High-Performance Maleimide and Nitrile-Functionalized Benzoxazines with Good Processibility for Advanced Composites Applications

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ABSTRACT: A maleimide and 2-aminobenzonitrile (MIan) based benzoxazine has been synthesized and characterized. This benzoxazine has maleimide and nitrile functionalities that can polymerize, resulting in a highly crosslinked material. Incorporation of the imide group increases the shear viscosity compared to monofunctional benzoxazines but not as high as difunctional benzoxazines, allowing good processibility, while maintaining excellent mechanical and thermal properties. Catalysts, epoxy copolymerization, and rubber interlayer methods are utilized to optimize the composite properties. The 60% carbon cloth-reinforced resin has achieved the flexural strength over 1 GPa. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 548–558, 2006

Key words: composites; high-performance polymers; fibers

INTRODUCTION

Recently, demand for high-performance materials has increased tremendously due to technological advancements. As a result, many thermosets, such as polyimides,[1] advanced epoxy resins,[2] and others, have been developed. Even though these resins have shown improvements in thermal and thermo-oxidative resistance, chemical resistance, and mechanical strength, they usually suffer from poor processibility.

In 1944, Holly and Cope discovered the synthesis of aromatic oxazines using phenol, formaldehyde, and amines through the Mannich reaction.[3] Burke et al. and others extensively studied the chemistry of low-molecular-weight benzoxazines.[4–10] Application of benzoxazine oligomers as a modifier for epoxy resin[11,12] and oligomer formation kinetics[13] have been reported. However, only recently has there been a detailed investigation into the polymerization of benzoxazine monomers.[14–18] During polymerization, benzoxazines undergo a thermally activated ring-opening reaction to form a Mannich base bridge.[14] The attractive characteristics of benzoxazine polymers include low melt viscosity, no release of volatiles during cure or need of harsh catalysts, high thermal stability, good mechanical properties, excellent electrical properties, and rich molecular design flexibility.[14–18] These characteristics enable benzoxazine polymers to be excellent candidates for high-performance composites.

By taking advantage of the molecular design flexibility of benzoxazine chemistry, thermal and thermo-oxidative stabilities of polybenzoxazine have been improved by altering the functional group on the amine and/or phenol. Low and Ishida had studied the thermal and thermo-oxidative degradation of polybenzoxazines and concluded that there are three stages in the thermal degradation of bisphenol-based polybenzoxazines. Evaporation of amine moiety first occurs below 300°C followed by degradation of the Schiff base between 300°C and 400°C. Finally, above 400°C, the evaporation of phenolic moiety occurs. This observation gave rise to the postulation that, if amine evaporation is reduced, the char yield can be greatly increased.[19]

Kim et al. synthesized acetylene-functionalized benzoxazines, in which acetylene-functionalized side chain could further crosslink upon thermal activation.[20] In a separate study, phthalonitrile-functionalized polybenzoxazines, which had low flammability due to their high char yield, were synthesized.[21,22]

Recently, Ishida and Ohba synthesized monofunctional benzoxazine with maleimide and aniline to develop low-viscosity benzoxazine monomers, with a glass-transition temperature above 200°C. Incorporation of the maleimide functionality into the monofunctional benzoxazine resulted in an increased char yield and glass-transition temperature without significantly increasing the viscosity of the monomer.[23]

Our current goal is to develop the benzoxazine polymer for high-performance composites with good processibility and excellent thermal properties. A monofunctional benzoxazine with maleimide and 2-aminobenzonitrile has been synthesized. Lewis acid catalysts have been utilized to further improve the thermal properties.

EXPERIMENTAL

Materials

All chemicals were used as-received. 4-Aminophenol (98%), maleic anhydride (96%), phosphorus pentoxide (98%), paraformaldehyde (95%), and 2-aminobenzonitrile (98%) were purchased from Aldrich Chemical Company (St. Louis, MO). Sulfuric acid, N,N′-dimethylformamide (DMF), chloroform, isopropanol, dichloromethane, and Lewis acid catalysts, including $FeCl_3$, $ZnCl_2$, $CuCl$, $CuCl_2$, $SnCl_2$, and $NiCl_2$, were obtained from Fisher Scientific Company (Hampton, NH). All catalysts and solvents used were certified ACS grade and used as-received. Carbon fiber woven fabric (TORAYCA T300) was kindly supplied by Toray Industries, Inc. (Siga, Japan), and used as-received. Liquid rubber, amine-terminated butadiene acrylonitrile (ATBN) (M_n = 5500, amine equiv. = 0.71) was purchased from Polysciences Inc. (Narrington, PA) and used as the fiber-coating material.

Synthesis

Synthesis of 1-(4-hydroxy-phenyl)-pyrrole-2,5-dione

1-(4-hydroxy-phenyl)-pyrrole-2,5-dione (HPMI) was synthesized according to Choi et al.[24] In a 100-mL round-bottom flask, 30 g (360 mmol) maleic anhydride and 30.6 g (280 mmol) p-aminophenol were mixed in 80 mL DMF at 0°C. A mixture of 15 g (106 mmol) P_2O_5 in 50 mL DMF and 8 g of concentrated H_2SO_4 was added to the flask over 30 min with stirring. The reaction mixture was stirred at 70°C for 3 h in an oil bath. The mixture was then poured into 500 mL of deionized ice water and yellow precipitation was observed. The precipitate was dried under vacuum for ~12 h and then purified by recrystallization in isopropanol. The product was in the form of yellow "needle like" crystals (30.1 g, yield 57%) with a melting point of 176°C.

Synthesis of maleimide and 2-aminobenzonitrile-based benzoxazine monomer, 2-[6-(2,5-dioxocyclopent-3-enyl)-2H,4H-benzo[e]1,3-oxazaperhydroin-3-yl]benzenecarbonitrile (MIan)

A mixture of HPMI, p-formaldehyde, and 2-aminobenzonitrile with a mole ratio of 1 : 2 : 1 was added to a flask and stirred at 110°C for ~30 min. The product

was then dissolved in dichloromethane, filtered, and washed with deionized water. The solvent was evaporated using a rotary evaporator and the product was vacuum dried at room temperature to produce a yellow powder.

Sample preparation

Coating process and composite fabrication

Dip coating in solution was the method selected to coat the carbon fiber in this study. The fabrics were immersed in a solution of 0.005% by fiber weight of ATBN rubber in THF. The coated carbon fiber cloths were dried in a vacuum oven at 100°C for 6 h. Thereafter, MIan resin was applied to the coated carbon fabrics by using the same approach but with concentrated benzoxazine solution. A 30-ton Carver compression molder was used to fabricate carbon fiber-reinforced MIan composite samples with an applied pressure of 9 MPa. Twelve plies of coated carbon fiber cloths were laminated and then subjected to a step cure procedure as follows: 150°C (1 h), 190°C (1 h), 210°C (2 h), and 250°C (30 min). The samples were then slowly cooled to room temperature.

Preparation of sample with catalyst

Lewis acid catalysts, including $FeCl_3$, $ZnCl_2$, $CuCl$, $CuCl_2$, $SnCl_2$, and $NiCl_2$, at 4 mol % were mixed with the benzoxazine monomers **1** and **4** using THF as a solvent at room temperature. The solution was mixed with a magnetic stirrer for several hours and then the solvent was evaporated under vacuum at room temperature.

Measurements

Fourier transform infrared (FTIR) spectra were obtained using a Bomem Michelson MB100 FTIR spectrometer, which was equipped with a deuterated triglycine sulfate (DTGS) detector. Coaddition of 16 scans was recorded at a resolution of 4 cm^{-1} after a 20 min purge with dry air. FTIR spectra of the monomers were taken using the KBr pellet technique while thin films were cast on a KBr plate for partially cured samples.

Thermal stability and curing behavior were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. TA Instruments High Resolution 2950 thermogravimetric analyzer was used, with nitrogen as a purging gas for all testings. A heating rate of 20°C/min with a nitrogen flow rate of 90 mL/min was used for all tests. TA Instruments DSC models 2910 (equipped with pressure DSC cell) and 2920 were used with heating rate of 10°C/min and a nitrogen flow rate of 65 mL/min for

all tests. All samples were crimped in hermetic aluminum pans with lids.

Dynamic mechanical analysis (DMA) was performed using a Rheometric Dynamic Mechanical Spectrometer (RMS-800) to determine the glass-transition temperature, T_g, storage modulus, G', and loss modulus, G''. A force rebalance transducer with 2000 g cm torque was used. Composites were cut into a rectangular shape with dimensions of 60 mm $\times$ 12 mm $\times$ 2 mm. All samples were analyzed under temperature sweep mode at a heating rate of 2°C/min. Measurements were taken at intervals of 2°C with a thermal soak time of 30 s until the temperature reached about 50°C above the material's T_g. A strain of 0.05% was used after a strain sweep to ensure that the strain used was within the linear viscoelasticity range. The test frequency was 1 Hz (6.28 rad/s).

Flexural properties of carbon fiber-reinforced MIan composites were measured using a three-point bending test according to ASTM 790–92. The L/D ratio used was 16/1. The dimensions of the specimens were 50 mm $\times$ 25 mm $\times$ 2 mm and the cross-head speed was 0.85 mm/min. All tests were conducted on an Instron model 5567 Universal Testing Apparatus at room temperature in air, and five samples were used to average for each test.

The end-notched flexural (ENF) test was carried out to determine the mode II delamination toughness of carbon fiber-reinforced polybenzoxazine composites fabricated from 18 plies of laminated carbon fiber cloths. A Teflon film of thickness about 75 μm was inserted as a crack starter and a sharp crack was introduced by using a razor blade. The dimensions of the ENF specimens were 100 mm $\times$ 20 mm $\times$ 3 mm. The cross-head speed was 2.5 mm/min and the span length was 80 mm. All experiments were run on the same tensile apparatus mentioned earlier.

G_{IIC} was calculated from the following equation:

$$G_{IIC} = \frac{9a^2 P_c \delta_c}{2W(2L^3 + 3a^3)}$$

where P_c is the load, δ_c is the displacement when crack growth is initiated, w is the specimen width, L is the half span length, and a is the crack length. The detailed test method is fully described in other references.[25–27]

RESULTS AND DISCUSSION

DSC analysis of maleimide and 2-aminobenzonitrile-based benzoxazine (MIan) and derivatives

Nonisothermal DSC thermograms of monomers **1**, **2**, and **3** (Scheme 1) are shown in Figure 1. Since the experiments were conducted up to 350°C, the DSC equipped with pressure DSC cell was used to prevent

the corrosive material produced as a consequence of the decomposition of the polymer, leading to the deterioration of the cell. The main exotherm peaks are at 256°C, 285°C, and 306°C, respectively. Benzoxazine monomers **2** and **3** were synthesized to compare the effect of different functionalities on the polymerization behavior of the system. In the case of monomer **3**, phenol has methyl-blocked ortho and para positions. Since polymerization of the oxazine rings occur mainly at the ortho position of the phenolic OH, methyl blocking should suppress the polymerization.[28,29] As a result, monomer **3** shows the highest exotherm temperature due to polymerization at meta position.

DSC thermogram (b) of compound **2** shows two separate peaks: the main exotherm peak centered at 285°C is followed by the broad exotherm at 340°C. We believe that the first exotherm represents both oxazine-ring polymerization and a nitrile reaction. Although the reaction of nitrile without any catalyst addition usually takes place above 250°C,[30] we believe that the second exotherm represents the remaining nitrile functionalities. This will be confirmed by FTIR study later. Scheme 2 displays ring-opening polymerization of benzoxazines on the basis of the nonfunctional primary amine, aniline. Oxazine ring-opening polymerization produces Mannich bridge (—CH$_2$—NR—CH$_2$—) and structures having phenolic hydroxyl functional groups. It is expected that these hydroxyls with an active hydrogen can promote nitrile polymerization at moderate curing conditions; thus, the second exotherm peak shifted to lower temperature. We did not observe the second exotherm peak in the DSC thermogram of monomer **3** due to the limited operating temperature of the instrument.

DSC thermogram (c) of compound **1** also shows two separate exotherm peaks shifted to lower temperature (256°C and 325°C, respectively). Surprisingly, by incorporating maleimide functionality, we could further reduce the polymerization temperature.

Several reports have shown that nitrile prepolymers can be converted to high-molecular-weight polymers in the presence of catalysts.[31–33] Cyclotrimerization and formation of linear polymer chains containing —C≡N— groups were the predominant products. As a result, Lewis acids containing metal atoms, such as FeCl$_3$ and ZnCl$_2$, were used for cationic ring-opening polymerization of benzoxazine and nitrile polymerization.

DSC thermograms of monomer **1** in the presence of metal catalysts are shown in Figure 1 (d, e). The main exotherm peak was lowered by 35°C using FeCl$_3$ and ~20°C using ZnCl$_2$. The second exotherm peaks were also lowered in both systems. The effect of the catalyst on the thermal stability of MIan benzoxazines will be discussed later.
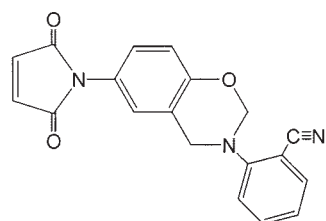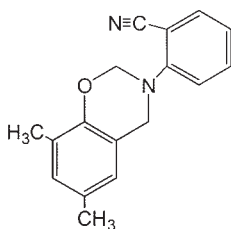
Maleimide and 2-aminobenzonitrile functional benzoxazine (MIan)
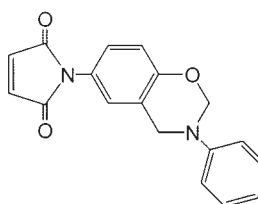
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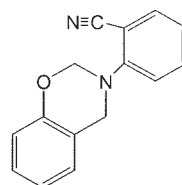
Phenol and 2-aminobenzonitrile functional benzoxazine (Phan)

2

2,4-Dimethyl Phenol and 2-aminobenzonitrile functional benzoxazine (24DMPan)

3

Maleimide and aniline functional benzoxazine (MIa)

4

Scheme 1 (**1**) 2-[6-(2,5-dioxocyclopent-3-enyl)-2H,4H-benzo[*e*]I,3-oxazaperhydroin-3-yl]benzenecarbonitrile. (**2**) 2-(2H,4H-benzo[*e*]1,3-oxazaperhydroin-3-yl)benzenecarbonitrile. (**3**) 2-(6,8-dimethyl-2H,4H-benzo[*e*]I,3-oxazaperhydroin-3-yl)benzenecarbonitrile. (**4**) 2-(3-phenyl-2H,4H-benzo[3,4-*e*]1,3-oxazaperhydroin-6-yl)cyclopent-4–3n3–1,3-dione.

Thermal properties of MIan and derivatives

To simplify our system and better understand the thermal properties of MIan, polybenzoxazine, maleimide, and aniline-based benzoxazine (abbreviated as MIa, monomer **4** in Scheme 1) was synthesized. TGA results are summarized in Table I. The polymer exhibits thermal stability up to 375°C as defined by 5% weight loss in the TGA thermograms. The char yield at 800°C under nitrogen was 56% when heated at 20°C/min. Our research has shown that degradation occurs in the sequence of evaporation of the amine followed by the simultaneous breakage of the phenolic linkage and degradation of the Mannich base.[19,34] In the case of the maleimide-based benzoxazine monomer, due to the incorporation of the imide group (which has a planar five-membered ring structure) and the partial conjugation with the benzene ring, the rotation of the imide residues are hindered. This phenomenon resulted in the increased stiffness and thermal stability of the material.[23]

The char yield results from MIa mixed with various Lewis acids are shown in Table II. By adding catalysts,
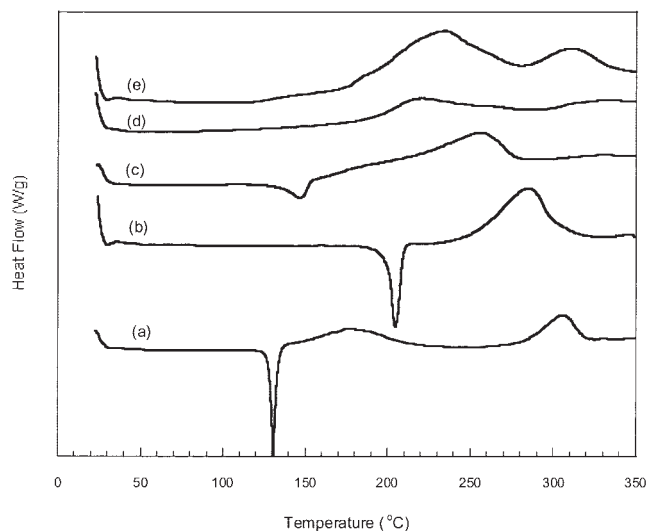
Figure 1 DSC thermograms of 24DMPan monomer (a), Phan monomer (b), MIan monomer (c), MIan monomer with 4 mol % FeCl$_3$ (d), and MIan monomer with 4 mol % ZnCl$_2$ (e), under high-pressure DSC.
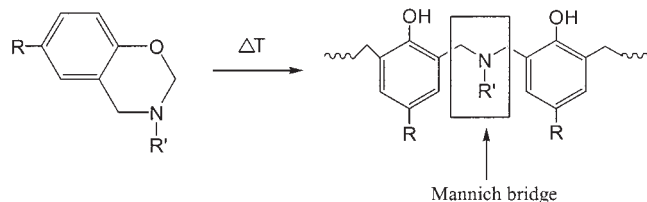
Scheme 2

the char yields could be improved as much as 12%. It is believed that metal chlorides help lower the polymerization temperatures and enhance the network formation. The FeCl₃ system exhibits the highest char yield of 68%.

Pendant phenyl groups connected to the Mannich bridge have been found to be the weak point from a thermal stability point of view (Scheme 2).[19] Increasing crosslink density and "end-capping" of the pendant phenyl group of amine derivative with thermally stable functionalities are considered to improve the thermal stability of benzoxazine.[20,21]

Thermal properties of MIan polybenzoxazine are shown in Table I. The temperature at 5% weight loss was 380°C and the char yield increased to 63%. It is presumed that the increase in char yield of MIan polybenzoxazine is a result of a more thermally stable structure formed upon intramolecular cyclization and linear polymerization, which will be discussed in the next section.

Char yields of catalyzed MIan polybenzoxazines are summarized in Table II. The char yields were improved up to 73% due to the further thermal polymerization of the nitrile (Scheme 3). This char yield is remarkably high considering the good processibility of the monomer.
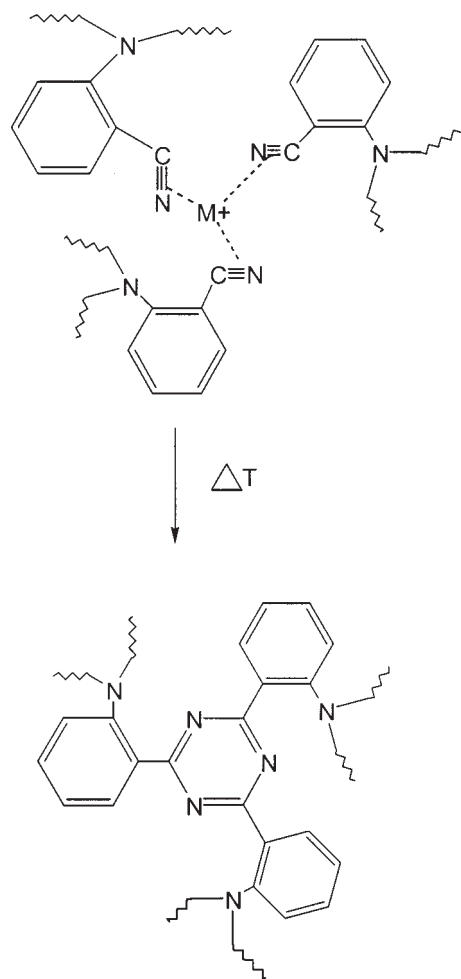
FTIR study of MIan benzoxazine

DSC of MIan monomer shows the melting point around 150°C and onset of the main exotherm peak at

TABLE I
Summary of TGA Results of MIa and MIan Polybenzoxazine

Monomer	Abbreviation	Char yield (%)	5% weight loss (°C)	10% weight loss (°C)
	MIa	56	375	392
	MIan	63	380	418

TABLE II
Effect of Metal Chloride Catalysts on Char Yield of MIa Polybenzoxazine

Catalyst	Char yield (%) of MIa polybenzoxazine	Char yield (%) of MIan polybenzoxazine
None	56	63
CuCl₂	66	73
FeCl₃	**68**	**73**
ZnCl₂	63	72
CuCl	64	69
SnCl₂	65	71
NiCl₂	64	66

200°C (Fig. 2). Thus, these temperatures are chosen to follow the polymerization process by FTIR.
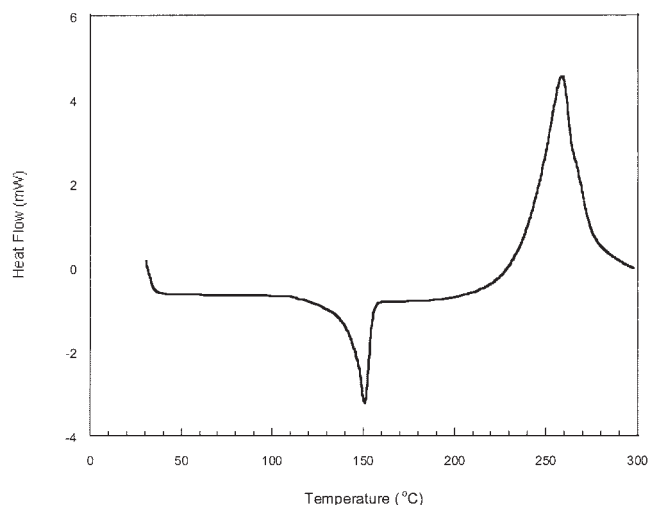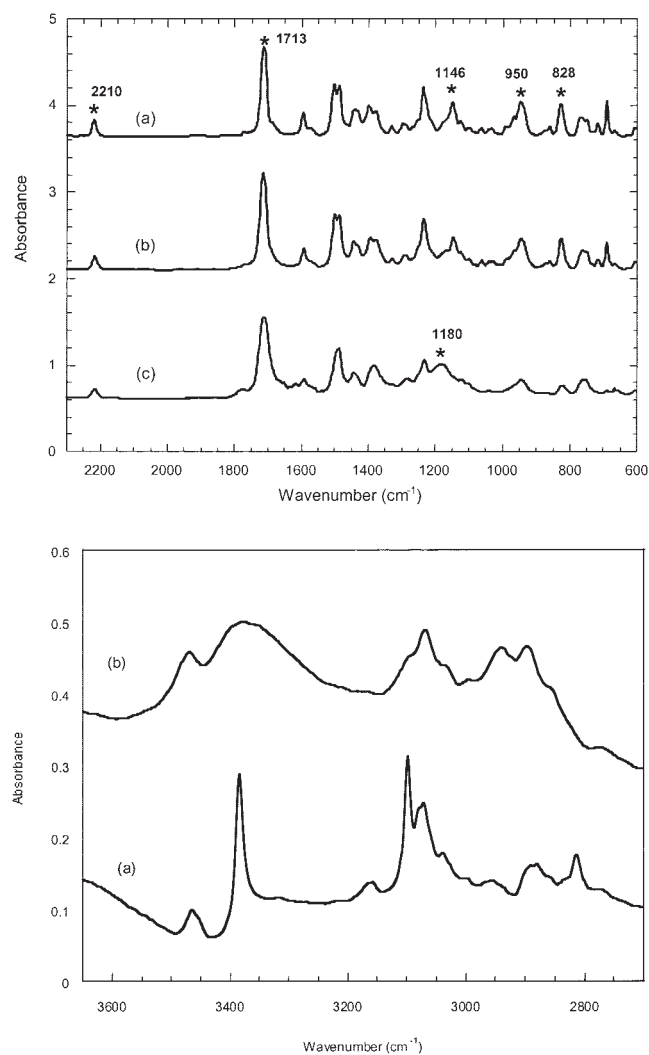
The band at 2210 cm⁻¹ associated with the stretching of —C≡N was used to monitor the polymerization of the nitrile groups. Oxazine ring-opening polymerization can be followed by the band at 950 cm⁻¹, which is the benzene ring mode with oxazine ring.[35] The prominent band at 1713 cm⁻¹ is attributed to the

Scheme 3
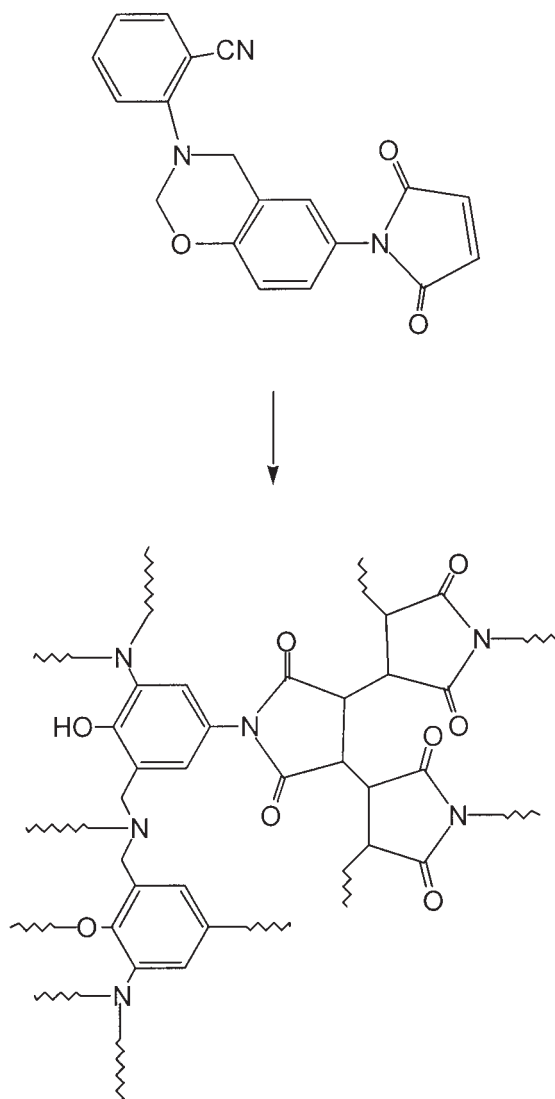
Figure 2 DSC thermogram of MIan benzoxazine monomer.

C=O of the maleimide group. The band at 828 cm^{-1} is assigned to the imide CH wagging of the vinylene group [Fig. 3(a)].[36]

At 150°C, 50% of the oxazine rings were consumed within 90 min [Fig. 4(a)] while the nitrile consumption was less than 20% [Fig. 4(b)]. It is noteworthy to see that oxazine ring opening occurred even at this temperature [Figs. 3 (a, b)]. The possible reaction at the benzoxazine site is shown in Scheme 4. By adding FeCl$_3$ to MIan benzoxazine, the oxazine ring consumption was increased to 70% during the same period of time for the system that did not contain catalyst. However, the maximum degree of conversion of the nitrile functional group was only about 40% even with FeCl$_3$ added.

It is interesting to see that, at 150°C after 90 min [Fig. 3(c)], the band at 1146 cm^{-1}, assigned to the C—N—C bending mode of the maleimide ring, shifted to 1180 cm^{-1}, which corresponds to the C—N—C bending

Figure 3 FTIR spectra of MIan monomer (a), polymerized at 150°C for 10 min (b) and 90 min (c), (top panel). FTIR spectra of MIan monomer (a) polymerized at 150°C for 90 min (b) (OH stretching region), (bottom panel). Baselines are shifted for clarity.
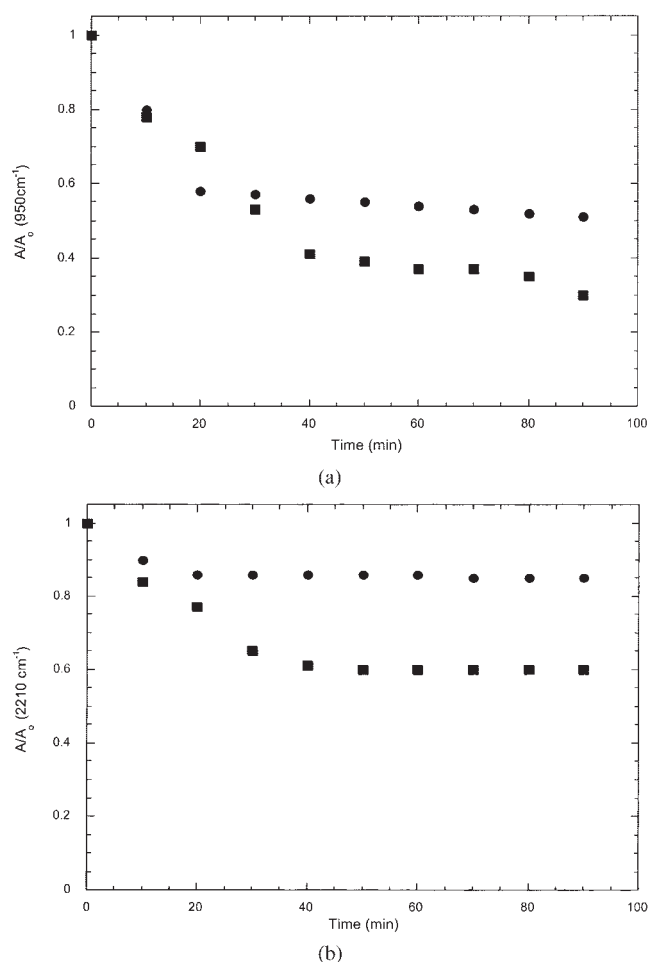
Figure 4 (a) Degree of conversion of oxazine groups (observed by the integrated intensity of the 950 cm$_1$ band) at 150°C. [●] No catalyst and (f) 4 mol % FeCl$_3$ added. (b) Degree of conversion of nitrile groups (observed by the integrated intensity of the 2210 cm$_1$ band) at 150°C. (●) No catalyst and (f) 4 mol % FeCl$_3$ added.

Scheme 4

showed consumption of only 60% of nitrile functionalities. It has been reported that $FeCl_3$ catalyzes not only the nitrile reaction, but also the oxazine ring polymerization.[21] Therefore, steric hindrance of the crosslinked network resulting from oxazine ring and maleimide polymerization caused lower conversion of the nitrile functionalities. Possible reactions on nitrile sites are shown in Scheme 5. It is presumed that thermal polymerization of the nitrile groups involves the formation of triazine and/or linear —C≡N— species. We observed the new bands at 1520 and 1360 cm^{-1}, which are the characteristic bands of triazine (Fig. 6). The model compound will be investigated in a separate study to confirm this statement.

Mechanical properties of MIan carbon fiber-reinforced polymer composites

The flexural strength of carbon fiber-reinforced MIan and MIan with $FeCl_3$ as a catalyst in comparison with

(a)

(b)
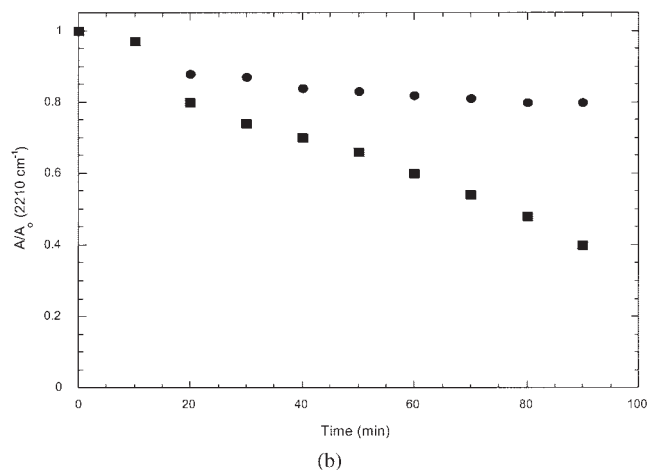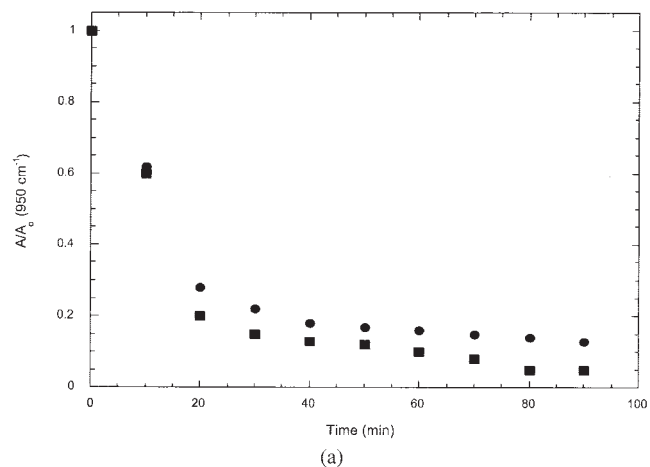
Figure 5 (a) Degree of conversion of oxazine groups (observed by the integrated intensity of the 950 cm^{-1} band) at 200°C. ([●]) No catalyst and (f) 4 mol % $FeCl_3$ added. (b) Degree of conversion of nitrile groups (observed by the integrated intensity of the 2210 cm^{-1} band) at 200°C. ([●]) No catalyst and (f) 4 mol % $FeCl_3$ added.

mode of the succinimide ring. A possible reaction at the maleimide site is the copolymerization of maleimide shown in Scheme 4. This indicates that the oxazine ring opening and maleimide polymerization occurred at 150°C. The oxazine ring opening took place before maleimide polymerization. The nitrile functional group requires higher temperature to achieve high degree of conversion.

Figures 5 (a, b) show the conversion of oxazine and nitrile functionalities at 200°C. More than 70% of the oxazine rings were consumed within 20 min and the conversion reached ~90% in 90 min. On the other hand, without the metal catalyst, the degree of nitrile consumption was low (20%) even at this temperature. When $FeCl_3$ was used as a catalyst, the polymerization of oxazine rings proceeded to 95%. The full consumption was not observed even in the case of the catalyzed system. The ferric chloride-catalyzed system of MIan
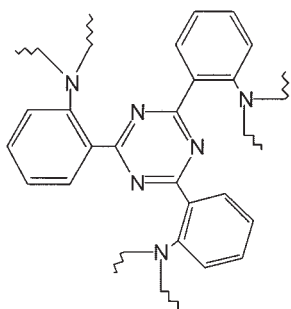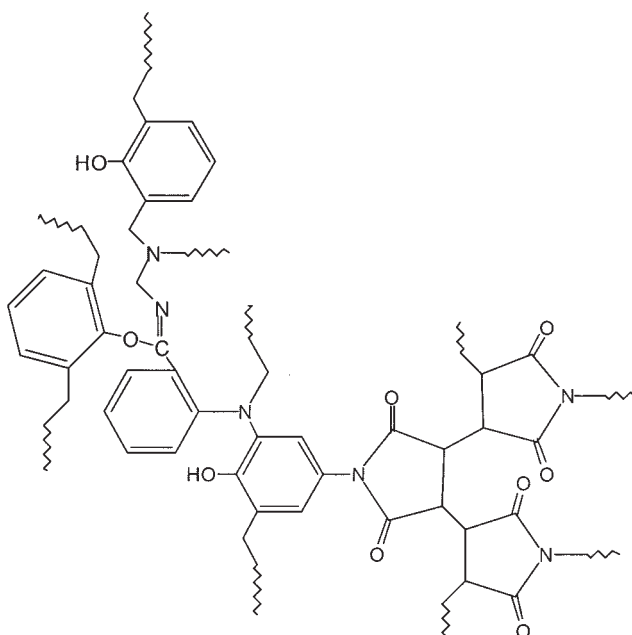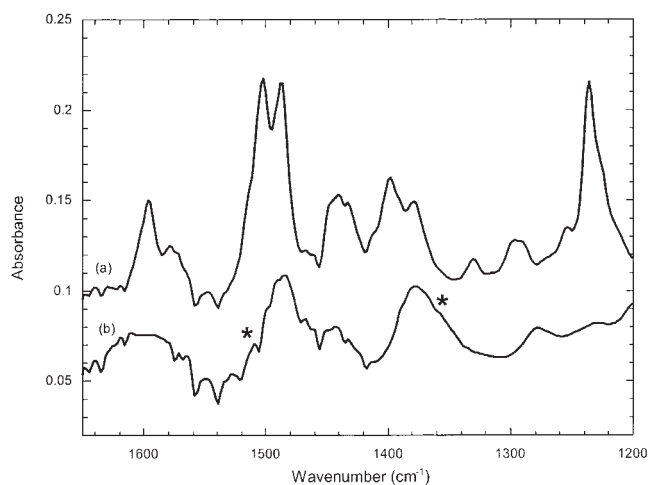
Triazine formation


Imine formation

Scheme 5

bisphenol A and 3,5-xylidine (BA-35X),[37] epoxy,[38] phenolic,[38] and MIa polybenzoxazine composites are shown in Figure 7. It should be mentioned that the data for carbon fiber-reinforced epoxy and phenolic composites were kindly provided by Toray Industries, Inc., and the epoxy and phenolic resins used were modified to achieve the optimum mechanical properties.

MIan carbon fiber-reinforced polymer (CFRP) composites showed a higher flexural strength when compared with a benzoxazine from bisphenol A and 3,5-xylidene (BA-35X), modified phenolic, and MIa composites. From the discussion earlier, using metal catalysts could intensify oxazine ring and nitrile polymerizations. Therefore, $FeCl_3$ was mixed into MIan. As expected, the flexural strength was improved by ~15% due to a higher degree of polymerization from both functionalities.

Recently, the rubber interlayer approach was used to enhance the mechanical properties of BA-35X CFRP composites.[37] Many studies have been done on the modification of surface properties of fibers by introducing functional groups (carboxylic, phenolic) on the fiber surface.[39,40] In our case, the carbon fiber woven fabric used contained epoxy groups in the sizing material[41] that can react with the amine group in ATBN liquid rubber.
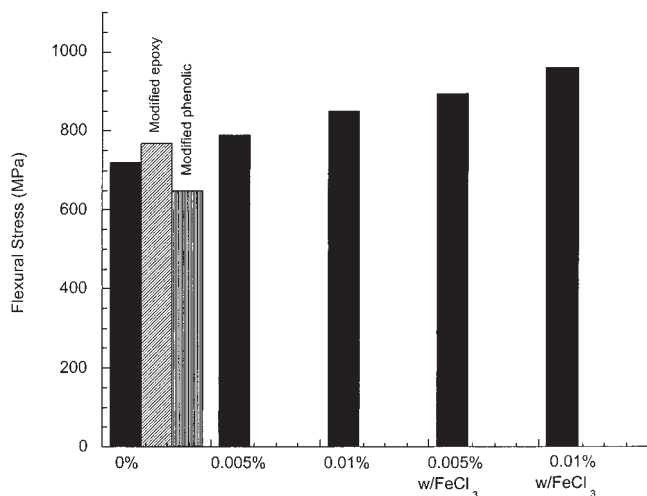
The effect of the rubber interlayer on flexural strengths of MIan CFRP composites are summarized in Figure 8. By applying both catalyst and rubber interlayer method, the flexural strength of MIan CFRP composite was increased by 33% over those of unmodified composites. The optimum ATBN rubber concentration for this system is 0.01% by fiber weight.

To improve the crosslink density and modify the mechanical properties of benzoxazine, copolymers of epoxy and bisphenol A-based benzoxazines were studied by Ishida and Allen.[42] They were able to op-

Figure 6 FTIR spectra of MIan monomer (a) and polymerized at 200°C for 30 min (b).
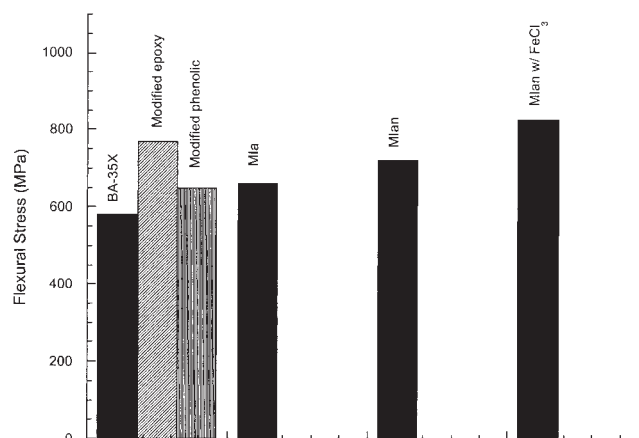
Figure 7 Flexural strength of MIan and modified MIan CFRP composites in comparison with BA-35X, modified epoxy, modified phenolic, and MIa CFRP composites.
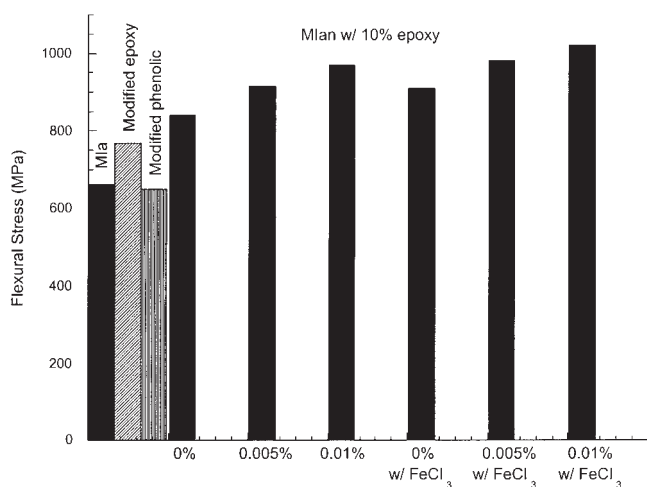
Figure 8 Effect of rubber interlayer on the flexural strength of MIan CFRP composites in comparison with those of modified epoxy and modified phenolic CFRP composites.
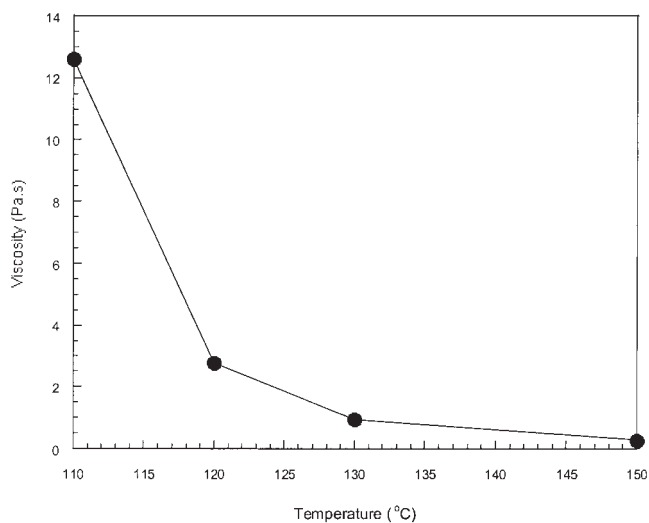

Figure 10 Shear viscosity of MIan monomer at various temperatures.

timize the copolymer system and an increase in glass-transition temperature, crosslink density, and flexural properties were observed.

Recently, our group studied the copolymerization of MIa polybenzoxazine.[43] The results showed that adding 10–15% by weight of diglycidyl ether of bisphenol A (DGEBA) will improve glass-transition temperature and flexural strain at breakage without reducing the strength and thermal properties of benzoxazine.

In this study, MIan copolymerized with 10% DGEBA CFRP composites showed an improvement in flexural strength of 17% over unmodified MIan CFRP composites. By adding a 0.01% ATBN rubber interlayer, a 35% increase in flexural strength was

achieved. The optimum conditions for MIan composites include utilizing catalyst, rubber interlayer, and epoxy copolymerization approaches together. As a result, a flexural strength of more than 1 GPa was achieved, as shown in Figure 9.

It is also important to note that incorporation of the imide group increased the viscosity compared to monofunctional benzoxazines but not above typical difunctional benzoxazines,[20] which allows for good processiblity. The shear viscosity of MIan benzoxazine monomer at various temperatures is shown in Figure 10.

The storage modulus (G') of the solid material under shear deformation provides information relating to the material stiffness. The storage moduli of MIan, epoxy-copolymerized MIan, and FeCl$_3$-catalyzed

Figure 9 Flexural strength of MIan polybenzoxazine modified with catalyst, epoxy copolymerization, and rubber interlayer CFRP composites in comparison with MIa, modified epoxy, and modified phenolic CFRP composites.
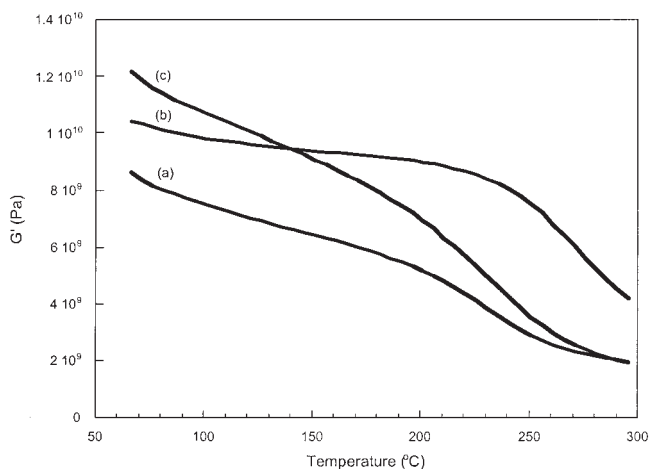

Figure 11 Storage modulus (G) of MIan polybenzoxazine (a), with 4 mol% FeCl$_3$ added (b), and copolymerized with 10% epoxy (c).
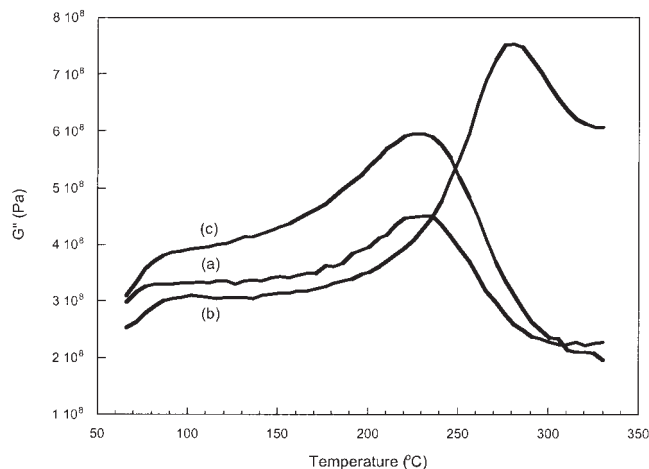
MIan CFRP composites are shown in Figure 11. By copolymerizing MIan with epoxy, the storage modulus increased significantly [Fig. 11(c)]. In the case of $FeCl_3$-modified MIan CFRP composite, the storage modulus was maintained at approximately the same value for a wide temperature range up to 200°C. This confirms the discussion given previously that $FeCl_3$ enhances the network formation [Fig. 11(b)].

The peak temperature of the α transition of the loss modulus (G″) at 1 Hz was taken as the glass-transition temperature (T_g) of the materials.[44] G″ and T_g of the MIan and epoxy-copolymerized, $FeCl_3$-modified MIan CFRP composites are shown in Figure 12. It should be noted that the epoxy-copolymerized composite exhibited strength improvement without compromising thermal properties. T_g's of both MIan and epoxy-copolymerized MIan CFRP composites are about 230°C. As expected, the T_g of the composite increased significantly (275°C) when $FeCl_3$ was added.

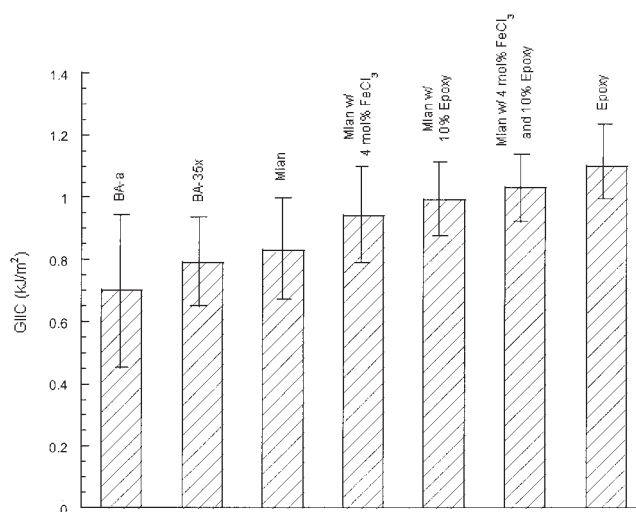The ENF test was carried out to study the mode II delamination of MIan CFRP composites. The strain energy release rate (G_{IIC}) of MIan and modified MIan composites are shown in Figure 13 in comparison with those of epoxy,[45] BA-a, and BA-35x CFRP composites. As we can see, the G_{IIC} increased with the addition of $FeCl_3$ and epoxy. From our previous study, it was found that the mode II delamination toughness of benzoxazine composites was increased by the rubber interlayer approach due to an improvement in adhesion.[37] Therefore, it is possible that the delamination toughness of modified MIan composite could be further improved by applying an ATBN rubber interlayer.

CONCLUSIONS

A polybenzoxazine with excellent thermal and mechanical properties and high processibility was syn-

Figure 13 Fracture toughness (G_{IIC}) of MIan polybenzoxazine modified with catalyst, epoxy copolymerization CFRP composites in comparison with those of BA-a, BA-35x, and epoxy[44] CFRP composites.

thesized by incorporating maleimide and nitrile functionalities. Lewis acid catalyst was used to improve the conversion of nitrile and oxazine groups during the polymerization. By utilizing catalyst, rubber interlayer and copolymerization with epoxy, MIan CFRP composites could be tailored for desired flexural properties without decreasing the thermal properties. A T_g of 275°C was observed for the optimized MIan CFRP composite. The highest flexural strength of the MIan CFRP composite exceeded 1 GPa.

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Figure 12 Loss modulus (G″) of MIan polybenzoxazine (a), with 4 mol % $FeCl_3$ added (b), and copolymerized with 10% epoxy (c).

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