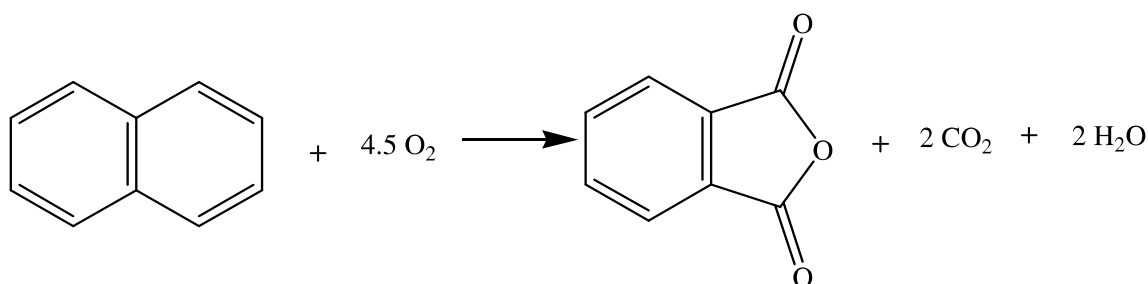


Figure 2.14 The production of phthalic anhydride

Table 2.6 Physical and chemical properties of PMDA [48]

Physical State	Powder
Color	white to light beige
Vapor Pressure	< 0.01hPa @ 20 °C
Boiling Point	397 - 400 °C @ 760mmHg
Freezing / Melting Point	283 - 287 deg C
Flash Point	380 deg C (716.00 deg F)
Solubility in water	Decomposes.
Solubility in other solvents	Soluble in acetone.

Molecular Formula	C ₁₀ H ₂ O ₆
Molecular Weight	218.12
Chemical Stability	Stable under normal temperatures and pressures. Moisture sensitive

- 3,3',4,4' –benzophenonetetracarboxylic dianhydride (BTDA)

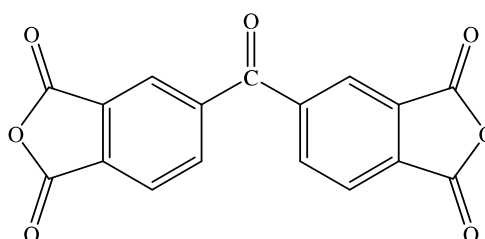


Figure 2.15 3,3', 4,4' –benzophenonetetracarboxylic dianhydride (BTDA)

Table 2.7 Physical and chemical properties of BTDA [49]

Synonyms	4,4'-Carbonyldipthalic anhydride
Empirical Formula (Hill Notation)	C ₁₇ H ₆ O ₇
Appearance	White or light yellow powder
Molecular Weight	322.23
Vapor density	1.4 (vs air)
Density	1.57 g/cm ³
Vapor pressure	<0.1 mmHg (0 °C)
Autoignition temp.	975 °F
Melting Point	218-222 °C
Chemical Stability	Sensitive to humidity
Assay	96 %

- **3,3',4,4' –biphenyltetracarboxylic dianhydride (s-BPDA)**

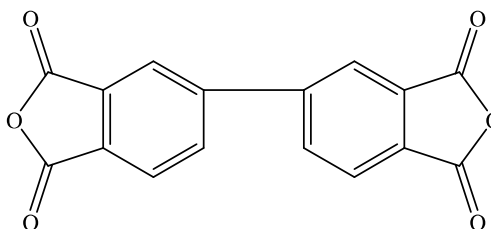


Figure 2.16 3,3', 4,4' –biphenyltetracarboxylic dianhydride (s-BPDA)

Table 2.8 Physical and chemical properties of s-BPDA [50].

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

2.9 Solvent

Dimethylformamide [51] is an organic compound which abbreviated as DMF. It is colourless liquid miscible with water and the majority of organic liquids. DMF is a common solvent for chemical reactions. Pure dimethylformamide is odorless whereas technical grade or degraded dimethylformamide often has a fishy smell due to impurity of dimethylamine. Its name is derived from the fact that it is a derivative of formamide, the amide of formic acid.

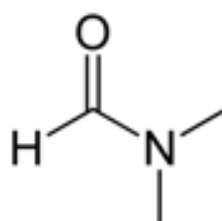


Figure 2.17 Dimethylformamide (DMF) [52]

Dimethylformamide is a polar (hydrophilic) aprotic solvent with a high boiling point. It facilitates reactions that follow polar mechanisms, such as S_N2 reactions. Dimethylformamide can be synthesized from methyl formate and dimethylamine or by reaction of dimethylamine with carbon monoxide. Dimethylformamide is not stable in the presence of strong bases like sodium hydroxide or strong acids such as hydrochloric acid or sulfuric acid and is hydrolyzed back into formic acid and dimethylamine, especially at elevated temperatures.

Dimethylformamide (DMF) is primarily used as a solvent in the production of polyurethane products and acrylic fibers. It is also used in the pharmaceutical industry, in the formulation of pesticides, and in the manufacture of synthetic leathers, fibers, films, and surface coatings [53-55]. DMF may be emitted to the environment as a result of its use in a variety of petrochemical industries [53]. The annual statewide industrial emissions from facilities reporting under the Air Toxics Hot Spots

Act in California based on the most recent inventory were estimated to be 18,249 pounds of DMF [56].

Table 2.9 Properties of Dimethylformamide (DMF) [56]

Molecular formula	C_3H_7NO
Molar mass	73.09 g/mol
Density	0.944 g/cm ³
Melting point	-61 °C
Boiling point	153°C

2.10 Reaction

Esterification proceeds of phthalic anhydride have two steps as shown in Figure 2.18 [57].

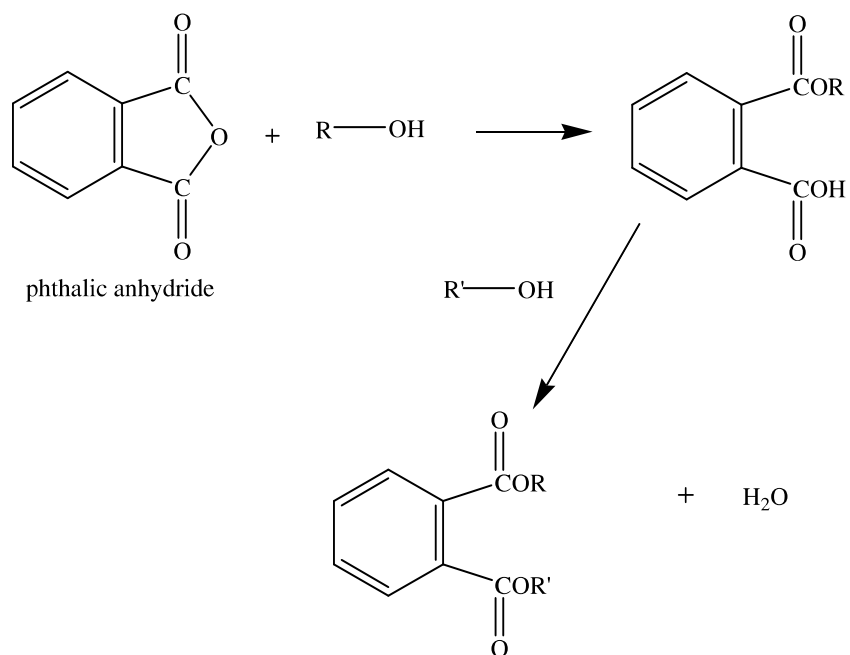


Figure 2.18 Esterification of phthalic anhydride [57]

CHAPTER III

LITERATURE REVIEWS

X. Ning, and H. Ishida, 1994 [34, 35] investigated the synthesis of bifunctional benzosazine precursors. These polyfunctional benzoxazine were found to exhibit excellent mechanical and thermal properties with good handling capability for resin processing and composites manufacturing, e.g., the glass transition temperature of 190°C, tensile modulus of 3.2 GPa, and tensile strength of 58 MPa. In addition, they offered greater flexibility than conventional phenolic resins in term of molecular design. They do not release by-products during curing reaction and there is no solvent needed in the resin production.

T. Takeichi, Y. Guo, S. Rimdusit, 2005 [44] studied the polymer alloys of polybenzoxazine (B-a) and polyimide (PI). The cast films were yellow and transparent, similar with that of the blend solution, and became deep wine-color and transparent after the cure at 240°C. From Figure 3.1, it is clear that all the samples of polymer alloys from PI/B-a have only one glass transition temperature (T_g) from both loss modulus (E'') and $\tan \delta$ maxima. And the T_g shifted to higher temperature as PI content increased.

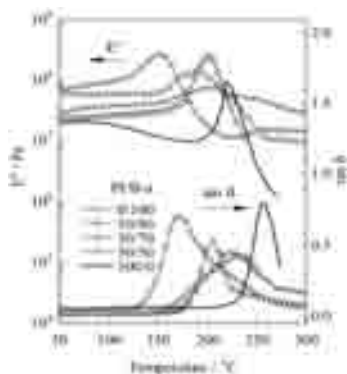


Figure 3.1 Loss modulus (E'') and $\tan \delta$ of PI/BA-a films with various ratios.

The stress–strain curves for PI/BA-a films are shown in Figure 3.2. The tensile properties of the PI/BA-a films confirmed that the polyBA-a enhanced the modulus of PI, while PI improved the toughness of polyBA-a.

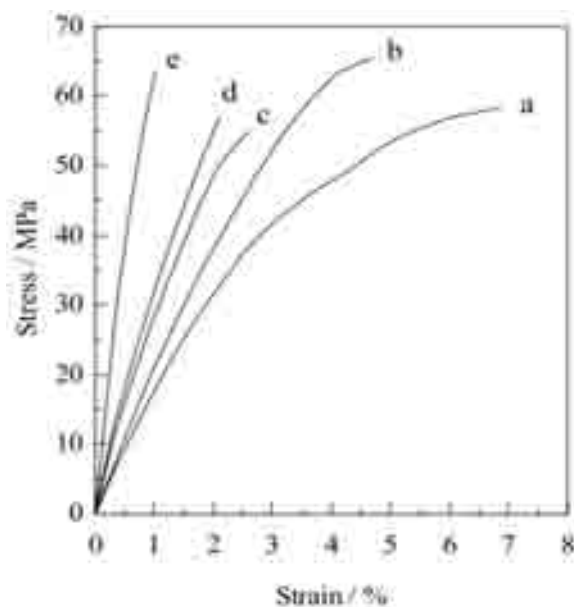


Figure 3.2 Tensile properties of PI/BA-a films after cured at 240°C/2 h with PI/BA-a ratio of 100/0 (a), 50/50 (b), 30/70 (c), 10/90 (d), and 0/100 (e).

The thermal stabilities of polymer alloy films from PI/BA-a were investigated by thermogravimetric analysis (TGA), and shown in Figure 3.3. The initial decomposition temperatures (defined at 5 and 10% weight loss) of the polymer alloys from PI/BA-a increased obviously with the increase of PI content due to higher thermal stability of PI than that of polyB-a. They also notice that char yield increased by the addition of only small amount of PI. These polymers have good thermal stability.

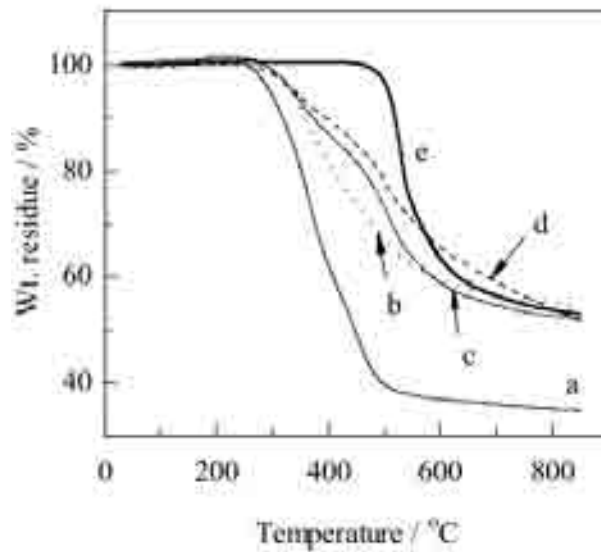


Figure 3.3 TGA of PI/BA-a films with PI/BA-a ratio of 0/100 (a), 10/90 (b), 30/70 (c), 50/50 (d), and 100/0 (e).

C. S. Tyberg, 2000 [5] explained that for prepregging process low viscosity matrices resins are required. The relatively low viscosities are less critical for preparing pre-impregnated because the impregnation temperature can be increased to decrease viscosity. The high viscosity resins are typically difficult to process such as high temperature processing, use of solution method. The high temperature and solvent were necessary to give a low enough viscosity to process the material. Low viscosities of the resins are critical to permit good wet-out of the reinforcing fiber tows and yield uniform resin content.

S. Rimdusit, and H. Ishida, 2000 [14] developed highly thermally conductive molding compounds for electronic packing application based on polybenzosazine system. They investigated thermal conductivity of boron nitride-filled benzoxazine resin as a function of filler content and particle size. The investigators used large aggregates of flake-like boron nitride crystals and were able

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

X. Zhao, Y. F. Li, S. J. Zhang, Y. shao, X. L. Wang, 2007 [58] studied polyimides that were prepared by polycondensation of 2-amino-5-[4-(40-aminophenoxy)phenyl]-thiazole (APPT) with various aromatic dianhydride, such as pyromellitic dianhydride (PMDA) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA). The thermal properties of the polyimides, which were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) methods, are listed in Table 3.1. DSC curves of the polyimides are shown in Figure 3.4. The experimental results indicate that APPT-PMDA have higher glass transition temperature than APPT-BTDA by dint of the structure of the dianhydride component.

Table 3.1 Data of thermal analysis of the polyimides.

Polymer	T _g ^a (°C)	In N ₂ ^b (°C)		In air ^b (°C)		Char yield ^c (%)
		T ₅	T ₁₀	T ₅	T ₁₀	
APPT-BTDA	320.2	489	523	439	482	59.31
APPT-PMDA	328.8	507	548	458	499	63.33

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

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

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

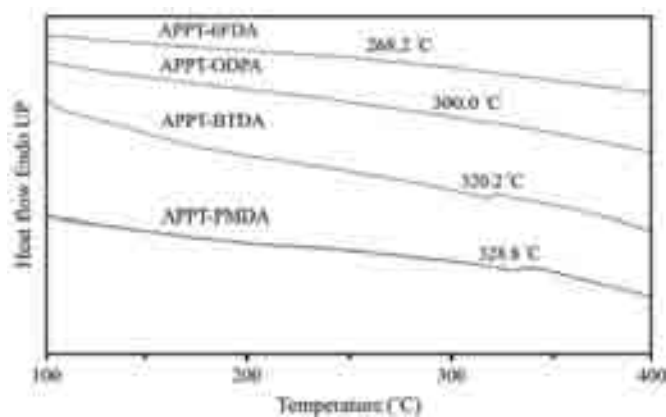


Figure 3.4 DSC thermograms of PIs at heating rate of 20°C/min in nitrogen.

B. Ramsiri, and S. Rimdusit, 2009 [16] prepared the novel high temperature film from mixture of benzoxazine resin (BA-a) and dianhydride, i.e. 3,3', 4,4' benzophenonetetracarboxylic dianhydride (BTDA), pyromellitic dianhydride

(PMDA), or 3,3', 4,4' biphenyltetracarboxylic dianhydride (s-BPDA). The glass transition temperature (T_g) values of BA-a/BTDA, BA-a/PMDA, and BA-a/s-BPDA films were observed to be significantly higher (T_g beyond 200°C) than that of the neat polybenzoxazine (PBA-a) ($T_g = 165^\circ\text{C}$). Moreover, the degradation temperature at 5% weight loss and char yield values at 800°C were enhanced by an addition of BTDA, PMDA, and s-BPDA of which the molecular structures consisted of aromatic ring are shown in table 3.2.

Table 3.2 Properties of BA-a/DA polymer blends.

Composition (molar ratios)	T_g ($^\circ\text{C}$)		E' at rubbery plateau (MPa)	Crosslink density (mol/m^3)	T_d ($^\circ\text{C}$)	Char yield (%)
	from DSC	from E''				
BA-a/BTDA						
100/0	165	166	45	4014	361	32.9
75/25	206	224	212	6311	396	58.8
60/40	239	262	302	6836	410	61.7
50/50	236	249	270	6670	420	61.5
BA-a/PMDA						
75/25	229	210	294	6796	375	57.0
60/40	306	305	554	7735	426	60.2
50/50	263	290	613	7885	418	55.7
BA-a/s-BPDA						
75/25	219	191	184	6101	389	55.8
60/40	257	269	325	6944	422	62.3
50/50	242	243	242	6507	439	59.2

Interestingly, the flexibility of BA-a/BTDA, BA-a/PMDA, and BA-a/s-BPDA were found to be greater than that of the neat (PBA-a). They obtained alloy

sample is appropriate for an application as polymeric film for high temperature applications.

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

Table 3.3 The thermal characteristics of polybenzoxazine composites and other high-performance composites.

Composites	T _g (°C)	T _d [*] (°C)	2 wt% Loss Temperature ^{**} (°C)	Char Yield (%)
CF/22Pa (290°C/1h)	268	330	260	87
CF/44Oa (290°C/1h)	350	370	260	92
CF/Bismaleimid	250-300	450-500	-	50-70
CF/Polyimide	230-380	560-600	-	-

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

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

J. Jang, and H. Yang, 2000 [2, 59] modified polybenzoxazine with liquid rubber (ATBN and CTBN) to improve the delamination toughness of carbon-fiber/polybenzoxazine composites. They conclude that ATBN improved the delamination toughness and interfacial bonding in the composites more effectively. Despite such improvement, there are some disadvantages from this rubber modified resin approach including the considerable reduction of strength, modulus, and glass transition temperature such as decrease in flexural strength with increase in CTBN (~380 MPa of 0% CTBN to ~200MPa of 20%CTBN). In addition, they have improved the mechanical properties of CF/polybenzoxazine composites using carbon fiber surface treatments. The influences of oxygen plasma treatment and nitric acid treatment on the mechanical properties were studied. The flexural strength of 60 min oxidized CF/polybenzoxazine composites is 2.4 times as high as that of untreated ones and is even more than that of plasma-treated ones (~850 MPa of nitric acid treatment, ~600 MPa of oxygen plasma treated, and ~380MPa of untreated). They observed the cohesive failure occurred in the matrix region due to the improvement of the interfacial adhesion strength between CF and matrix by the nitric acid treatment.

H. Ishida, and T. Chaisuwan, 2003 [1] improved the mechanical properties of carbon fiber-reinforced polybenzoxazine composites by rubber interlayering. The resin used is BA-35X because it shows the highest thermal stability achieved from neat benzoxazine based on bisphenol-A and unfunctionalized aniline derivatives ($T_g = 236^\circ\text{C}$ of BA-35X and $T_g = 170^\circ\text{C}$ of BA-a). Carbon fiber woven fabric (T300) was used either as-received or desized condition. The fiber content of the composite is about 60% by volume. They reported the optimizing concentration of ATBN rubber provided the mechanical properties comparable or superior to those of modified epoxy and phenolic matrices i.e. flexural strength: ~800 MPa of rubber interlayered BA-35X, 780 of modified epoxy, and 650 of modified phenolic; flexural modulus: 58 GPa of rubber interlayered BA-35X, 58 GPa of modified epoxy, and 56GPa of modified phenolic.

S. Rimdusit, P. Jongvisuttisun, C. Jubsilp, W. Tanthapanichakoon, 2009 [17] evaluated characteristics of the ternary systems of benzoxazine, epoxy, and phenolic resin systems for utilizing as a matrix of carbon fiber prepreps such as viscosity, gelation time, shelf-life, and curing properties as well as the mechanical and thermal properties of their fully cured polymers and their carbon fiber composites. The ternary mixtures can provide a relatively wide processing window ranging from 50 to 200°C by maintaining their low A-stage viscosity for a relatively long time which is crucial in the fiber pre-impregnating process. Furthermore, relatively long shelf-life of the ternary mixtures stored at room temperature (~30°C) up to 270 days is obtained with minimal effect on their processability. Furthermore, the carbon fiber composite based on BEP362 was found to exhibit a relatively high modulus value of 57.7 GPa. comparing with about 4.0 GPa. of the neat BEP362 alloy are shown in Figure 3.5.

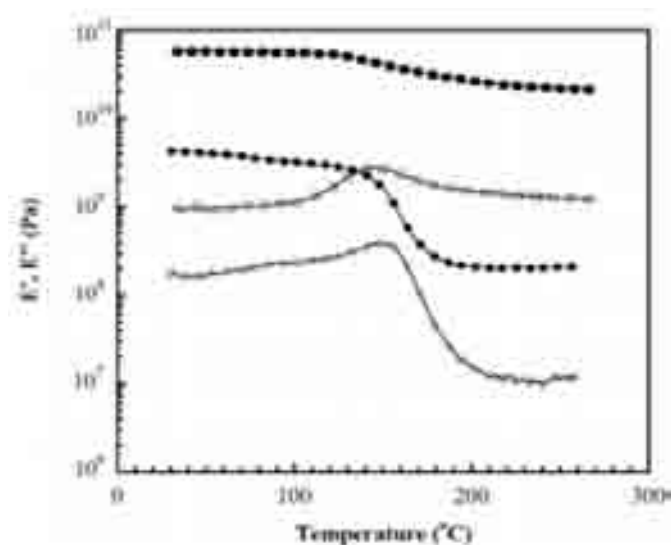


Figure 3.5 Dynamic mechanical properties of BEP362 alloy (●) storage modulus, (○) E'' loss modulus and carbon fiber-reinforced BEP362 composite (■) storage modulus, (□) E'' loss modulus.

CHAPTER IV

EXPERIMENTAL

4.1 Raw Materials

The materials used in this research are benzoxazine resin, Pyromellitic dianhydride (PMDA) and carbon fiber. Benzoxazine resin is based on bisphenol-A, aniline and formaldehyde. The bisphenol-A (polycarbonate grade) was provided by Thai Polycarbonate Co., Ltd. (TPCC). Paraformaldehyde (AR grade) was purchased from Merck Co. while aniline (AR grade) was contributed by Panreac Quimica S.A. Co. Pyromellitic dianhydride (PMDA; 99%) purchased from Acros organics. Dimethylformamide (DMF; AR grade) solvent purchased from Fisher Scientific UK Limited. All chemicals were used as-received. Carbon fiber plain fabric (BN CC200P) in 3k-tows with a fiber areal weight of 200 g/m² was purchased from Rattanakosin Composites Ltd., Partnership. It was used as-received without any additional surface modification.

4.2 Synthesis of Benzoxazine Monomers

Benzoxazine resin is synthesized using bisphenol-A, formaldehyde, and aniline at the stoichiometric mole ratio of 1:4:2. The mixture was heat to 110°C in an aluminum pan and was mixed until a homogeneous mixture was obtained for 30 minutes to yield a light yellow solid monomer product, according to the patented solventless technology [12]. The product is then ground into fine powder and can be kept in a refrigerator for future-use.

4.3 Preparation of Benzoxazine-PMDA Mixture

The benzoxazine monomer (BA-a) was blended with various amount of Pyromellitic dianhydride (PMDA), i.e., BA-a:PMDA (1:1), BA-a:PMDA (1.5:1), BA-a:PMDA (2:1), BA-a:PMDA (3:1) and BA-a:PMDA (4:1) in Dimethylformamide (DMF) and stirred at 80°C until the clear homogenous mixture was obtained.

4.4 Prepreg and Composite Manufacture

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

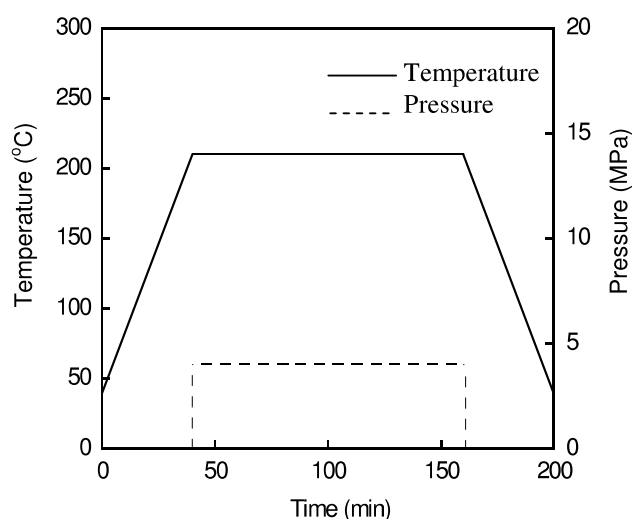


Figure 4.1 Curing cycle of carbon fiber reinforced composites based on BA-a:PMDA.

4.5 Physical Properties

4.5.1 Density Measurement

A density of each specimen was determined by a water displacement method according to ASTM D 792-91 (Method A). All specimens were prepared in a rectangular shape (50 mm x 25 mm x 1 mm). The density was calculated by the following equation:

The average value from at least three specimens was calculated.

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

where ρ = Density of the specimen (g/cm^3)

A = Weight of the specimen in air (g)

B = Weight of the specimen in liquid (g)

ρ_0 = Density of the liquid at the given temperature (g/cm^3)

4.5.2 Fiber Content (weight/weight) Calculation

The percent fiber content was calculated from the completely cured PMDA modified polybenzoxazine reinforced with carbon fiber composites with known weight of carbon fiber and composites, according to the following equation.

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

where M_{fiber} = Mass of the carbon fiber in the composite

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

4.5.3 Interfacial Bonding Examination

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

4.6 Mechanical Properties

4.6.1 Flexural Property Measurement

Flexural modulus and flexural strength of composite specimens were determined utilizing a Universal Testing Machine (model 5567) from Instron Instrument. The test method used was a three-point bending mode with a support span of 32 mm at the crosshead speed of 1.7 mm/min. The dimension of the specimens was 50 mm x 25 mm x 1 mm. The flexural properties were determined using ASTM D 790 - 03 according to the following equations:

$$E_B = \frac{L^3 m}{4bd^3} \quad (4.3)$$

$$S = \frac{3PL}{2bd^2} \quad (4.4)$$

where E_B = Flexural modulus (MPa)

S = Flexural strength (MPa)

P = Load at a given point on the load-deflection curve (N)

L = Support span (mm)

b = Width of beam tested (mm)

d = Depth of beam tested (mm)

m = Slope of the tangent to the initial straight-line portion of the load-deflection curve (N/mm)

4.6.2 Dynamic Mechanical Measurement

The dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH was used to investigate the dynamic mechanical properties. The dimension of the specimen was $50 \times 10 \times 1 \text{ mm}^3$. The samples were tested in three point bending mode. In a temperature sweep experiment, a frequency of 1 Hz and a strain value of 0.1% were applied. The temperature was scanned from 30°C to a temperature above the glass transition temperature (T_g) of the specimen with a heating rate of 2°C/min under nitrogen atmosphere. The storage modulus (E'), loss modulus (E''), and loss tangent or damping curve ($\tan \delta$) were then obtained. The glass transition temperature was taken as the maximum point on the loss modulus curve in the DMA thermogram.

4.7 Thermal Properties

4.7.1 Thermogravimetric Analysis (TGA)

A thermogravimetric analysis model TGA/DSC 1 from Mettler-Toledo model TGA/DSC 1 was used to evaluate the degradation temperature (T_d) and char yield of the cured composites. The testing temperature program was ramped at a heating rate of 20°C/min from room temperature to 1000°C under nitrogen atmosphere. The sample mass used was measured to be approximately 8-15 mg. Weight loss of the sample was measured as a function of temperature. The degradation temperature (T_d) of cured composites was reported at their 5% weight loss and char yields were also reported at 800°C.

4.7.2 Differential Scanning Calorimetry (DSC)

The glass transition temperature (T_g) of the cured composites was examined using a differential scanning calorimeter (model 2910) from TA Instruments in a temperature range of 30-300°C. A sample mass of 5-10 mg was placed in a non-hermetic aluminum pan with lid. The experiment was performed at a heating rate of 10°C/min under nitrogen purging. The purge nitrogen gas flow rate was maintained to be constant at 50ml/min. The glass transition temperature was obtained from the temperature at half extrapolated tangent of the step transition midpoint.

4.7.3 Limited Oxygen Index Test (LOI)

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

$$LOI = \frac{O_2}{O_2 + N_2} \quad (4.5)$$

4.7.4 UL-94 Flame Test

4.7.4.1 UL-94 Vertical Test

UL-94 tests were performed on vertical testing apparatus as shown in Figure 4.2. Five specimens 120 mm × 12 mm × 1 mm were used for testing. The specimen was placed in a holder in a vertical position the lower end of specimen is contacted by a flame for 10 second thus initiating burning. A second ignition was made after self-extinguishing of the flame at the sample for 10 second. The burning process is characterized by the times t_1 and t_2 pertaining to the two burning steps. The parameters t_1 and t_2 denote the time between removing the methane flame and self-

extinguishing of the sample. Moreover, it is always noted whether drips from the sample are released or drips make absorbent cotton flame during the burning times t_1 and t_2 . If $t_1 + t_2$ were less than 10 second with no dripping, it would be considered a V-0 material.

4.7.4.2 UL-94 Thin Material Vertical Test

This test includes three classifications: VTM-0, VTM-1 and VTM-2. Materials that are thin gauge, typically ≤ 10 mil or very flexible may distort, shrink or flex during the 94 vertical test. These materials can be tested using 94VTM. This differs in ways from 94 vertical test :

- The specimen size is 8" \times 2".
- The two flame applications have duration of three seconds instead of ten.

The test is performed in the same manner as 94 vertical test with the above mentioned differences.

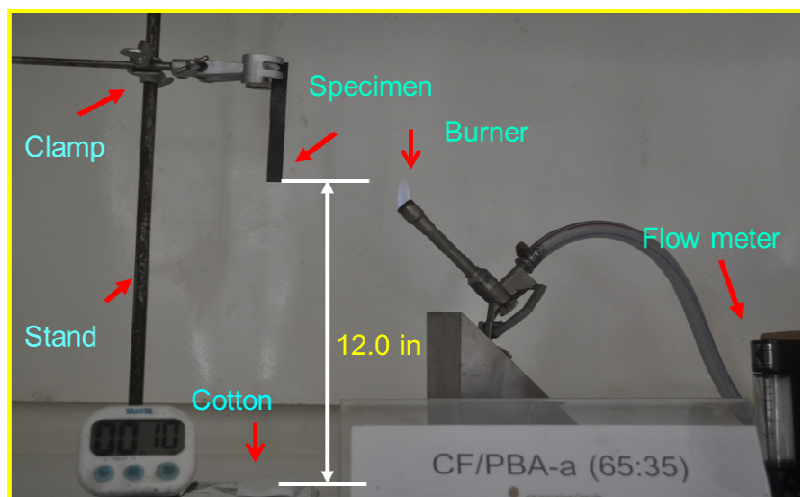


Figure 4.2 UL-94 Vertical test.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Effects of Carbon Fiber Contents on Properties of Carbon Fiber (CF)/PBA-a:PMDA Composites

5.1.1 Density of CF/PBA-a:PMDA Composites at Various CF Contents

One of the quantification methods to evaluate the maximum packing of carbon fibers in PMDA-modified polybenzoxazine (PBA-a) composed of BA-a = 1.5 mole and PMDA = 1 mole can be evaluated by density measurement [60, 61]. The density at room temperature calculated using equation 4.1 of the carbon fiber-reinforced polybenzoxazine modified with PMDA composite as a function of carbon fiber content is shown in Figure 5.1. The theoretical densities of the composites were calculated based on the density of carbon fiber of 1.75 g/cm^3 and the density of PMDA-modified polybenzoxazine prepared from benzoxazine resin (BA-a) = 1.5 mole and PMDA = 1 mole of 1.26 g/cm^3 . The maximum packing density of the composite was defined by the maximum density value, corresponding to the theoretical density. From the figure, the actual density of all composites insignificantly reduced to be lower than the theoretical density. This characteristic may be due to the presence of a few voids as a defect which often occurs in the composite prepared by solvent [62]. Based on the result, the CF/PBA-a:PMDA composite at 65% by weight of fiber provided the maximum density value, corresponding to the theoretical density.

5.1.2 Flexural Properties of CF/PBA-a:PMDA Composites at Various CF Contents

Flexural properties such as flexural strength and modulus of PMDA-modified polybenzoxazine (PBA-a) composed of BA-a = 1.5 mole and PMDA = 1 mole reinforced with CF at different CF contents ranging from 60 to 80% by weight are shown in Figures 5.2-5.3. Figure 5.2 exhibits the flexural strength represented an ability of materials to absorb maximum force at rupture of the composites. We can see that the flexural strength of the composite increased with increasing CF content and reached to the highest flexural strength value, i.e. 652 MPa at 65% by weight of CF (57vol%). In case of flexural modulus as seen in Figure 5.3, the composite showed the flexural modulus increased to be approximately 65 GPa with an incorporation of CF content at 65% by weight, and then the flexural modulus value slightly decreased at higher CF content which may be related to void formation as reported in published work [63]. As expected, in Figure 5.3, the void content decreased from 7.9% to 4.2% with decreasing CF content from 80% by weight to 65% by weight. However, the flexural modulus and strength values of the resulting carbon fiber composites, i.e. 61-64 GPa and 439-625 MPa, were still high than 56vol% carbon fiber-reinforced bisphenol-A based epoxy composites having 38 GPa for the flexural modulus and 380 MPa for flexural strength. [64].

5.1.3 Glass Transition Temperature of CF/PBA-a:PMDA Composites at Various CF Contents

Glass transition temperatures (T_g) of PMDA-modified polybenzoxazine (PBA-a) composed of BA-a = 1.5 mole and PMDA = 1 mole reinforced with CF at different CF contents ranging from 60 to 80% by weight evaluated by differential scanning calorimetry (DSC) with a heating rate of 10°C/min in a temperature range of 30-300°C are displayed in Figure 5.4. Generally, the T_g of the fully cured composites were taken as the midpoint temperature of the change in specific heat in the transition region and the numerical results are summarized in Table 5.1. From the

table, we can see that the T_g of the fully cured CF/PBA-a:PMDA composites at various CF contents were observed to be 230, 232, 225, 221, and 220°C for 60wt%, 65wt%, 70wt%, 75wt%, and 80wt% CF contents, respectively. These values were higher than that of CF/epoxy composites which was reported to be in range of 111-115°C [65].

5.1.4 Dynamic Mechanical Analysis (DMA) of CF/PBA-a:PMDA Composites at Various CF Contents

Recently, DMA at a selected fixed frequency over a range of temperature has grown as useful analytical techniques for the characterization of polymeric materials, such as homopolymers, copolymers, and composites [66, 67]. The evaluation is based on the determination of the temperature dependence of the dynamic moduli, stress relaxation, mechanical loss, and damping phenomena. In this work, the effect of CF content on DMA properties as dynamic moduli and mechanical loss of PMDA-modified polybenzoxazine (PBA-a) composed of BA-a = 1.5 mole and PMDA = 1 mole reinforced with CF are depicted in Figures 5.5-5.6. The results from DMA study give information about the glass transition temperature and associated features. Thus, the DMA method is suitable for making sensitive conclusions about changes in molecular mobility of the composites.

Figure 5.5 illustrates the storage modulus (E') as a function of temperature ranging from 30 to 300°C of PMDA-modified polybenzoxazine (PBA-a) composed of BA-a = 1.5 mole and PMDA = 1 mole reinforced with CF at different CF contents ranging from 60 to 80% by weight. From the figure, the storage modulus (E') related to the stiffness of the composites expectedly increases with an increasing amount up to 65% by weight of carbon fiber. Beyond 75% by weight of carbon fiber, the storage modulus value slightly decreases. In addition, the storage modulus at 35°C of the composites having a CF content of 65% by weight has a value up to 45.3 GPa which is very high compared to that of 70wt% CF reinforced bisphenol-A epoxy composite with a value of 12 GPa [65]. Furthermore, the curve in transition region is observed to be less steep when the fiber content is increased. This may be due to

content of the fiber which greatly restricts the motion of the polymer molecules and imparts higher thermal stability to the composites.

The glass transition temperature (T_g) of PMDA-modified polybenzoxazine (PBA-a) composed of BA-a = 1.5 mole and PMDA = 1 mole reinforced with CF at different CF contents ranging from 60 to 80% by weight can be obtained from the maximum point on the loss modulus curve as presented in Figure 5.6. The T_g values of composites were determined as 234, 237, 235, 230, and 229°C for the composite composed of 60wt%, 65wt%, 70wt%, 75wt%, and 80wt% CF contents, respectively. It is clearly seen that the highest T_g was observed in 65wt% CF composite. Moreover, the T_g as a function of carbon fiber content showed a behavior nearly identical to that of the T_g determined by DSC.

5.2 Effects of PMDA Contents on Properties of CF/PBA-a:PMDA Composites

5.2.1 Glass Transition Temperature of 65wt% CF/PBA-a:PMDA Composites at Various PMDA Mole Ratios

Thermal properties of PBA-a:PMDA composites based on BA-a:PMDA = 4:1, 3:1, 2:1, 1.5:1 and 1:1 mole reinforced with 65% by weight of carbon fiber were evaluated from DSC are shown in Figure 5.7 and the numerical results are also summarized in Table 5.2. From the figure, we can see that the exothermic peaks of all 65wt% CF/PBA-a:PMDA composites were not observed. This are confirmed that the fully cured composites were achieved after curing at 210°C for 2 hours and post-cured at 230-240°C for 3 hours. The T_g values were taken as the midpoint temperature of the change in specific heat in the transition region. The T_g values of the fully cured 65wt% CF/PBA-a:PMDA composites were observed to be 210, 215, 227, 235, and 230°C for PBA-a:PMDA matrix based on BA-a:PMDA = 4:1, 3:1, 2:1, 1.5:1 and 1:1 mole 4:1, 3:1, 2:1, 1.5:1 and 1:1 mole ratios, respectively. The value is relatively high than that of the fully cured 65wt% CF-reinforced neat polybenzoxazine (PBA-a) composite (i.e. $T_g = 175^\circ\text{C}$).

5.2.2 Thermomechanicsl Properties of 65wt% CF/PBA-a:PMDA Composites at Various PMDA Mole Ratios

Storage modulus (E') values of 65wt% carbon fiber (CF)-reinforced PBA-a and PBA-a modified with PMDA composites at five mole ratios between BA-a and PMDA = 1:1, 1.5:1, 2:1, 3:1 and 4:1 as a function of temperature are shown in Figure 5.8. From this figure, the storage modulus of CF/PBA-a:PMDA composites at room temperature of 35°C exhibited values in the range of 43-46 GPa, which are slightly higher than that of the neat CF/PBA-a composite i.e. 41 GPa. This

observation indicated that the addition of PMDA can help improving the storage modulus of the specimens. This could be related to more benzene ring in PMDA molecular structure which enhanced rigidity of the 65wt% CF/PBA-a:PMDA composites as similarly reported in previous work [68]. Moreover, the highest storage modulus of PBA-a:PMDA reinforced with 65wt% carbon fiber was observed at 46 GPa which is clearly higher than that of 60vol% carbon fiber reinforced benzoxazine composite (28.5 GPa) [4].

Glass transition temperature (T_g) of 65wt% CF reinforced PBA-a and PMDA-modified PBA-a composites at various mole ratios of PMDA are depicted in Figure 5.9. The T_g of 65wt% CF/PBA-a composite determined from the maximum of loss modulus curve from dynamic mechanical analysis was about 183°C which was found substantially enhanced by an incorporation of PMDA. All of the PMDA-modified PBA-a reinforced with 65wt% of CF composites showed T_g in the range of 203 to 237°C. From the results, the T_g value increased with the incorporation of PMDA into the composites. This phenomenon is due to the presence of greater aromatic content and the increased crosslink density via ester linkage between phenolic hydroxyl group of PBA-a and anhydride group of PMDA in the copolymer structures [68]. Moreover, it can be noticed that the highest T_g (237°C) observed from DMA thermograms belonged to the composite composed of BA-a:PMDA = 1.5:1 mole.

Loss tangent ($\tan\delta$) of 65wt% CF-reinforced PBA-a and 65wt% CF-reinforced PMDA-modified PBA-a composites at various mole ratios of PMDA are illustrated in Figure 5.10. A magnitude of $\tan\delta$ decreased with an addition of PMDA and the peak shifted to high temperature. The results suggested that an increase in the crosslink density caused a restriction of the chain's segmental mobility in PBA-a:PMDA matrix thus a more elastic nature compared to the PBA-a. In addition, the incorporation of stiff fibers reduced the $\tan\delta$ peak height by restricting the movement of polymer molecules [66, 69]. Thus, 65wt% CF-reinforced PMDA-modified PBA-a composites will increase the elasticity and decrease in the viscosity. Hence, less energy will be used to overcome the friction forces between molecular as to decrease mechanical loss.

5.2.3 Thermal Degradation and Thermal Stability of 65wt% CF/PBA-a:PMDA Composites at Various PMDA Mole Ratios

Thermal stability, thermal degradation temperature (T_d) and char yield, of the 65wt% CF/PBA-a:PMDA composites at various PMDA contents was evaluated by TGA at the programmed temperature range of 35 to 1000°C. The TGA curves of all composites are shown in Figure 5.11. Thermal decomposition in carbon fiber composites reinforced polybenzoxazine resin modified with PMDA was found to occur in one stage attributed to decomposition of the polymer matrix at temperature between 350°C and 600°C. The degradation temperatures at 10% weight loss (T_{d10}) of the 65wt% carbon fiber reinforced neat benzoxazine resin was observed to be 404°C whereas 65wt% CF reinforced PMDA-modified PBA-a composites at various mole ratio between BA-a:PMDA = 1:1, 1.5:1, 2:1, 3:1 and 4:1 was ranging from 458°C to 498°C. However, 65wt% CF reinforced PMDA-modified PBA-a composites exhibited higher degradation temperatures than those of the PBA-a:PMDA matrix, as illustrated in Table 5.3. It is due to the effect of high degradation temperature of the carbon fiber. Furthermore, the greater T_d of the composite with higher amount of the PMDA fraction in the PBA-a:PMDA copolymer matrix. This is possibly due to the enhanced crosslink density of the PBA-a with an addition of PMDA as mentioned previously [68].

Another important feature in the thermograms is the amount of carbonized residues (char yield) at 800°C of the composites which is related to the flammability of materials. The char yield was found to be 75.7 for 65wt% carbon fiber reinforced neat PBA-a composite. For the char yield of 65wt% CF-reinforced PBA-a modified with PMDA composites at various PMDA mole ratio, the values systematically increased from 80.7% to 82.2% with an incorporation of the PMDA, as depicted in Table 5.3. In addition the values were all greater than those of the the PBA-a:PMDA copolymer matrix compared at the same PMDA content.

According to char yield can be applied as decisive factor for estimating its limiting oxygen index (LOI) using Van Krevelen and Hoftyzer equation (Eq. 5.1) [70-73].

$$\text{LOI} = 17.5 + 0.4\text{CR} \quad (5.1)$$

Where CR is char yield.

Thermogravimetric analyzer was also used to determine the amount of fiber in the composites. This research, the carbon fiber content in the composites was calculated using the resulting char yields from thermogravimetric analysis (TGA) following an empirical formula based on the rule of mixtures to calculate the fiber fraction.

$$X = a(W_f) + b(1 - W_f) \quad (5.2)$$

Where X is the percentage weight of TGA residue, W_f is the weight fraction of fiber, a is the percentage residual weight when 100% fiber is degraded and b is the percentage residual weight when 100% neat matrix is degraded [74].

The percent of carbon fiber content of 68wt% for PBA-a , 66wt% for PBA-a:PMDA 4:1, 65wt% for PBA-a:PMDA 3:1, 65wt% for PBA-a:PMDA 2:1, 65 %wt for PBA-a:PMDA 1.5:1 and 65wt% for PBA-a:PMDA 1:1 were obtained as shown in Table 5.3. The calculated results confirmed that the carbon fiber content in each composite was about 65% by weight as prepared in the pre-impregnation stage.

5.2.4 Limiting Oxygen Index (LOI) of PBA-a:PMDA Matrix at Various PMDA Mole Ratios

Ignitability and fire resistivity of composites can be characterized by a limiting oxygen index (LOI). The relative flammability is determined by adjusting the concentration of oxygen. The LOI is the lowest oxygen gas concentration which a material will burn [75]. Figure 5.12 presents the LOI values of neat PBA-a and PBA-a:PMDA 1.5:1 copolymer films. The LOI values of PBA-a and PBA-a:PMDA copolymer films were about 23 and 28, respectively. This means the PBA-a:PMDA copolymer films can be classified as self-extinguishing polymers which require LOI value to be at least 26. As depicted in Figure 5.12, LOI value of CF composites were 26 for 65wt%CF/PBA-a and 47.5 for 65wt% CF/PBA-a:PMDA (1.5:1). The LOI of composites were remarkably higher than the matrices. This result suggested that incorporation carbon fiber can improve flame retardance due to the high thermal stability, especially char yield as mention in TGA result. Furthermore, the LOI values of the carbon fiber composites were in range of 32.5-49.5. This indicates that incorporating PMDA shows a significant effect on promoting the flame retardance of the carbon fiber composite. This is due to the fact that the char formed during combustion can act as a protective layer to prevent the oxygen diffusion to the surface. Consequently, more oxygen is needed for combustion [76]. Interestingly, the LOI values of our carbon fiber composites are significantly higher than that of the flame-retarded carbon fiber composite, e.g., 70wt% CF/epoxy (LOI = 33.2-47.7) [77].

5.2.5 UL-94 Vertical Test of 65wt% CF/PBA-a:PMDA Composites at Various PMDA Mole Ratios

The UL-94 results of films (i.e. PBA-a and PBA-a:PMDA) and CF/PBA-a:PMDA composites are presented in Table 5.4. Normally, the standard requirements of the sample thickness should be at least 3 mm. In our investigation, the composite

thickness was fixed at 1 mm for having a more severe condition for UL-94 vertical flame test. As the result from Table 5.4, the 65wt% CF/PBA-a composite is classified as V-1 in UL-94 vertical flame test which were higher than that of 70wt% CF/epoxy composite (3 mm) classified as horizontal burning (HB), the lowest UL-94 classification[80]. In addition, all CF-reinforced PBA-a:PMDA composites showed total after flame time (t_1+t_2 for the 5 specimens) to be less than 50 seconds which can be classified as V-0, the maximum flame resistant class of UL-94 vertical rating. The photographs of specimens are shown in Figure 5.13-5.18.

Furthermore, an increasing of PMDA content resulted in reduced burning time, suggesting that an addition of the PMDA into the PBA-a matrix of the CF composites can help improve the fire resistance of the CF/PBA-a composite. This result is in good agreement with our previous work [68] reported that the char yield value of polybenzoxazine modified with dianhydrides copolymers were much higher than that of the neat PBA-a. In principle, the higher char residue of the copolymer can provide a sample with enhanced flammability because char formation can inhibit volatile products from diffusing to the flame and shield the polymer surface from heat and air [78].

5.2.6 Water Absorption at of CF/PBA-a:PMDA Composites at Various PMDA Mole Ratios

The water absorption for the 65wt% CF/PBA-a:PMDA composites at different PMDA contents are exhibited in Figure 5.19. The percentage of water absorbed plotted against time for all specimens revealed a similar behavior, i.e., the specimens absorbed water more rapidly during first stages (0–24 h). The water adsorption values of all CF/PBA-a:PMDA composites at various PMDA content were 0.26, –1.61% after 7 days of the immersion. These values were significantly lower than the water absorption values of previous works such as a carbon fiber reinforced with epoxy (1.7% at 168 hr) [79]. Generally, the water absorption is concerned with the hydrophilic property of the fiber and the matrix and by the

adhesion between the fiber and the matrix. Therefore, the water absorption of our composites depend on PBA-a:PMDA matrix and interface between the CF and the PBA-a:PMDA matrix since CF is hydrophobic materials [80]. As shown in Figure 5.21, the water absorption of all composites was also observed to increase with increasing PMDA content. It is due to the fact that PMDA easily absorb water due to its hydrophilic characteristic [81]. It is essential to study the kinetic water sorption to have better understanding of the water sorption mechanism and to minimize water absorption of the composites.

The generalized equation for explaining the diffusion in materials can be expressed as Eq. (5.3)

$$M_t/M_\alpha = kt^n \quad (5.3)$$

Where M_t is the moisture content at time t , M_α is moisture content at equilibrium, and k and n are constants.

The diffusion behaviors can be classified as follows: super caseII ($n > 1$), case II ($n = 1$), anomalous ($1/2 < n < 1$), classical/Fickian ($n = 1/2$), or pseudo-Fickian ($n < 1/2$) [82]. Figure 5.19 illustrates the relationship between $\log M_t/M_\alpha$ and $\log t$ plots which show the slopes ranging from 0.43-0.53. Therefore, we can conclude that our composite materials exhibited a behavior close to Fickian type diffusion.

5.2.7 Flexural Properties of CF/PBA-a:PMDA Composites at Various PMDA Mole Ratios

Generally, the strength, modulus and mode of failure of fiber-reinforced composite depend on properties of constituents and interfacial interaction between the fiber and the matrix. However, the critical controlling mechanism identified for

the composite quality was fiber interfacial wetting. A property that can indicate the fiber interfacial wetting of a considering carbon fiber-reinforced polybenzoxazine modified with PMDA is the bending characteristics.

Flexural properties of a composite are very important for structural applications, as it is comprised of both the tensile and compressive strength components of the composites. During flexural testing, upper part is dominated by compressive force and the lower part by tensile force in the longitudinal direction. It is reported that tensile response of the composite (rather than the compressive) has a critical influence on flexural strength [83]. Flexural properties of 65wt% carbon fiber (CF)-reinforced PBA-a and 65wt% CF-reinforced PMDA-modified PBA-a composites at mole ratios between BA-a:PMDA = 1:1, 1.5:1, 2:1, 3:1 and 4:1 mole were examined. In Figure 5.20, flexural strength values of the 65wt% CF reinforced PMDA-modified PBA-a composites variation with PMDA mole ratio was observed to be in the range of 637 to 652 MPa. The values are slightly higher than the flexural strength value of the CF-reinforced polybenzoxazine (PBA-a) observed to be 636 MPa. Furthermore, the flexural strength of carbon fiber composite in this work was found to be higher than that of 70wt% carbon fiber reinforced bisphenol-A epoxy composite with a published value of 488 MPa [65]. Additionally, the flexural strength of the composites tended to increase with increasing amount of PMDA in the polybenzoxazine. This behavior was attributed to an enhancement in crosslink network density from additional esterification reaction between the phenolic hydroxyl group of polybenzoxazine and the carboxylic carbonyl group of PMDA as reported in previous work [16]

Figure 5.21 presents the flexural modulus of the PMDA-modified PBA-a composites at various PMDA mole ratios. The flexural modulus values were also observed to slightly increase with an incorporation of PMDA into the PBA-a matrix having values ranging from 61 to 65 GPa. The values are also higher than that of the neat CF/PBA-a composite i.e. 55 GPa. The enhancement in the composite flexural properties with PMDA addition was possibly due to the improved interfacial adhesion between the carbon fiber and the matrix resin with increasing content of the PMDA. In addition, the flexural modulus of the 65wt% CF-reinforced PBA-a modified with PMDA composites showed a maximum value at a composite

composed of BA-a:PMDA = 1.5:1 mole. It may possible due to an increase aromatic in structure of PMDA. The tendency is in good agreement with the results from DMA mentioned above.

5.2. Fracture Surface of the CF/PBA-a:PMDA Composites

Wettability of the PBA-a:PMDA matrix on the carbon fiber and interfacial adhesion between the fiber and the matrix have been inspected using scanning electron microscopic (SEM) technique. The micrographs show phase information and fracture characteristics reflecting the reasons why the mechanical properties have been changed and in turn determining the mechanical properties of polymeric composites [84].

The surface morphology of the carbon fiber and the fractured surfaces from flexural specimen test of the carbon fiber composites using a polybenzoxazine alloy matrix at a mole ratio between PBA-a:PMDA = 1.5:1 are illustrated in Figure 5.22. From Figure 5.22(a), the SEM picture indicates the relative smooth, defect-free carbon fiber and also reveals the fibers' cylindrical morphology with a diameter about 8 microns. Furthermore, the surface fracture in the weft region and in the warp region of the 65wt% CF/PBA-a:PMDA composites is displayed in Figure 5.22(b) and 5.22(c), respectively. From Figure 5.22(b), the fracture surface in the weft region of the carbon fiber is extensively embedded with the PBA-a:PMDA alloy. This implies that cohesive failure occurred in the PBA-a:PMDA alloy matrix region due to the significant interfacial adhesion between the carbon fiber and the matrix. In addition, in Figure 5.22(c), the pull-out length is short. This phenomenon confirmed that the carbon fibers were potentially adhered by the PBA-a:PMDA alloy matrix, as can be seen from the pieces of matrix attached to the fiber. The results from the SEM micrographs agree well with the observed enhancement in mechanical properties of these composites.

Table 5.1 The glass transition temperature (T_g) of CF-reinforced PBA-a:PMDA composites at various carbon fiber contents from DSC.

Sample CF/PBA-a:PMDA	T _g (°C)
60/40	230
65/35	232
70/30	225
75/25	221
80/20	220

Table 5.2 The glass transition temperature (T_g) of 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios from DSC.

CF/PBA-a:PMDA	T _g (°C)
1:0	175
4:1	210
3:1	215
2:1	227
1.5:1	235
1:1	230

Table 5.3 The thermal stability of 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios.

Samples CF/PBA-a:PMDA	Td at 10 wt% loss		Percent residual weight at 800°C		Percent fiber content
	Matrix	Composite	Matrix	Composite	
1:0	361	404	32.9	75.7	68
4:1	373	458	52.2	80.7	66
3:1	375	472	57.0	81.4	65
2:1	401	482	58.5	81.8	65
1.5:1	426	498	60.2	82.0	65
1:1	394	482	59.0	82.2	65

Table 5.4 UL-94 flame test of films and composites:

-Vertical thin material of neat PBA-a and PBA-a:PMDA = 1.5:1 films.

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

Criteria Conditions	PBA-a:PMDA film (mole ratio)		CF/PBA-a:PMDA (mole ratio)					
	1:0	1.5:1	1:0	4:1	3:1	2:1	1.5:1	1:1
- Afterflame time for each individual specimen t1 or t2 (s)	3.7, 1.1	1.6, 1.7	12.0, 4.5	4.8, 3.5	1.9, 5.1	0.4, 3.4	0.4, 2.8	0, 0.8
- Total afterflame time for any condition set (s) (t1 + t2 for the 5 specimens)	23.4	17.3	82.7	41.9	31.1	23.5	16.2	4.1
- Afterflame plus afterglow time for each individual specimen after the second flame application (t2 + t3) (s)	1.1	1.5	4.5	3.5	5.1	3.4	2.8	0.8
- Afterflame or afterglow of any specimen up to the holding clamp	No	No	No	No	No	No	No	No
- Cotton indicator ignited by flaming particales of drops	No	No	No	No	No	No	No	No
UL-94 Classification	VTM-0	VTM-0	V-1	V-0	V-0	V-0	V-0	V-0

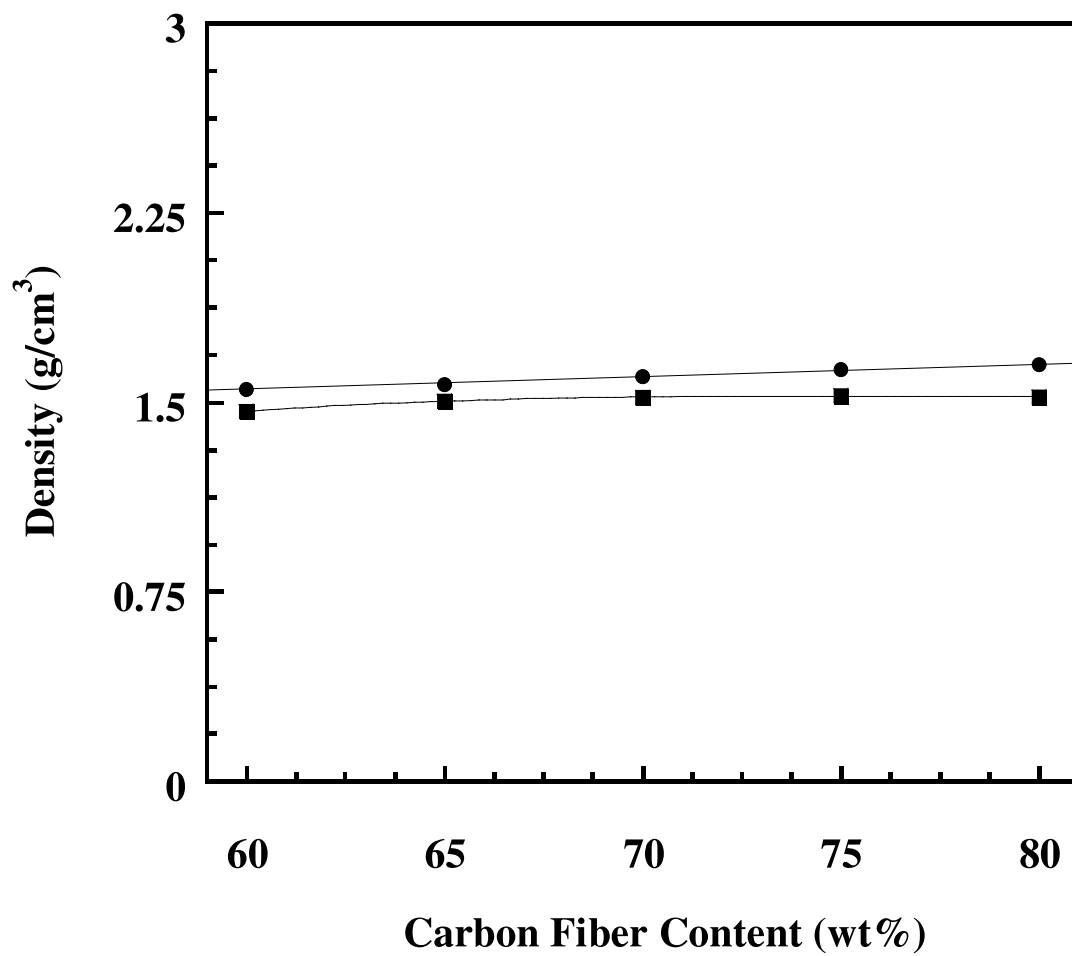


Figure 5.1 The maximum packing density of CF-reinforced PBA-a:PMDA composites at various fiber contents. (●) theoretical density and (■) actual density.

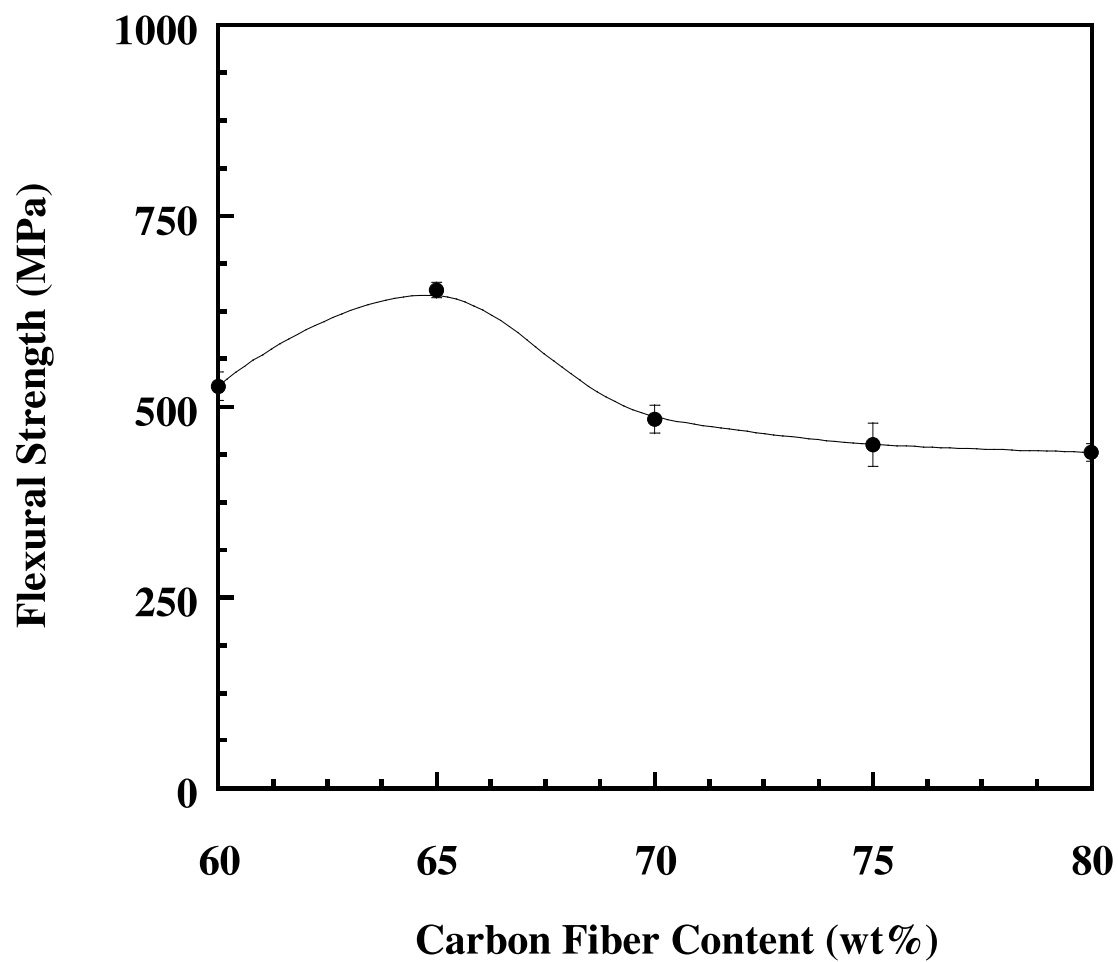


Figure 5.2 Flexural strength of CF-reinforced PBA-a:PMDA composites at various fiber contents.

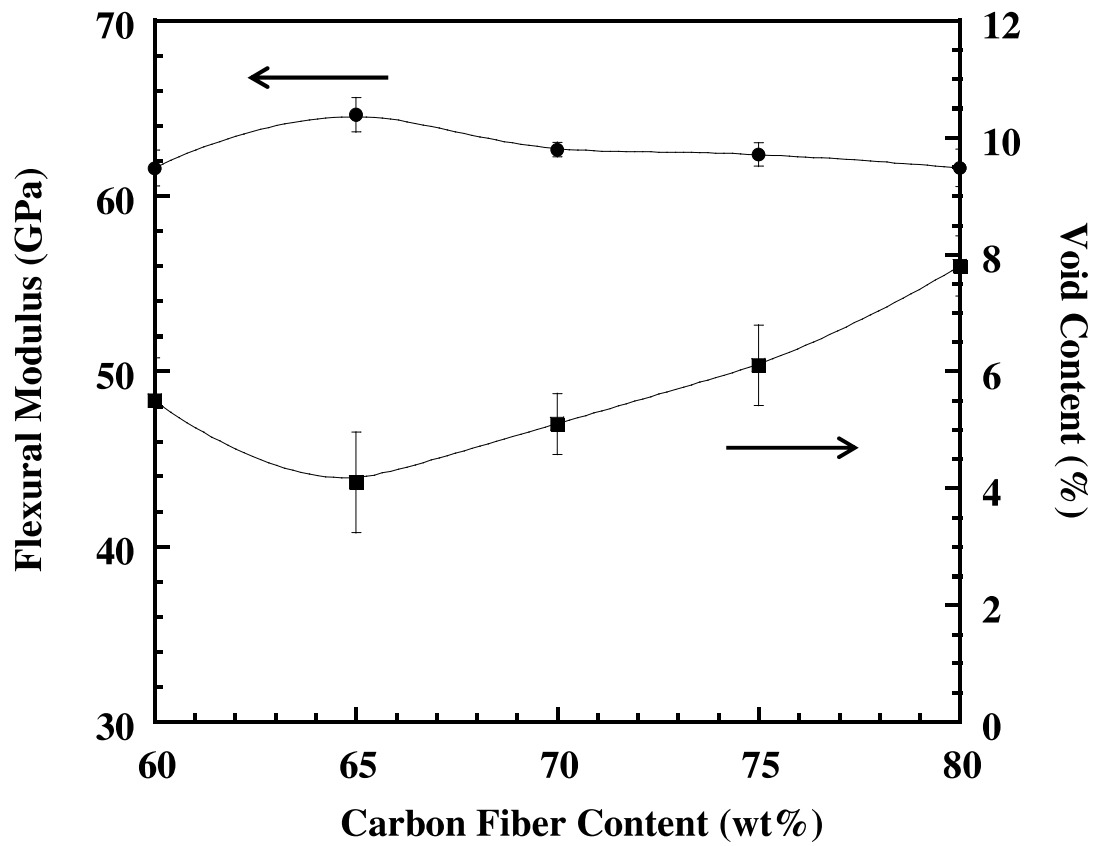


Figure 5.3 Flexural modulus (●) and void content (■) of CF-reinforced PBA-a:PMDA composites at various fiber contents.

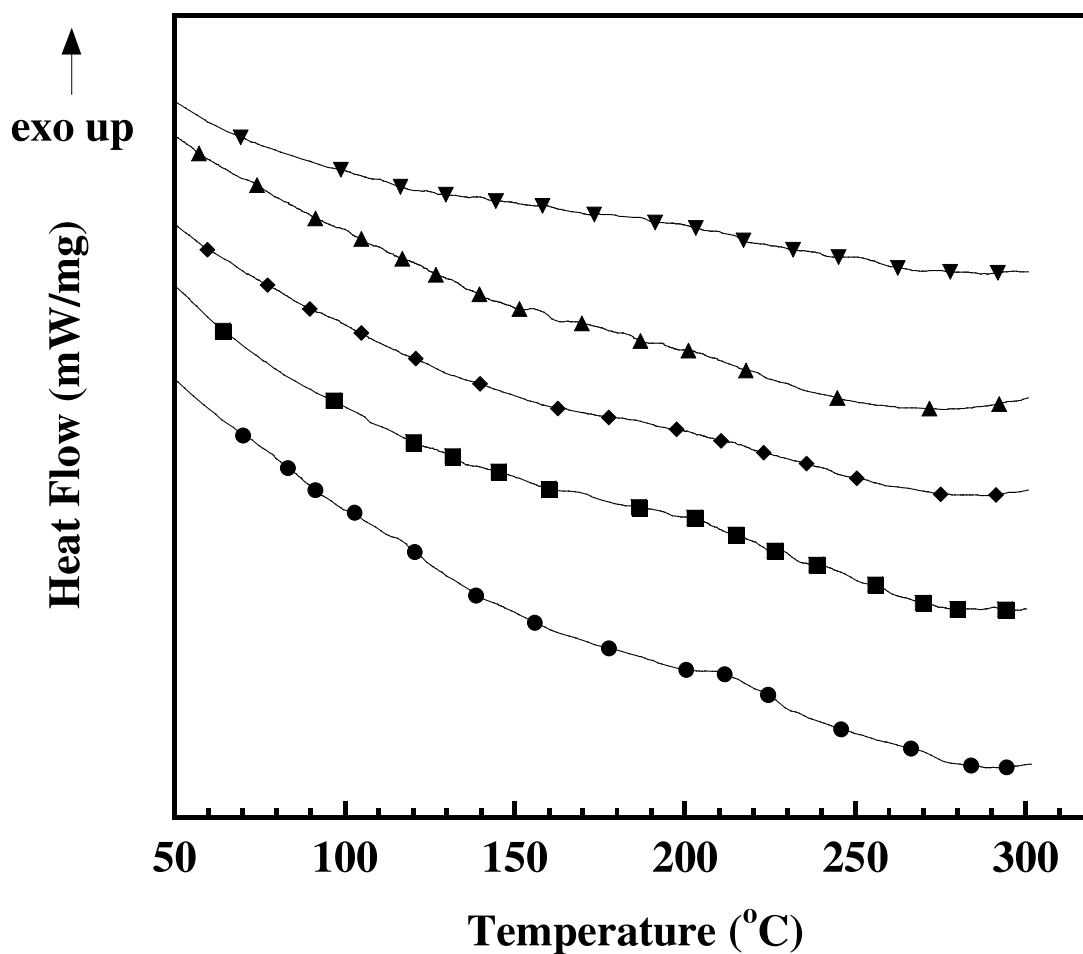


Figure 5.4 DSC thermograms of CF-reinforced PBA-a:PMMA composites at various carbon fiber contents. (●) CF/ PBA-a:PMMA = 60/40, (■) CF/ PBA-a:PMMA = 65/35, (◆) CF/ PBA-a:PMMA = 70/30, (▲) CF/ PBA-a:PMMA = 75/25, (▼) CF/ PBA-a:PMMA = 80/20.

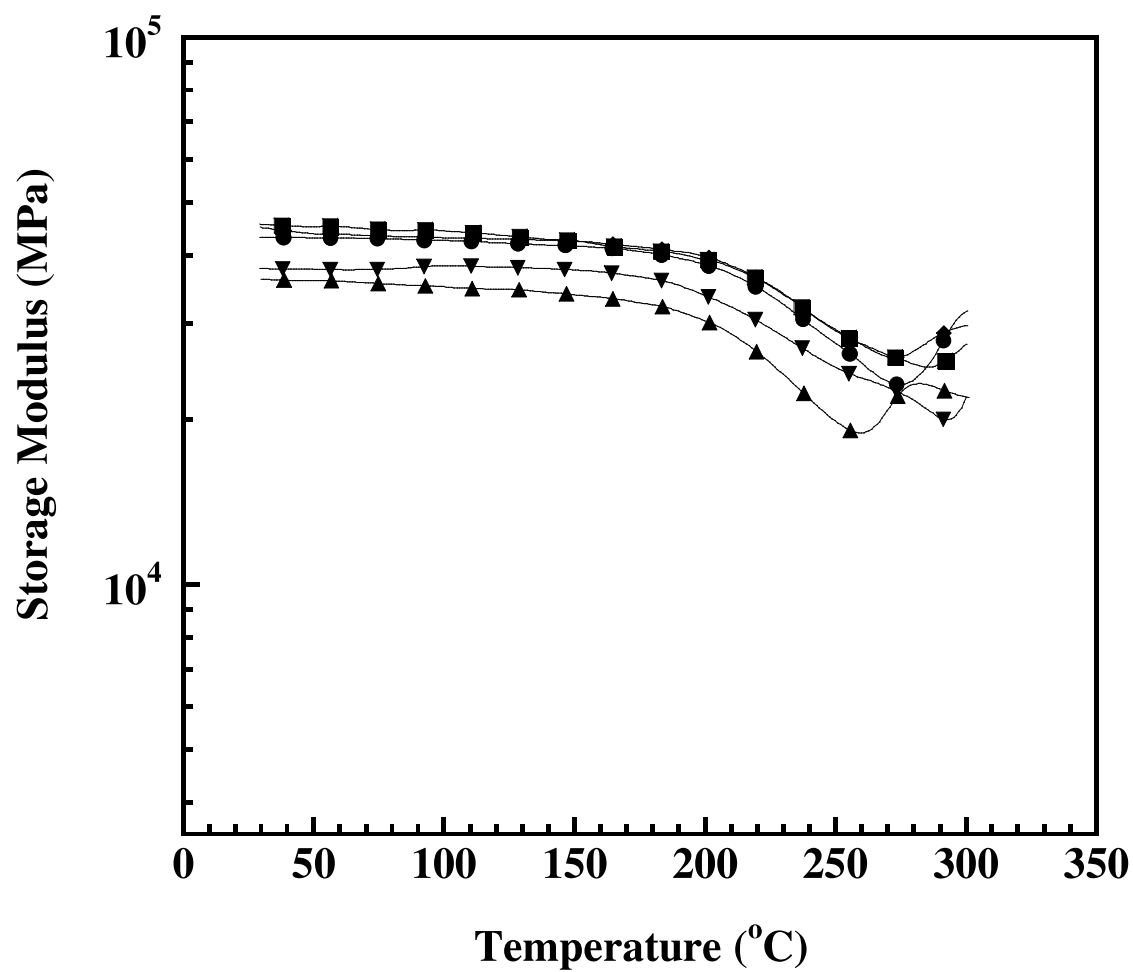


Figure 5.5 Storage modulus of CF-reinforced PBA-a:PMDA composites as a function of temperature at various carbon fiber contents. (●) CF/ PBA-a:PMDA = 60/40, (■) CF/ PBA-a:PMDA = 65/35, (◆) CF/ PBA-a:PMDA = 70/30, (▲) CF/ PBA-a:PMDA = 75/25, (▼) CF/ PBA-a:PMDA = 80/20.

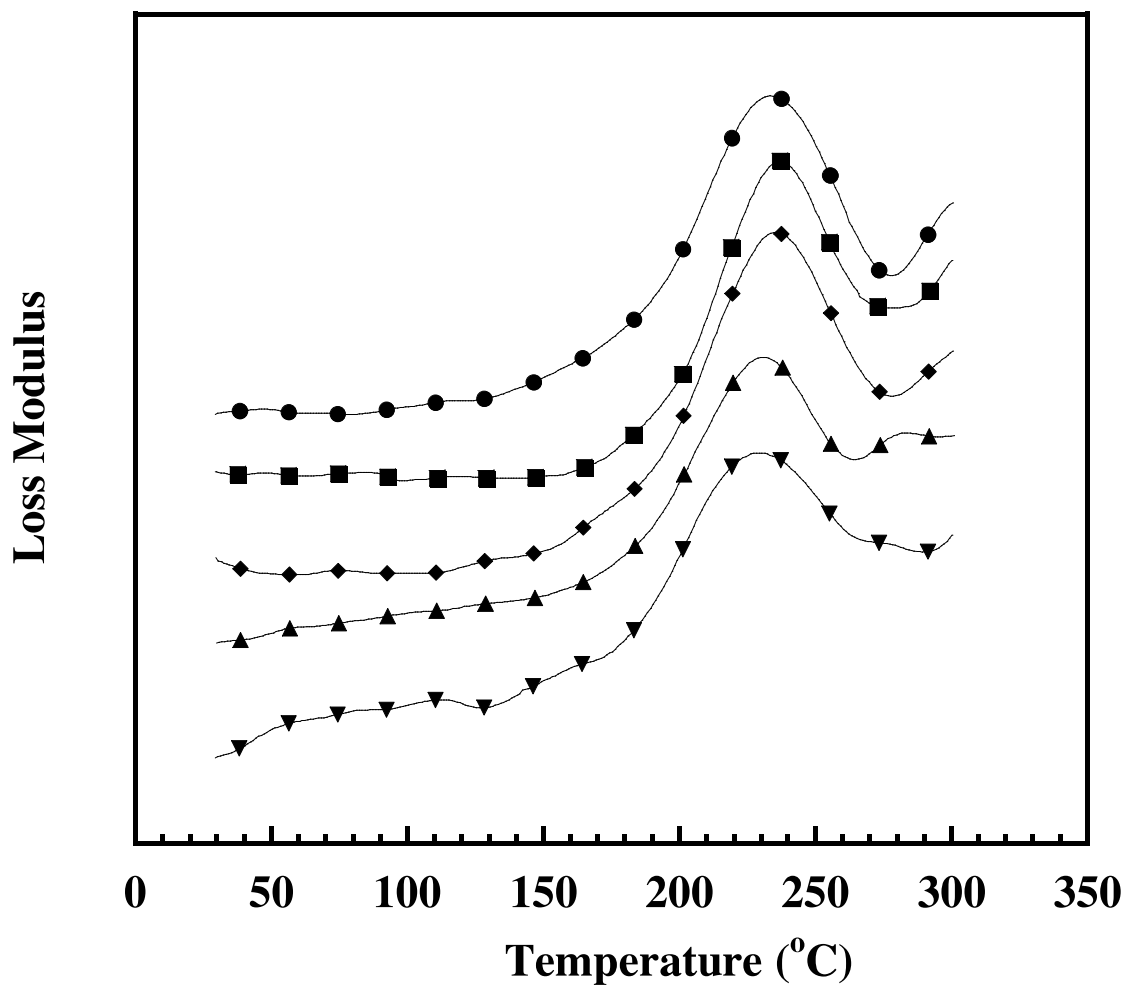


Figure 5.6 Loss modulus of CF-reinforced PBA-a:PMDA composites as a function of temperature at various carbon fiber contents. (●) CF/ PBA-a:PMDA = 60/40, (■) CF/ PBA-a:PMDA = 65/35, (◆) CF/ PBA-a:PMDA = 70/30, (▲) CF/ PBA-a:PMDA = 75/25, (▼) CF/ PBA-a:PMDA = 80/20.

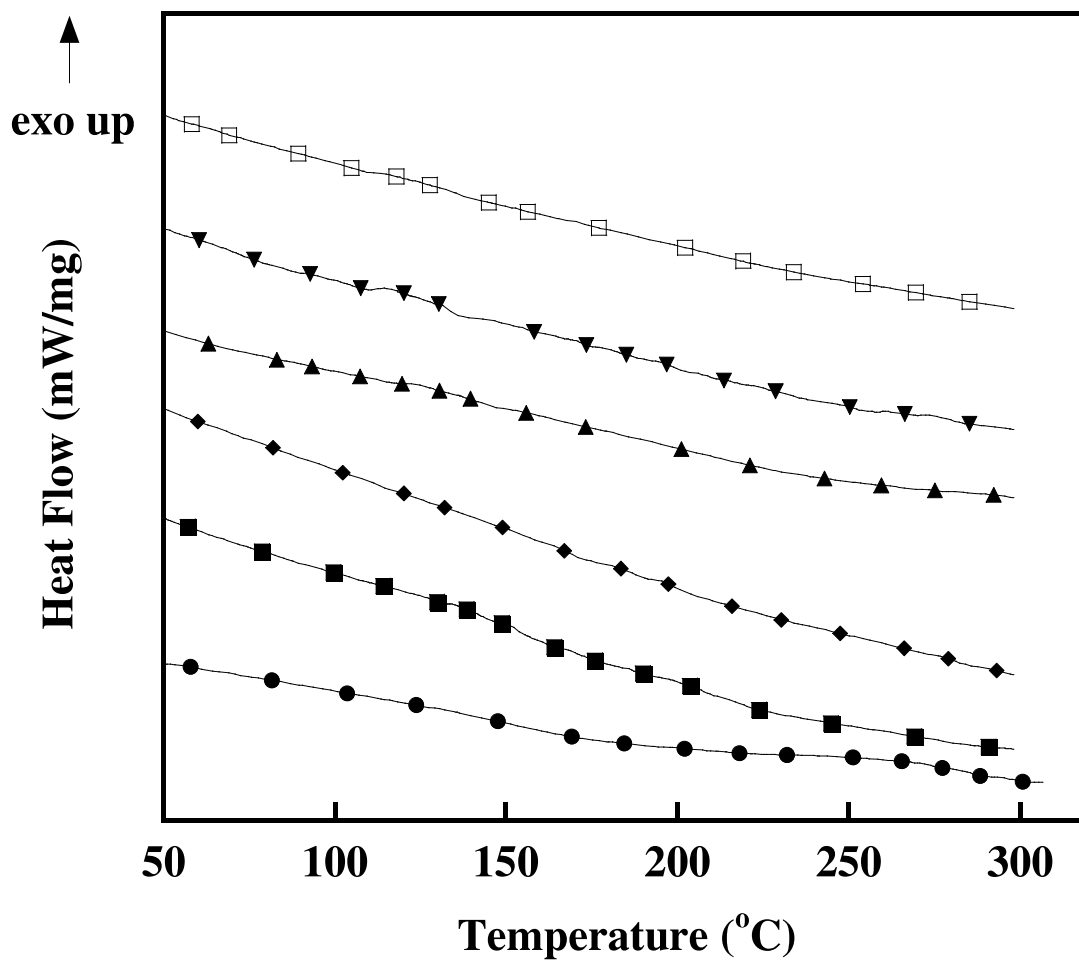


Figure 5.7 DSC thermograms of 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios. (●) CF/PBA-a, (■) CF/PBA-a:PMDA = 4:1, (◆) CF/PBA-a:PMDA = 3:1, (▲) CF/PBA-a:PMDA = 2:1, (▼) CF/PBA-a:PMDA = 1.5:1, (□) CF/PBA-a:PMDA = 1:1.

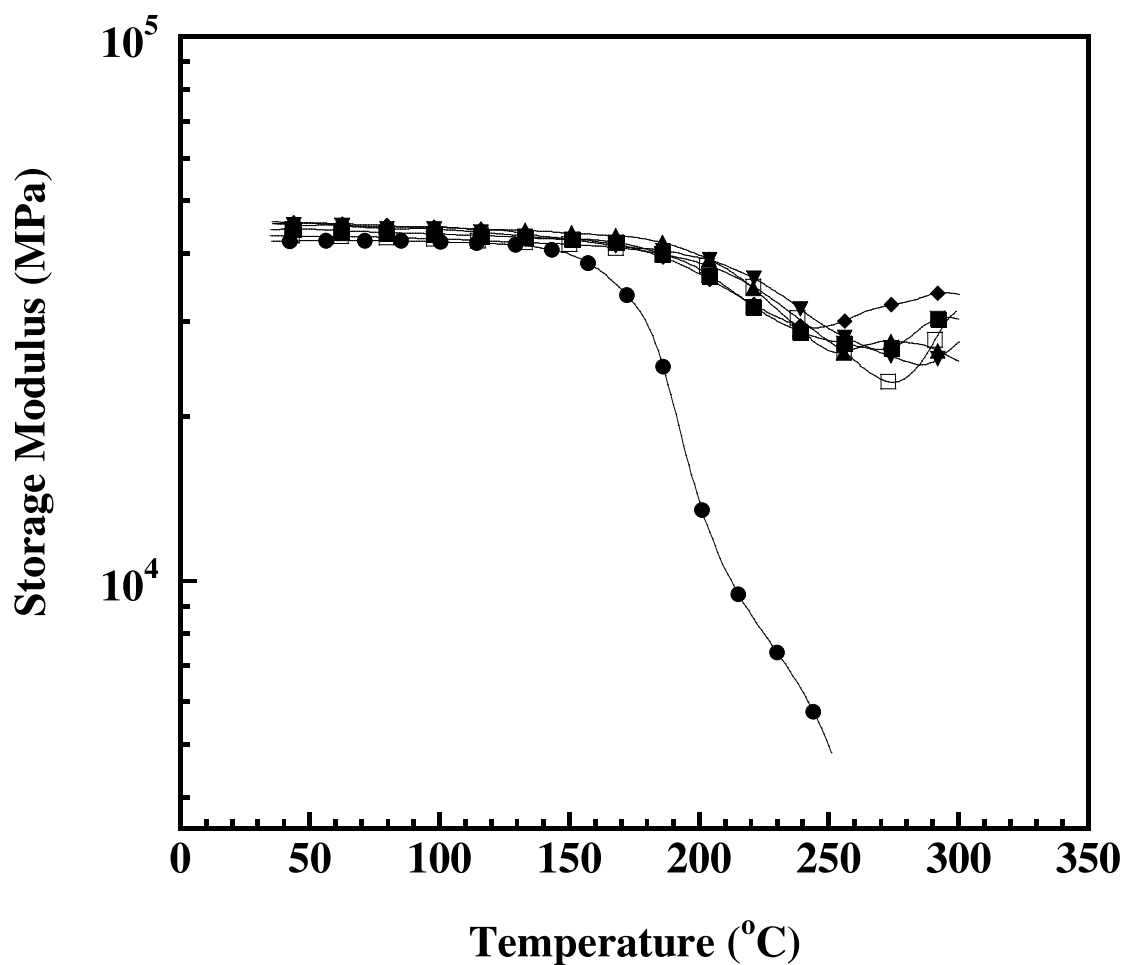


Figure 5.8 Storage modulus of 65wt% CF-reinforced PBA-a:PMMA composites as a function of temperature at various PMMA mole ratios. (●) CF/PBA-a, (■) CF/ PBA-a:PMMA = 4:1, (◆) CF/ PBA-a:PMMA = 3:1, (▲) CF/PBA-a:PMMA = 2:1, (▼) CF/PBA-a:PMMA = 1.5:1, (□) CF/PBA-a:PMMA = 1:1.

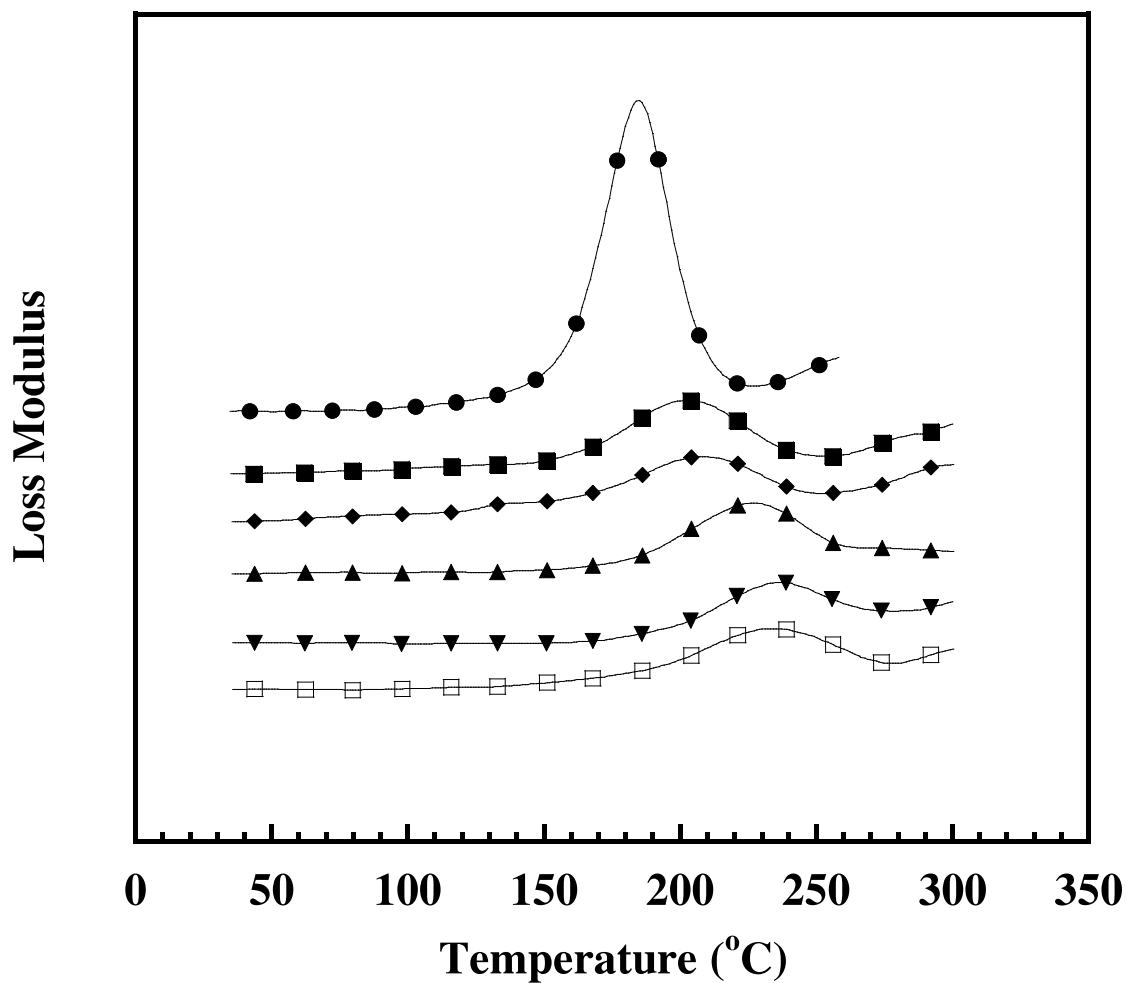


Figure 5.9 Loss modulus of 65wt% CF-reinforced PBA-a:PMDA composites as a function of temperature at various PMDA mole ratios. (●) CF/PBA-a, (■) CF/ PBA-a:PMDA = 4:1, (◆) CF/ PBA-a:PMDA = 3:1, (▲) CF/PBA-a:PMDA = 2:1,(▼) CF/PBA-a:PMDA = 1.5:1, (□) CF/PBA-a:PMDA = 1:1.

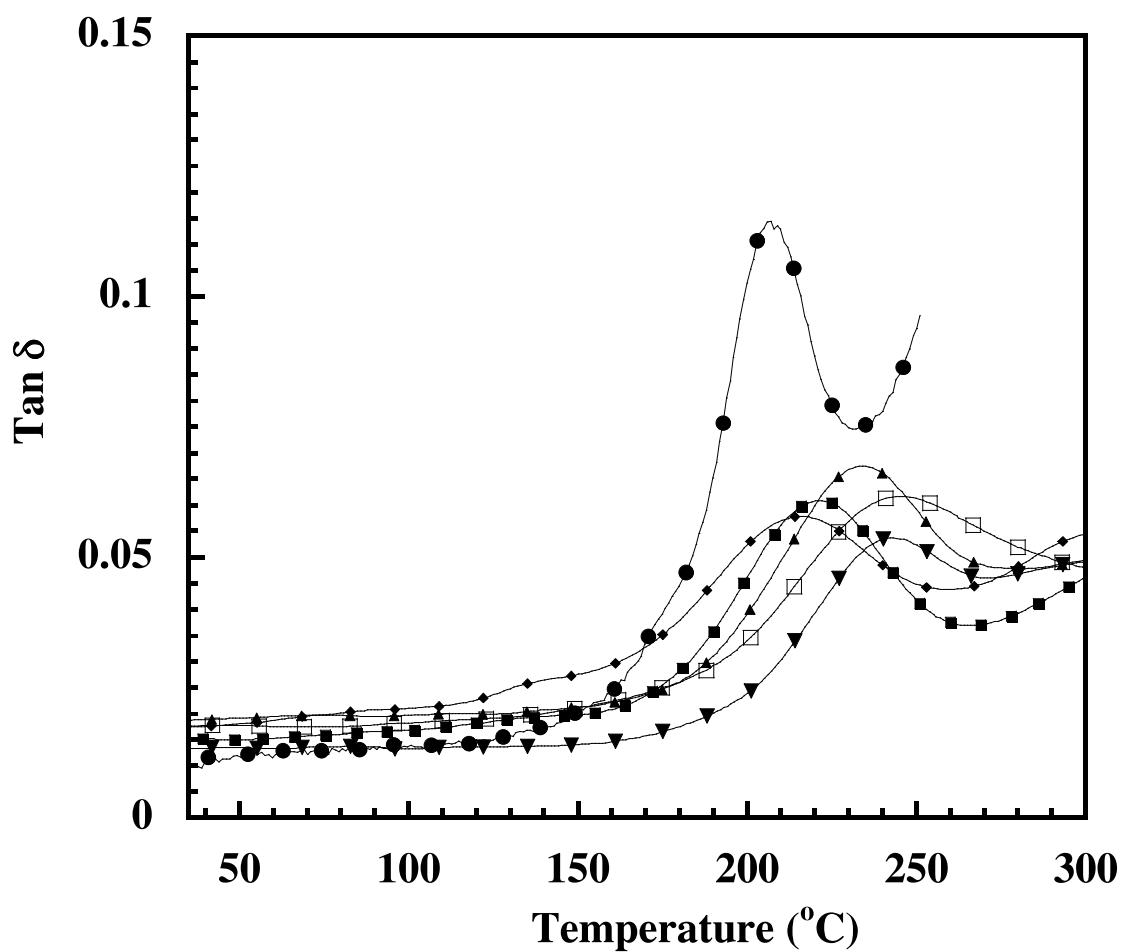


Figure 5.10 $\text{Tan } \delta$ of 65wt% CF-reinforced PBA-a:PMDA composites as a function of temperature at various PMDA mole ratios. (●) CF/PBA-a, (■) CF/ PBA-a:PMDA = 4:1, (◆) CF/ PBA-a:PMDA = 3:1, (▲) CF/PBA-a:PMDA = 2:1,(▼) CF/PBA-a:PMDA = 1.5:1, (□) CF/PBA-a:PMDA = 1:1.

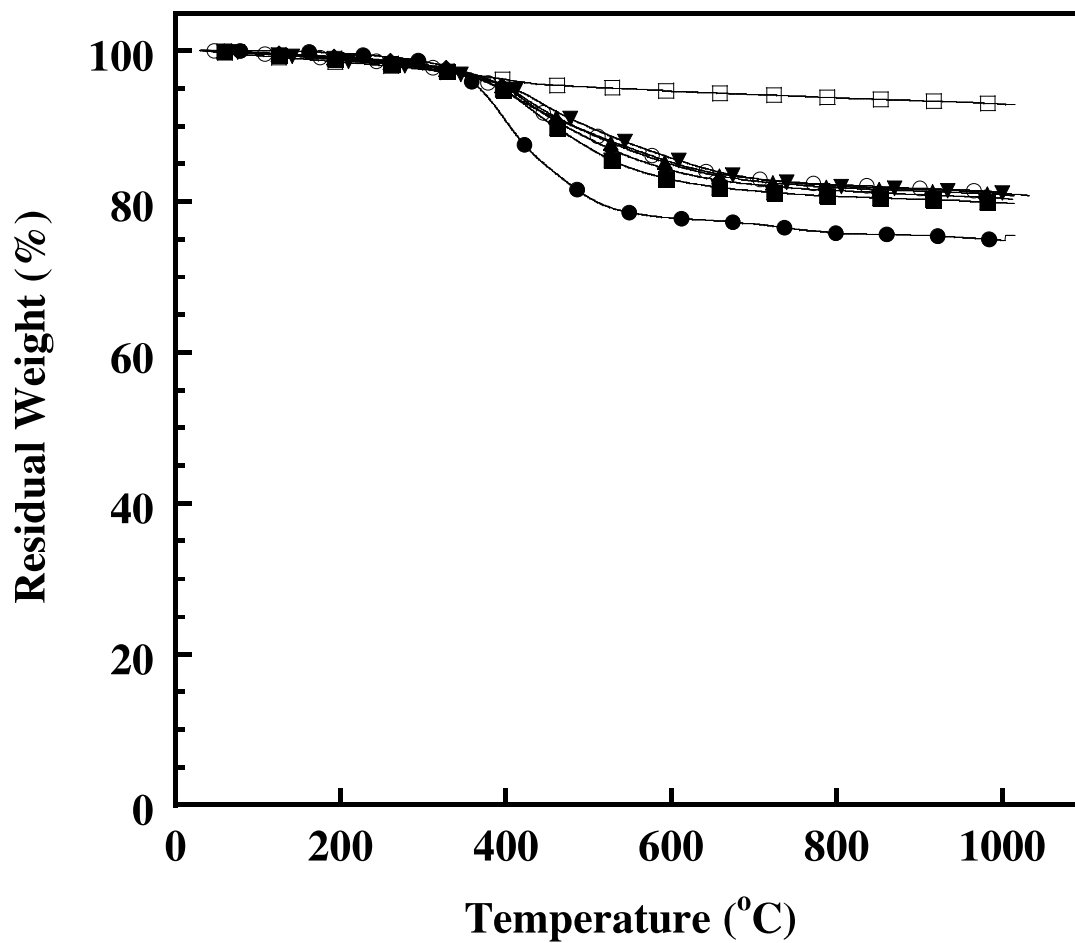


Figure 5.11 TGA thermograms of (□) carbon fiber and 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios. (●) CF/PBA-a, (■) CF/ PBA-a:PMDA = 4:1, (◆) CF/ PBA-a:PMDA = 3:1, (▲) CF/PBA-a:PMDA = 2:1, (▼) CF/PBA-a:PMDA = 1.5:1, (○) CF/PBA-a:PMDA = 1:1.

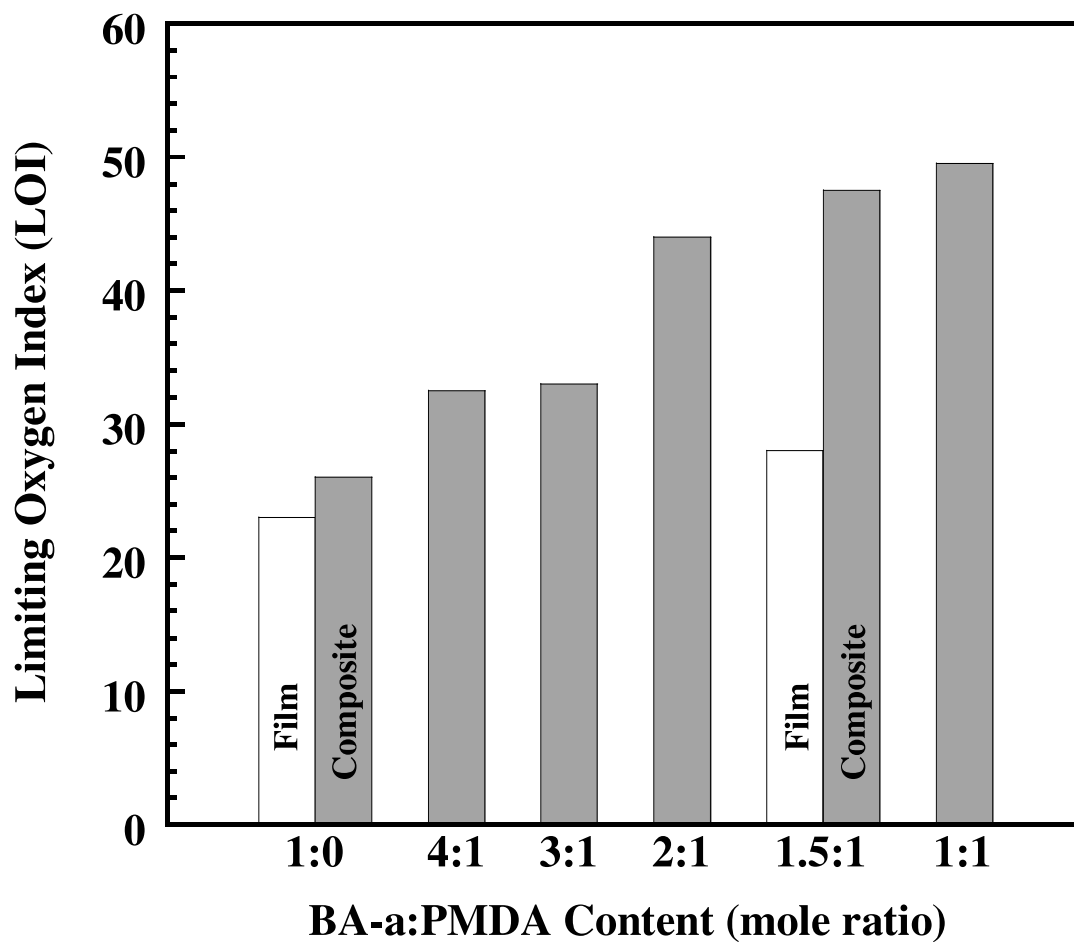
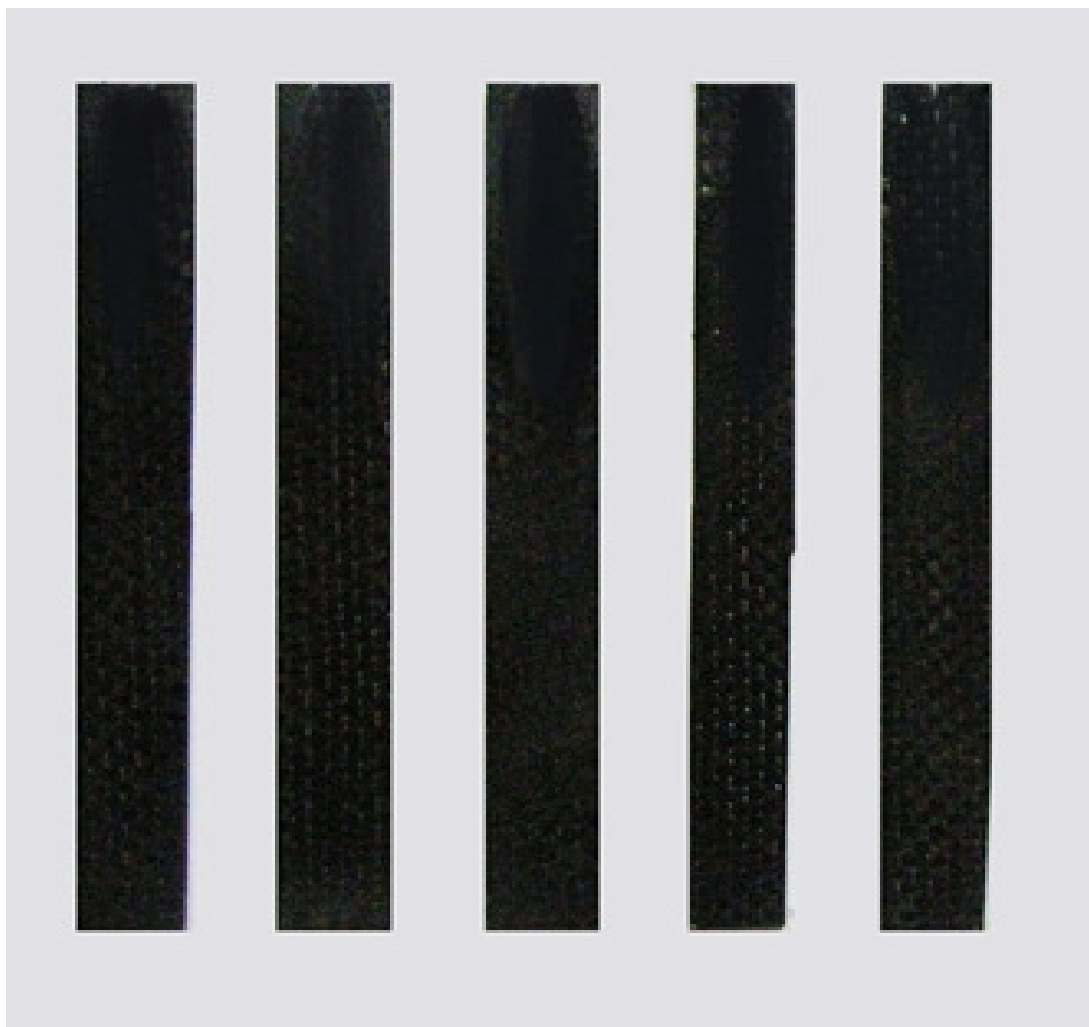
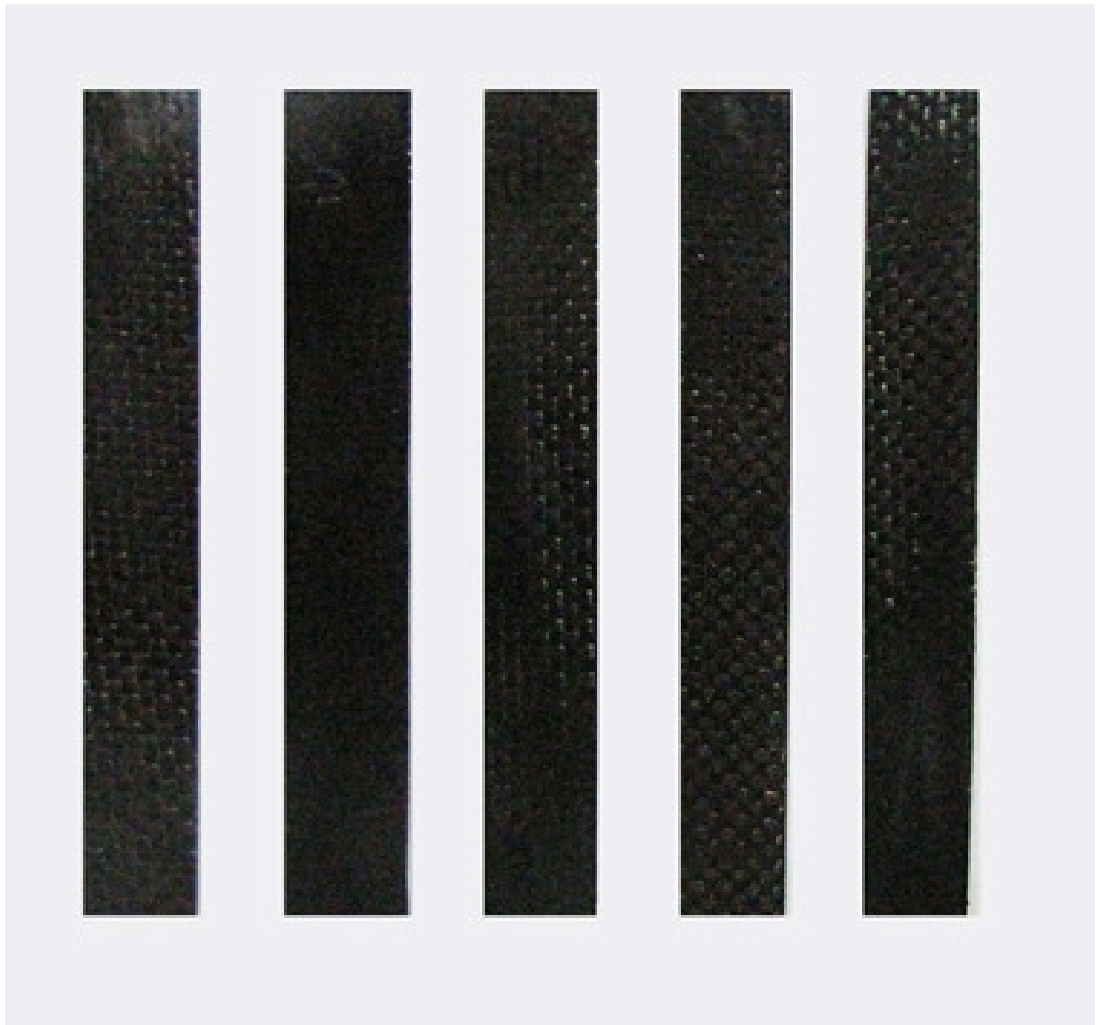


Figure 5.12 Limiting oxygen index (LOI) of (□) neat PBA-a and PBA-a:PMDA 1.5:1 alloy films and (■) 65wt% CF/PBA-a:PMDA composites at various PMDA mole ratios.



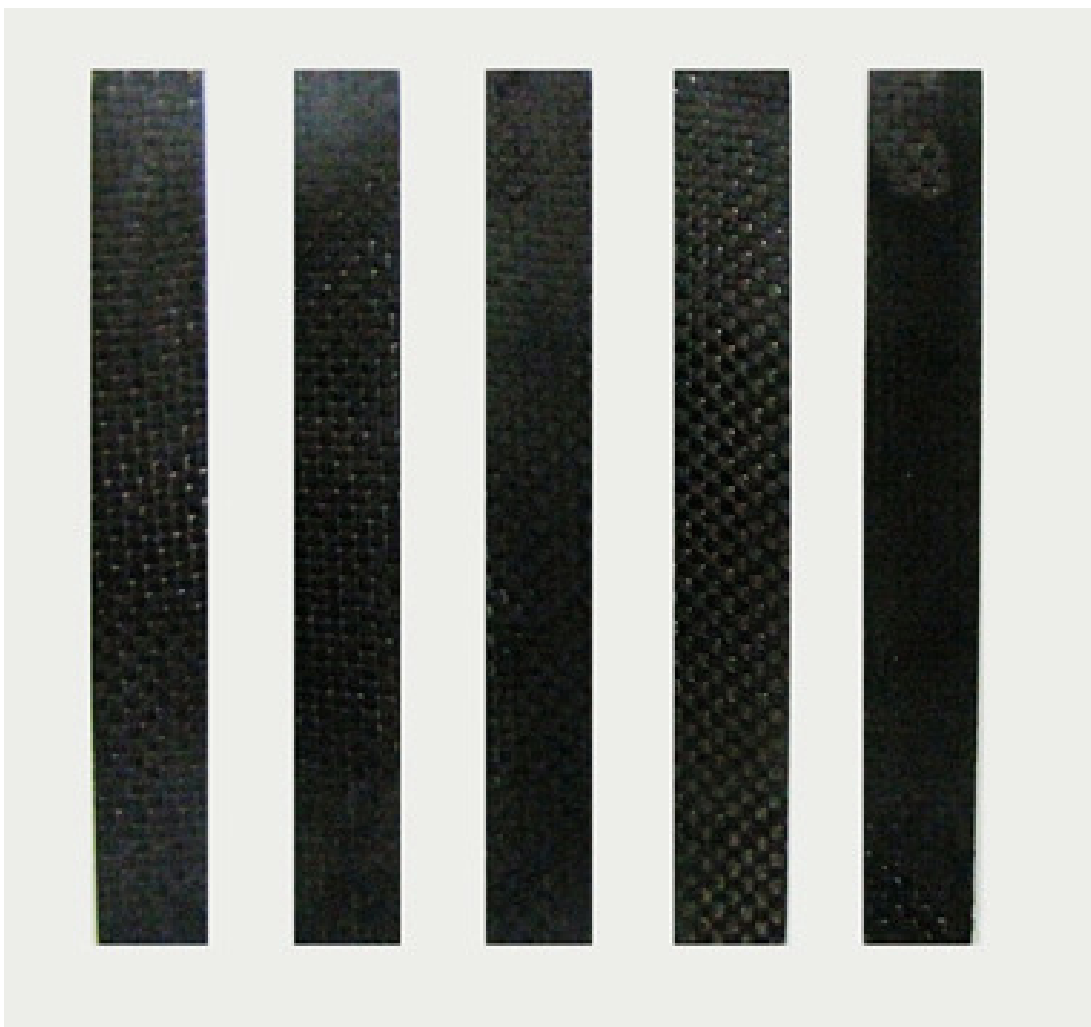
V-1

Figure 5.13 UL-94 vertical test of 65wt% CF-reinforced neat PBA-a composites.



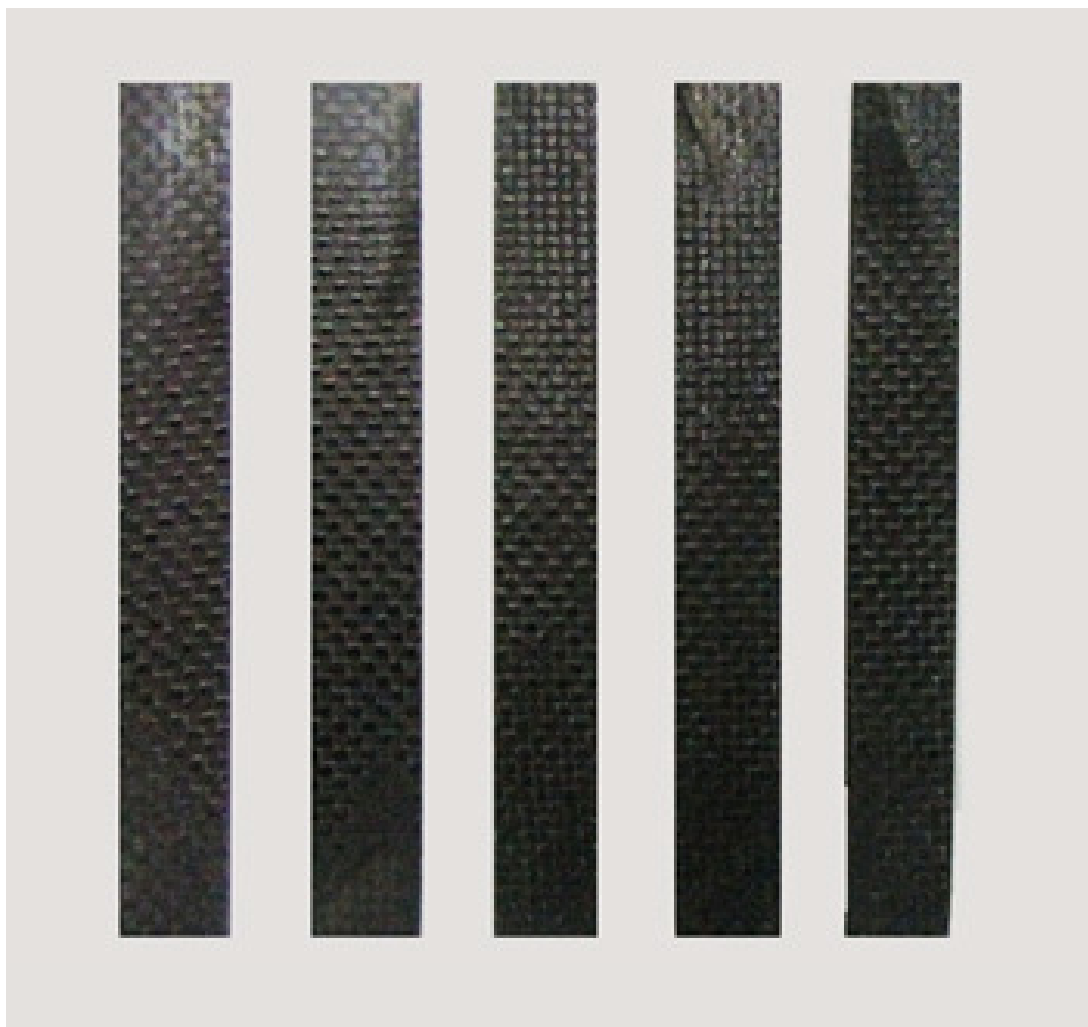
V-0

Figure 5.14 UL-94 vertical test of 65wt% CF-reinforced PBA-a:PMDA (4:1) composites.



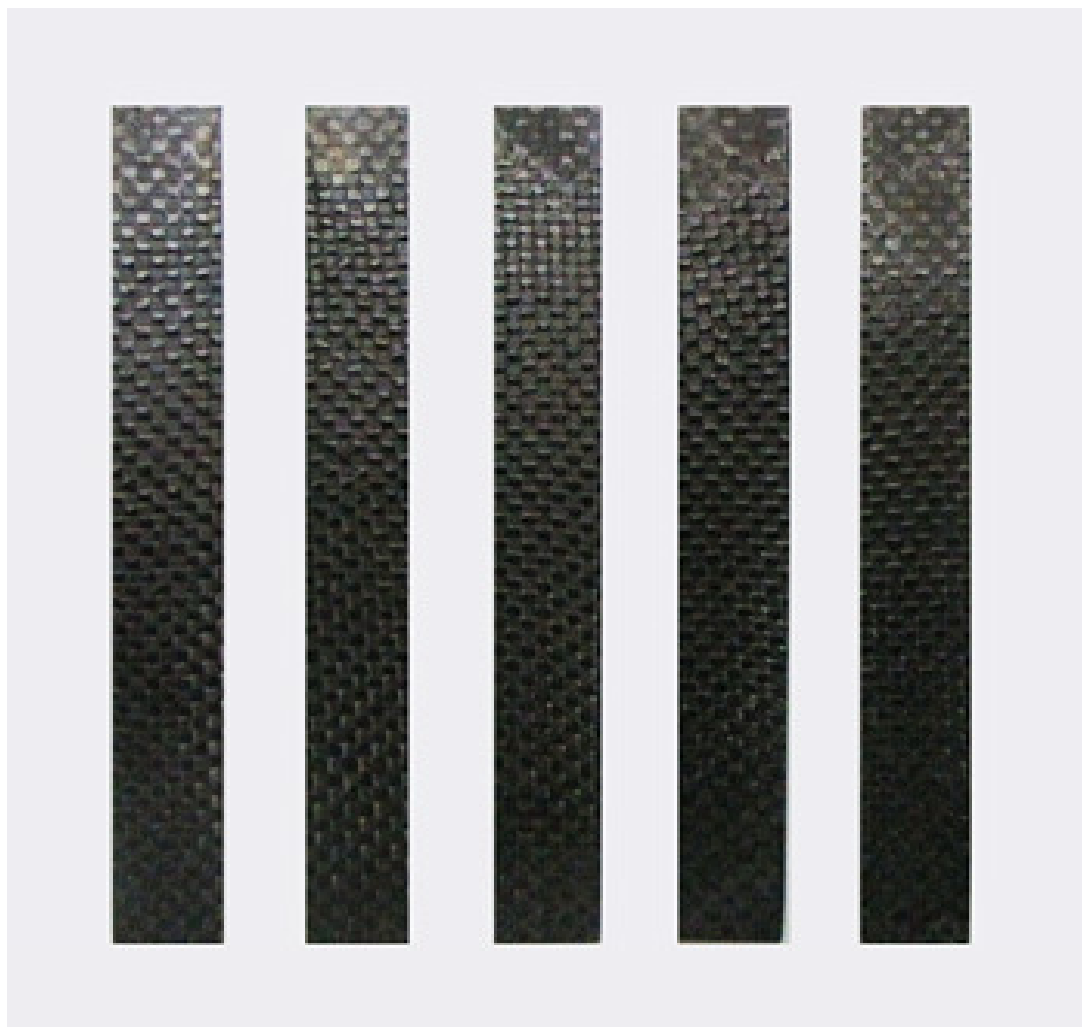
V-0

Figure 5.15 UL-94 vertical test of 65wt% CF-reinforced PBA-a:PMDA (3:1) composites.



V-0

Figure 5.16 UL-94 vertical test of 65wt% CF-reinforced PBA-a:PMDA (2:1) composites.



V-0

Figure 5.17 UL-94 vertical test of 65wt% CF-reinforced PBA-a:PMDA (1.5:1) composites.



V-0

Figure 5.18 UL-94 vertical test of 65wt% CF-reinforced PBA-a:PMDA (1:1) composites.

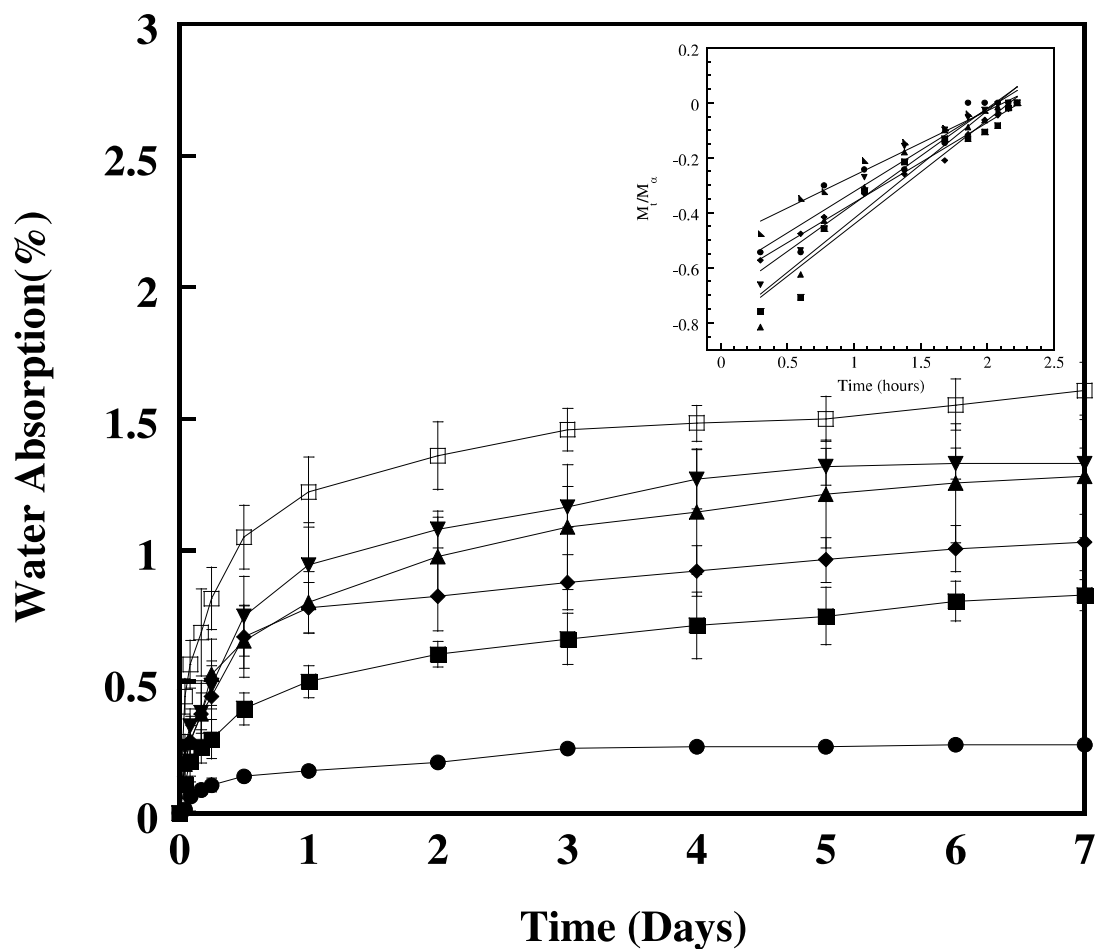


Figure 5.19 Water absorption of 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios. (●) CF/PBA-a, (■) CF/PBA-a:PMDA = 4:1, (◆) CF/PBA-a:PMDA = 3:1, (▲) CF/PBA-a:PMDA = 2:1, (▼) CF/PBA-a:PMDA = 1.5:1, (□) CF/PBA-a:PMDA = 1:1.

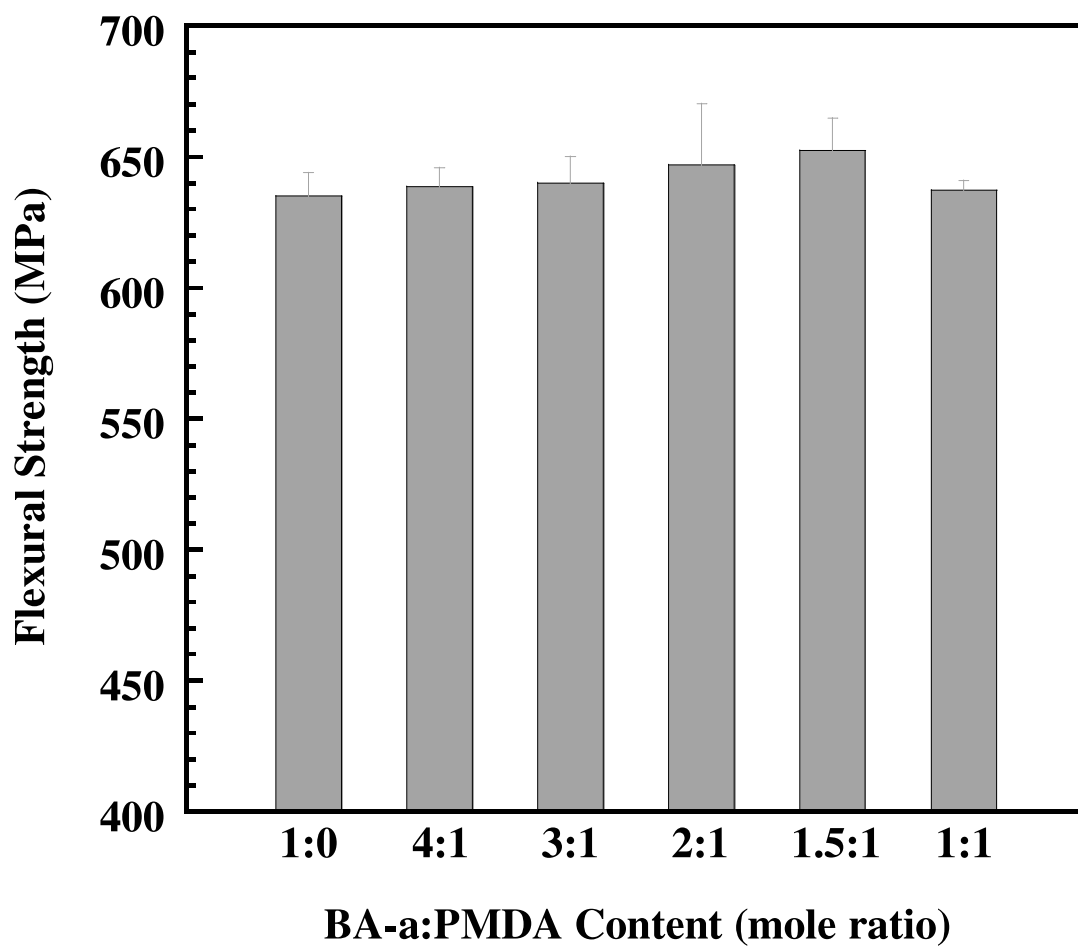


Figure 5.20 Flexural strength of 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios.

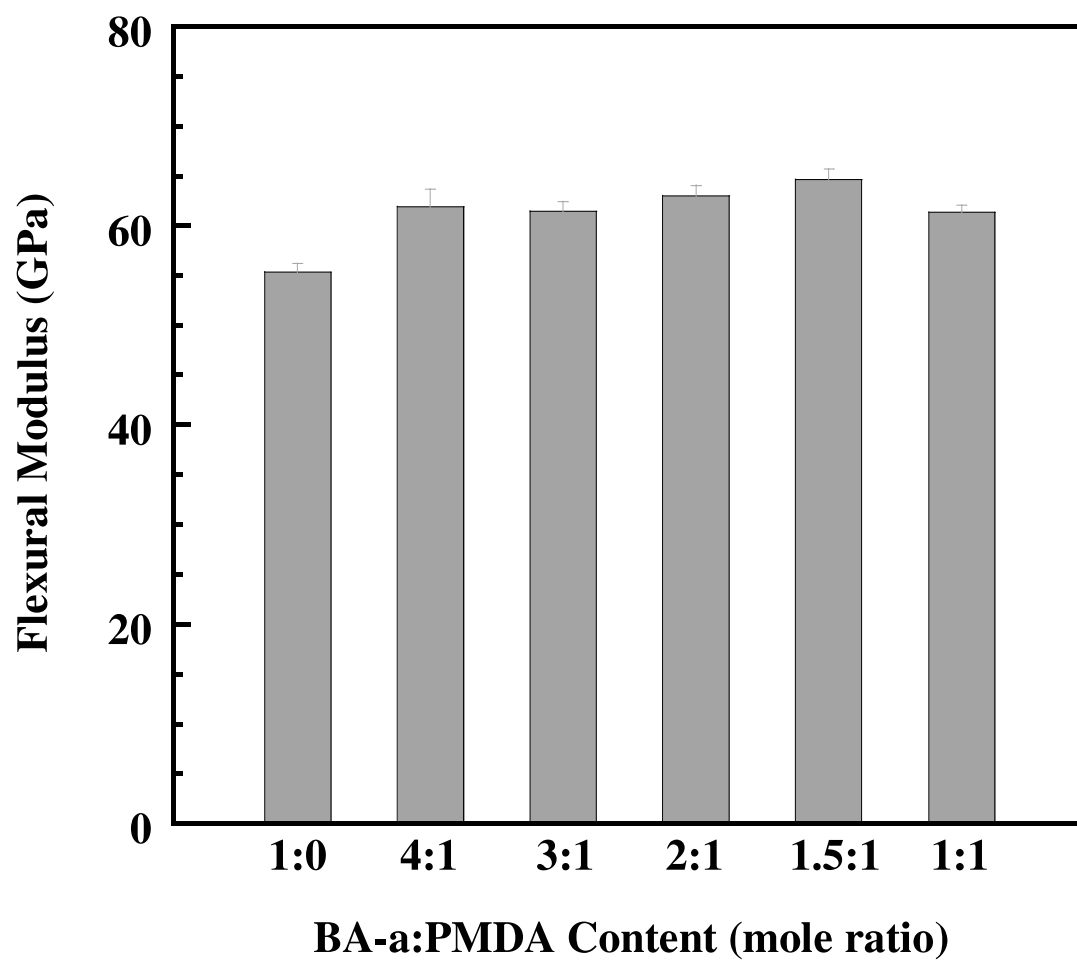
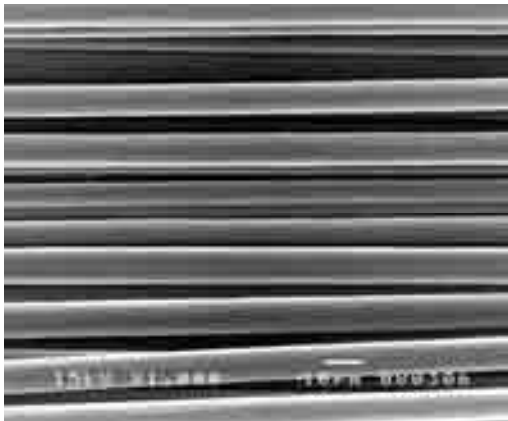
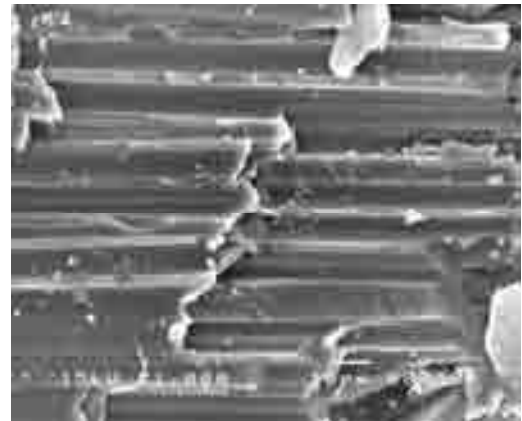


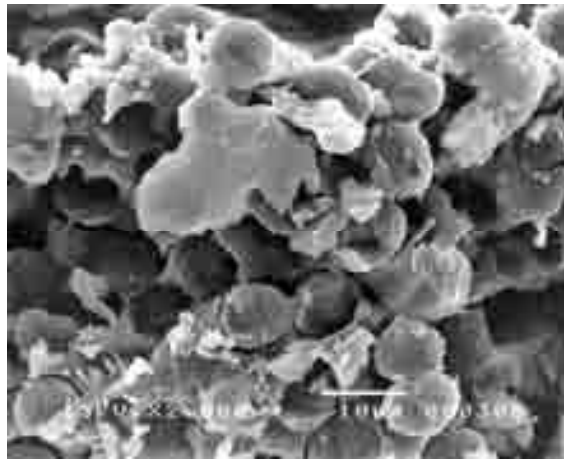
Figure 5.21 Flexural modulus of 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios.



(a)



(b)



(c)

Figure 5.22 SEM micrographs (a) carbon fiber morphology (b) fractured surface of CF/PBA-a:PMDA = 1.5:1 composite in weft region (c) fractured surface of CF/PBA-a:PMDA = 1.5:1 composite in warp region.

CHAPTER VI

CONCLUSIONS

The effects of carbon fiber (CF) and PMDA contents on flammability, mechanical, and thermal properties of CF-reinforced bisphenol A-aniline based polybenzoxazine (PBA-a) modified with PMDA composites can be summarized as follows. The maximum packing density of CF in PBA-a:PMDA composites belonged to 65wt% CF with the highest mechanical properties, i.e. flexural modulus and strength, and thermal property as glass transition temperature (T_g).

From above-mentioned results, the 65wt% CF-reinforced PBA-a:PMDA composites with various PMDA contents were conducted through flammability, mechanical, and thermal properties. The incorporation of PMDA into benzoxazine resin based on bisphenol-A and aniline (BA-a) can be achieved relatively flammability. Limiting oxygen index (LOI) values of the 65wt% CF-reinforced PBA-a:PMDA composites substantially increased with increasing PMDA content compared with the 65wt% CF-reinforced PBA-a. Importantly, all 65wt% CF-reinforced PBA-a:PMDA composites as thin as 1 mm passed the highest V-0 classification of UL-94 vertical flame test. Furthermore, the highest T_g value of the composite consisted of BA-a:PMDA = 1.5: 1 mole was approximately 237°C. The degradation temperature (T_{d10}) and char yield at 800°C of the 65wt% CF-reinforced PBA-a:PMDA composites was remarkably higher than those of the 65wt% CF/PBA-a. The increase of PMDA content was found to enhance the char yield of the composites up to 82% for the molar ratio of BA-a:PMDA = 1.5:1 reinforced with 65wt% CF. In addition, the flexural modulus and strength of the 65wt% CF-reinforced PBA-a:PMDA composites increased with increasing PMDA. The modulus and strength under flexure mode of the 65wt% CF/PBA-a:PMDA = 1.5:1 mole was recorded as 65 GPa and 652 MPa, respective, compared to the 65wt% CF/PBA-a composite which displayed the values of the flexural modulus and strength to be 55 GPa and 635 MPa, respectively. Scanning electron micrographs showed good fiber-matrix interfacial adhesion as observed tight interfaces between

the carbon fiber and the matrix. Moreover, the resulting composites exhibited outstanding property such as low water absorption. The optimum mechanical and thermal properties of 65wt% CF-reinforced PBA-a:PMDA composites were obtained at 1.5:1 mole ratio.

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APPENDICES

APPENDIX A

Effects of Carbon Fiber Contents on Properties of Carbon Fiber (CF)/PBA-a:PMDA Composites

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

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

Appendix A-2 The flexural properties of CF-reinforced PBA-a:PMDA composites at various carbon fiber contents.

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

Appendix A-3 The storage modulus (E') at 35°C and the glass transition temperature (T_g , loss modulus), of CF-reinforced PBA-a:PMDA composites at various carbon fiber contents which were determined from DMA.

Sample	Storage modulus (E') at 35°C (GPa)	T_g (°C) DMA
CF/PBA-a:PMDA (60/40)	43.1	233
CF/PBA-a:PMDA (65/35)	45.3	237
CF/PBA-a:PMDA (70/30)	44.5	235
CF/PBA-a:PMDA (75/25)	35.9	230
CF/PBA-a:PMDA (80/20)	37.7	229

APPENDIX B

Effects of PMDA Contents on Properties of CF/PBA-a:PMDA Composites

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

Sample	Storage modulus (E') at 35°C (GPa)	T_g (°C) DMA
CF/PBA-a:PMDA (1:0)	41.3	183
CF/PBA-a:PMDA (4:1)	44.1	203
CF/PBA-a:PMDA (3:1)	45.6	208
CF/PBA-a:PMDA (2:1)	45.3	227
CF/PBA-a:PMDA (1.5:1)	45.3	237
CF/PBA-a:PMDA (1:1)	43.05	234

Appendix B-2 The Limiting oxygen index (LOI) of films and composites:

- Neat PBA-a and PBA-a:PMDA = 1.5:1 films.
- 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios.

Samples	PBA-a:PMDA film (mole ratio)		CF/PBA-a:PMDA (mole ratio)					
	1:0	1.5:1	1:0	4:1	3:1	2:1	1.5:1	1:1
LOI values	23	28	26.0	32.5	33	44	47	49.5

Appendix B-3 Water absorption of 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios.

Samples CF/PBA-a:PMDA	24 hr (%)	7days (%)
1:0	0.16 ± 0.05	0.26 ± 0.02
4:1	0.5 ± 0.06	0.83 ± 0.06
3:1	0.78 ± 0.11	1.03 ± 0.09
2:1	0.80 ± 0.23	1.28 ± 0.12
1.5:1	0.94 ± 0.06	1.33 ± 0.16
1:1	1.22 ± 0.1	1.61 ± 0.13

Appendix B-4 Diffusion case selection parameters and diffusion coefficients of the carbon fiber composites.

Sample	n	Diffusion Coefficient $\times 10^{-12}$ (m ² /sec)
CF/PBA-a:PMDA (1:0)	0.28	0.28
CF/PBA-a:PMDA (4:1)	0.38	0.27
CF/PBA-a:PMDA (3:1)	0.45	0.25
CF/PBA-a:PMDA (2:1)	0.51	0.23
CF/PBA-a:PMDA (1.5:1)	0.55	0.23
CF/PBA-a:PMDA (1:1)	0.37	0.14

Appendix B-5 The flexural properties of 65wt% CF-reinforced PBA-a:PMDA composites at various PMDA mole ratios.

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

Appendix B-6 The mechanical and the thermal properties of CF/PBA-a:PMDA systems composites and other high-performance composites.

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

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

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

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

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

- ⁵ Ref.: Chowdhury, F. H., Hosu,r M. V., and Jeelani, S. Investigations on the thermal and flexural properties of plain weave carbon/epoxy-nanoclay composites by hand-layup technique. J. Mater. Sci. 42 (2007): 2690–2700.
- ⁶ Ref.: Gabr, M. H., Elrahman, M. A., Okubo, K., and Fujii, T. A Study on mechanical properties of bacterial cellulose/epoxy reinforced by plain woven carbon fiber modified with liquid rubber. Composites: Part A 41 (2010): 1263–1271.
- ⁷ Ref.: Cho, D., and Lee, J. Effect of quasi-carbonization processing parameters the mechanical properties of quasi-carbon/phenolic composites. J. appl. Polym. Sci. 107 (2008): 3350–3357.

VITAE

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List of publications:

1. C. Panyawanitchakun, C. Jubsilp, and S. Rimdusit, "High Performance PMDA-Modified Polybenzoxazine Composites Reinforced with Carbon Fiber," Proceeding of Asian International Conference on Materials, Minerals, and Polymer (MAMIP 2012), Mar. 23-24, 2012, Penang, Malaysia, p. 31 (Oral presentation).
2. C. Panyawanitchakun, C. Jubsilp, and S. Rimdusit, "Characterization of High Performance PMDA-Modified Polybenzoxazine Composites Reinforced with Carbon Fiber," Proceeding of 6th Pure and Applied Chemistry International Conference 2012 (PACCON 2012), Jan. 11-13, 2012, Chiang Mai, Thailand, p. 1068 (Oral presentation).