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Processing and characterization of carbon fibre-reinforced polynaphthoxazine composite

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In order to attain a high-temperature resistant composite with good performance as well as processability, a polynaphthoxazine composite with 60% by volume of carbon fibre has been successfully developed. The naphthoxazine monomer was modified to obtain lower melting point and higher solubility for improved processability. The density and void content of this composite were measured at room temperature. The T_g and the activation enthalpy of the glass transition process were measured by dynamic mechanical analysis, and the effect of cure temperature on the T_g of the composite was studied. The thermal characteristics of this composite were studied in terms of the weight loss after isothermal ageing, the decomposition temperature from thermogravimetric analysis, and the change in dynamic storage moduli at high temperatures. Flexural and interlaminar shear tests were performed to evaluate the mechanical properties of this composite. A good balance between strength and toughness of this composite was achieved. A very high char yield of 90% was gained after carbonization in a nitrogen atmosphere. This polynaphthoxazine composite compares favourably with the *bis*maleimide composites in terms of mechanical properties and thermal stabilities.

1. Introduction

Thermally resistant structural materials play a key role in the progress of the electronic and aerospace industries. Many different polymer composites have been developed in the past decades for high-temperature applications. The basic requirements for heat-resistant composites are retention of mechanical properties at high temperatures, good processability, ease of inspection, and acceptable repair methods. They can only be partially met by some of the commercial polymer composites, but none can fulfil all of them [1, 2].

Phenolic composites provide some good characteristics including flame retardance, low smoke generation and fairly high-temperature resistance. They are extensively used in aircraft interiors. However, there are some shortcomings associated with them, such as brittleness, release of by-products during curing, use of strong acids and alkalis as catalysts, and limited shelf life. Phenolics show a good retention of strength at 200 °C for 1000 h but a sudden drop in mechanical properties occurs after thermal ageing to longer times [2–4].

Polybenzoxazines and polynaphthoxazines [5–9] can be deemed as alternatives to traditional phenolics. Both are synthesized from the ring-opening polymerization of the aromatic oxazines. A much higher freedom in molecular design can be obtained from such a synthesis route. Furthermore, no by-products are produced in the polymerization process, and strong catalysts are unnecessary [5, 6]. Some polybenzoxazines were proved to have near-zero shrinkage or volumetric expansion upon curing. The thermal and mechanical properties of polybenzoxazines and polynaphthoxazines were measured on resin specimens cured in an autoclave process [8, 9].

The main objective of this study was to develop a carbon fibre-reinforced polynaphthoxazine composite with good mechanical properties and thermal stabilities. The naphthoxazine monomer was first synthesized in this laboratory [9] and was derived from the reaction of formaldehyde and aniline with 1,5-dihydroxynaphthalene (abbreviated 15N). Specific curing cycles were developed according to a differential scanning calorimetry (DSC) study. The composite was made by filament winding and compression moulding. Subsequently, the density, fibre volume content, and void content were measured. Dynamic mechanical analysis (DMA) was performed to study the storage modulus (G′), loss modulus (G″), and glass transition temperature, T_g, of composites associated with different curing temperatures. The thermo-oxidative stability of these composites was investigated using thermogravimetric analysis (TGA) and isothermal ageing tests. Mechanical behaviour of these composites was evaluated by means of flexural and interlaminar shear properties. Finally, scanning electron microscopy (SEM) was used to examine the fractured surface of the flexural specimens.

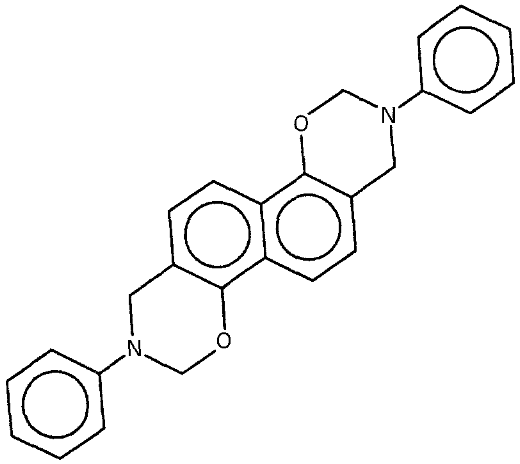
2. Experimental procedure

2.1. Materials

Formaldehyde (37% in water), aniline (99.5%), and 1,5-dihydroxynaphthalene (97%) were purchased from Aldrich Chemical Company. All the chemicals were used as-received. The Thornel carbon fibre T-650/42 6 K (without sizing, courtesy of Amoco Performance Products, Inc.), was used as-received without any additional modification.

2.2. Monomer preparation

Detailed synthesis procedures for the preparation of the naphthoxazine monomer *bis*(4,5-dihydro-5-phenyl-6*H*-3,5-oxazinyl) [2,1-a, 2′, 1′-f] naphthalene (abbreviated 15 Na), were presented elsewhere [9]. The chemical structure of the 15 Na monomer is shown in structure I. The 15 Na naphthoxazine precipitated from the reaction medium as a brownish powder with a melting point (T_m) of 204–206 °C. After preheating quickly at 208 ± 2 °C for 4 min in an oven, it melted and changed to the preheated 15 Na with a black colour and a melting point of 155–160 °C.



(I) 15Na

Based on the results of DSC, it was found that the melting point of the pure naphthoxazine was too high and very close to the curing temperature. Therefore, preheated 15 Na naphthoxazine was used for composite fabrication.

2.3. Composite fabrication

The laminates were prepared from unidirectional carbon fibre-reinforced prepregs prepared by brush application of a naphthoxazine solution on to a drum-wound unidirectional carbon fibre. The naphthoxazine solution was 6% by weight in tetrahydrofuran (THF) and was prepared in such a way as to obtain a fibre volume content of 60% after curing. The prepreg was removed soon after brushing and was placed on a flat surface for 30 min at room temperature. The prepreg was cut and then dried at 90 °C under 0.5 mm Hg for 2 h in a vacuum oven to remove any volatiles.

Eight plies of the prepregs were stacked unidirectionally and compression moulded to obtain a laminate having a cured thickness of 0.8–0.9 mm. The laminate was compression moulded by placing the prepreg stacks into a flat metal die at room temperature and then inserting the die into the compression moulder. The heating rates for the different steps were all 3.5 °C min^{-1}. After the die reached 160 °C for 10 min, a pressure of 4.1 MPa (600 p.s.i) was applied. When the die reached the final cure temperature ranging from 240–316 °C, the laminate was cured for 1 h and then cooled under pressure to room temperature at a rate of 1.2 °C min^{-1}. Detailed curing cycles for the CF/15 Na composite are shown in Fig. 1.

2.4. Characterization

The water-replacement method according to ASTM D792-86 was used to measure the density of the composites cured at different temperatures. Fibre contents and void contents of the composites, indicated as volume fractions, were measured as follows. The hot sulphuric acid chemical digestion technique according to ASTM D3171-76 (reapproved 1990) was applied to measure the fibre weight. The fibre contents were then calculated from the density of composites and the carbon fibre (1.78 g cm^{-3}). The density of pure polynaphthoxazine, 1.272 g cm^{-3} was used to calculate the resin volume content. The void content was taken as unity minus the fibre and resin contents.

A Perkin–Elmer DSC-7 differential scanning calorimeter was used to study the curing parameters of the naphthoxazine monomer. For isothermal tests, samples were heated in the DSC instrument at a heating rate of 300 °C min^{-1}, equilibrium was established in 50 s, then the rate of enthalpy production at the experimental temperature was monitored with time. For non-isothermal tests, the temperature sweep was performed from room temperature to 250–290 °C with a heating rate of 10 °C min^{-1} and the heat flow from the sample pan was monitored.

Dynamic mechanical tests were performed on a Rheometrics RMS-800 dynamic mechanical spectrometer equipped with a 2000 gcm force dual-range rebalance transducer. Specimens with dimensions of approximately 55 mm × 12 mm × 0.9 mm were tested in a rectangular torsion fixture. A constant strain of 0.15% was applied sinusoidally, which was checked in a strain sweep to ensure it was in the linear viscoelastic region. The glass transition temperature (T_g) was reported as the maximum point on the G'' curve in the

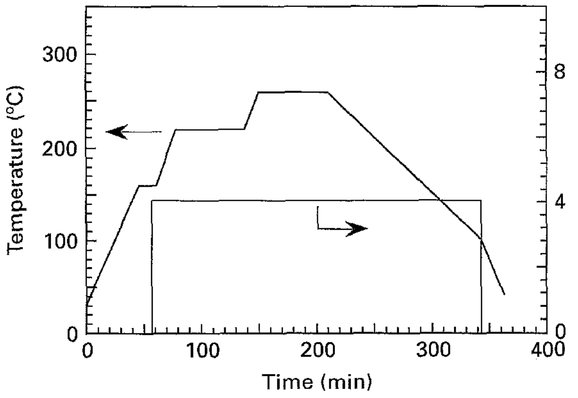


Figure 1 A typical curing cycle for CF/15 Na composite. The heating rates are all 3.5 °C min^{-1} and the cooling rate is 1.2 °C min^{-1} down to 100 °C.

temperature sweep test. The test frequency was 1 Hz (6.28 rad s^{-1}) for temperature-sweep tests. A frequency range between 0.4–60 rad s^{-1} was applied to the temperature/frequency sweep tests to obtain the activation enthalpy of the glass transition process.

The average heating rate was approximately 1.8 °C min^{-1} for temperature-sweep mode and 0.9 °C min^{-1} for temperature/frequency-sweep mode. Test data were collected in 2 °C intervals between room temperature and at least 50 °C above the T_g for each sample. The specimens were held for a thermal soak time of 30 s for each temperature before the measurement was performed.

A Perkin–Elmer System 4 Model TGS-2 apparatus was used to perform the thermogravimetric analysis (TGA) with a heating rate of 20 °C min^{-1} in a nitrogen atmosphere. Isothermal ageing tests were conducted in an oven without air circulation. The temperature fluctuation in the oven was ± 2 °C. The specimen dimensions were approximately 40 mm × 20 mm × 1 mm. Specimens were predried at 120 °C for 1 h and put in the oven and periodically taken out to measure the weight loss.

Specimens with the dimensions of 60 mm × 25 mm × 0.8 mm were used to measure flexural properties under a three-point loading with a span-to-depth ratio of 48:1 and bending speed of 2.0 mm min^{-1} according to ASTM D790-92. The flexural toughness of the composites was reported as the area under the stress–strain curve of the flexural test. Short-beam shear specimens with the dimensions of 25.4 mm × 6.4 mm × 2.8 mm were used for interlaminar shear test with a span-to-depth ratio of 4:1 and bending speed of 1.3 mm min^{-1} in accordance with ASTM D2344-84 (reapproved 1989). Both tests were carried out at room temperature on an Instron Model 1125 universal testing apparatus. The property values reported are averages of five specimens.

A Jeol JSM-840-A scanning electron microscope (SEM) was applied to observe the fractured surface of flexural specimens. Specimens with the dimensions of 6 mm × 3 mm × 0.8 mm were cut with a diamond saw and then were sputtered with gold for a thickness of approximately 6 nm. The fibre/matrix interphase was observed in a cross-section view either perpendicular to the fracture surface or parallel to the delaminated plane.

3. Results and discussion

3.1. Curing parameters

Fig. 2 shows the non-isothermal DSC thermograms of the 15 Na naphthoxazine, both in the pure and the preheated form. The 15 Na monomer has a high melting point which is very close to the curing temperature, (T_{cure}). Once the monomer melts it starts to cure at a fast rate, which makes the composite fabrication process difficult and results in poor quality of the product. After melting and partially curing to the oligomer-containing material, preheated 15 Na shows much lower T_m at 155–160 °C, which can improve the processability. So the carbon fibre-reinforced composites were fabricated from the preheated 15 Na.

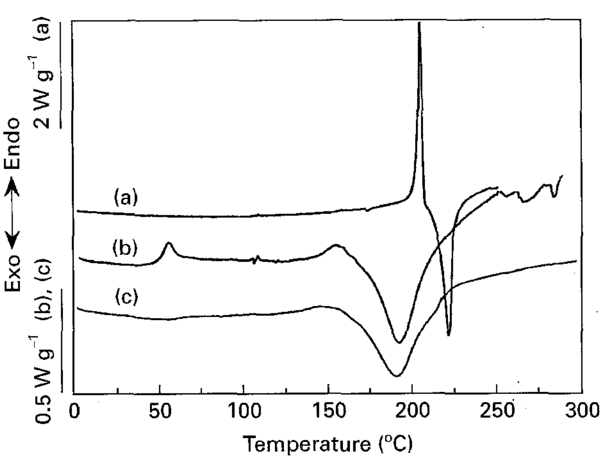


Figure 2 Non-isothermal DSC scans of 15 Na naphthoxazines: (a) pure, (b) preheated, and (3) preheated then annealed at 155 °C.

There is a heat capacity change at 56 °C on the DSC thermogram of the preheated 15 Na, and a peak also appears at 61 °C. They could be associated with the T_g of the preheated 15 Na which is in the partially cured form. The peak might be due to the quenching of the molten 15 Na, which disappears after annealing at 155 °C for 2 min and then cooling at a rate of 3 °C min^{-1}. In the meantime, the T_g shifts to 87 °C due to further curing in the annealing process.

In addition, the solubility of the 15 Na in THF was 3% and was increased to 10% for the preheated 15 Na. This improvement in the solubility can make the prepreg processing much easier. Most of the currently available high-performance composites have the processing problems of low solubility and high melt viscosity. A certain powder prepreg process was developed to improve the processability for some composite systems [10].

3.2. Physical properties

The main physical characteristics of the CF/15 Na composite including density, fibre volume content, void content, and T_g, are listed in Table I. Corresponding data for epoxy composites, polyimide composites, and *bis*maleimide composites are quoted for comparison [11–15]. The processing procedures were optimized to control the fibre volume content in the range of 60% ± 1.5%. The void content of CF/15 Na was determined to be 4.2% ± 0.2%, which is fairly low in comparison with the general composites [16].

3.3. Dynamic mechanical analysis

The dynamic mechanical spectra of the CF/15 Na composite and the 15 Na resin, both cured at 260 °C for 1 h, are shown in Fig. 3. In comparison with the pure resin, the CF/15 Na has a much lower peak height (– 30%) on the tanδ peak, which can be related to higher crosslink density [17–19]. The increase in G' and G'' after the α-transition could be associated with the decomposition and charring of the 15 Na resin [19].

TABLE I The physical properties of the polynaphthoxazine composite and other high-performance composites

Fibres	Resins	Curing conditions	Density ($g cm^{-3}$)	Fibre volume content (%)	Void content (%)	T_g (°C)
T-650/42, 6K	Polynaphthoxazine1 5 Na	260 °C for 1 h	1.528–1.590	60 ± 1.5	4.2 ± 0.2	353
T-650/42, 6K	Polybenzoxazine 22Pa[a] [8]	290 °C for 1 h	1.542–1.569	60 ± 2	0.4 ± 0.3	268
T-650/42, 6K	Polybenzoxazine 44Oa[b] [8]	290 °C for 1 h	1.541–1.583	60 ± 2	1.0 ± 1.7	350
Carbon fibre	Epoxy [11]	–	1.46–1.58	54–56	–	150–261
T-300	Bismaleimide [11, 12]	–	1.60	68.3	–	250–300
T-650/35, 6K C-6000	PMR-15 [13–15]	316 °C for 16–24 h	–	~60	–	340–380

[a] Polybenzoxazine based on the 8,8′- *bis*(3,4-dihydro-3-phenyl-2*H*-1,3-benzoxazine).
[b] Polybenzoxazine based on the 6,6′- *bis*(2,3-dihydro-3-phenyl-4*H*-1,3-benzoxazinyl) ketone.

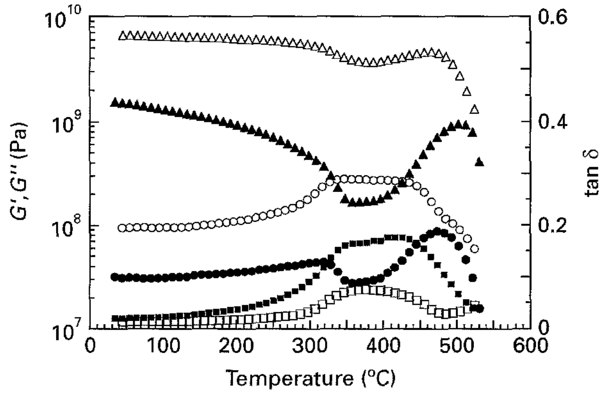


Figure 3 Dynamic mechanical spectra of 15 Na (▲, G′; ●, G″, ■, tan δ) and its carbon fibre composite (△, G′, ○, G″, □, tan δ); both were cured at 260 °C for 1 h.

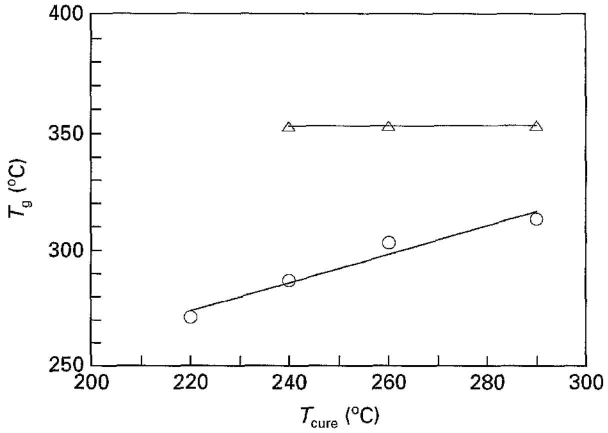


Figure 4 The glass transition temperature (T_g) of (○) 15 Na polynaphthoxazines and (△) their composites, as a function of cure temperature.

Fig. 4 shows the glass transition temperatures of CF/15 Na composites cured at different temperatures. As the curing temperature increases, the T_g of the pure resin linearly increases. However, the T_g of CF/15 Na composite remains almost constant and is much higher than that of the pure resin cured at the same temperature. Such a significant increase in T_g could also be attributed to the interaction of resin and fibre at the interface, and/or some structural changes in the resin near the interphase.

In order to examine if any reaction occurs between the resin and the fibre, isothermal DSC studies were conducted. Fig. 5 presents the isothermal DSC thermograms of pure 15 Na monomer, as well as with the 20% and 40% by weight of carbon fibres. As the carbon fibre content increases, the resin curing rate becomes faster. It can be concluded that the carbon fibre exhibits a catalytic and/or initiation effect on the curing of the 15 Na naphthoxazine. The major contribution might come from the phenol groups on the surface of the carbon fibres [5]. These effects would result in the higher T_g in the composite than in the pure resin.

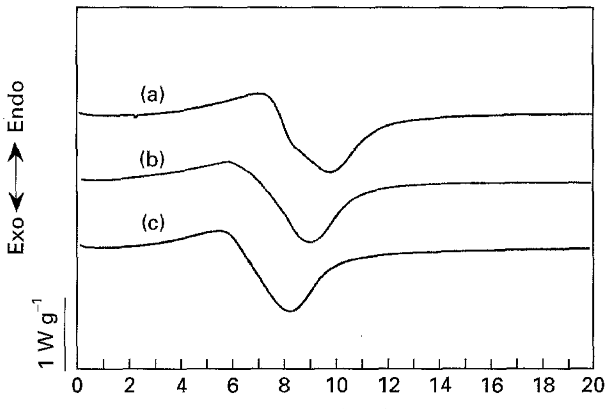


Figure 5 Isothermal DSC scans of 15 Na naphthoxazines: (a) pure, (b) with 20% by weight carbon fibre, and (c) with 40% by weight carbon fibre.

It is noteworthy that the CF/15 Na composites have T_gs higher than their cure temperatures. This T_g-higher-than-T_{cure} characteristic could be an advantage: being able to process at 240 °C and exhibiting an extra-high T_g of 353 °C. This T_g-higher-than-T_{cure} characteristic has been found in only a few thermosetting resins [20].

By using the frequency/temperature sweep, the activation energy (more accurately, the activation enthalpy) of the glass transition process can be obtained from the following equation [21]

$$\frac{\ln \omega_1}{\ln \omega_2} = \frac{\Delta H}{R}\left(\frac{1}{T_{g2}} - \frac{1}{T_{g1}}\right) \quad (1)$$

where ΔH is the activation enthalpy, R is the gas constant, T_{g1}, T_{g2} are the glass transition temperatures (K) which are related to the test frequencies ω_1 and ω_2, respectively. The Arrhenius plots of frequency versus T_g^{-1} of the 15 Na polynaphthoxazine and its composite are shown in Fig. 6. Under the same curing conditions, the ΔH of the CF/15 Na composite is 27% higher than the 15 Na polymer (200 versus 157 kcal mol^{-1}). Such a result can be explained in terms of the crosslink density. In comparison with the pure resin, the composite matrix has a higher crosslink density which could restrain the polymer molecular relaxation in the glass transition process and results in a higher ΔH.

3.4. Thermal stability

Table II lists the thermal properties of CF/15 Na composite including the decomposition temperature, T_d, defined as the temperature with 5% weight loss of resin or 1.5% of composites with the resin content of 30% by weight when subjected to TGA test in nitrogen [22], the weight loss after 200 h isothermal ageing in static air, and the char yield from TGA test when subjected to 800 °C in nitrogen. Reference data of composites with the resins of epoxies, *bis*maleimides and polyimides are also listed for comparison [2, 11–15, 22].

The TGA curves of the CF/15 Na cured at 260 °C for 1 h in both air and nitrogen atmospheres are shown in Fig. 7, with the data of pure 15 Na resin and carbon fibre as reference. This composite moderately decomposes from 200 °C both in air and nitrogen, then oxidizes in air at 450 °C. The T_d of CF/15 Na composite is 240 °C, which is inconsistent with the results of pure resin. A char yield of 90% was obtained for this composite after carbonizing to 800 °C in a nitrogen atmosphere. Such a high char yield could make the composite a good candidate for carbon/carbon composites. Fig. 8 presents the isothermal weight loss of CF/15 Na composite in static air. The temperature at which 3% weight loss occurs for CF/15 Na composite is 260 °C. Severe weight loss occurs between 260 and 290 °C.

In order to evaluate the maximum service temperature of the CF/15 Na composite, the storage moduli

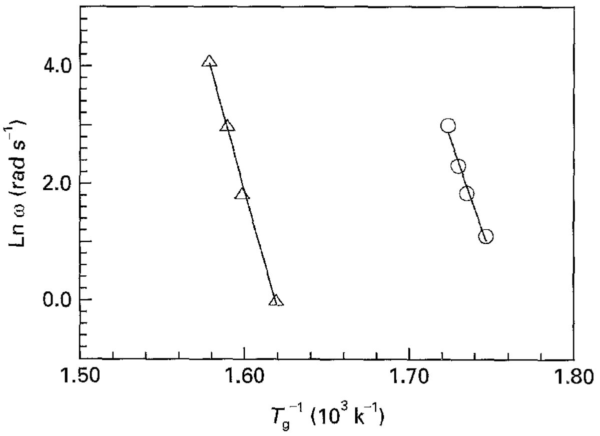


Figure 6 Arrhenius plots of test frequency versus glass transition temperature for (○) 15 Na polynaphthoxazine and (△) its composites, both cured at 260 °C for 1 h.

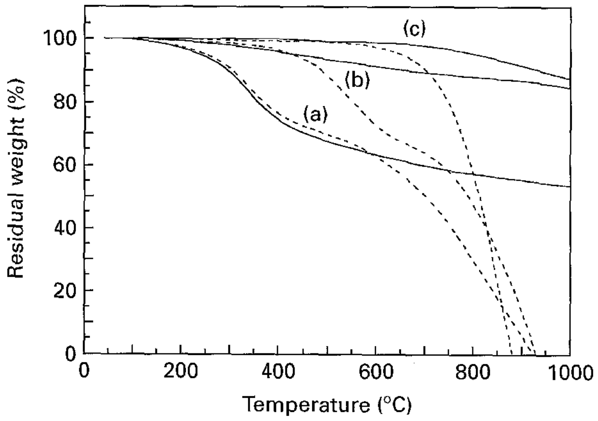


Figure 7 TGA curves of (a) 15 Na polynaphthoxazine, (b) CF/15 Na composite, and (c) T650/42 carbon fibre, at a heating rate of 20 °C min^{-1}, (– – –) in air, (——) in N$_2$.

TABLE II The thermal characteristics of the polynaphthoxazine composite and other high-performance composites

Materials	Curing conditions	T_g (°C)	T_d^{a} (°C) [22]	3% wt loss temperature^b (°C)	Char yield (%)
CF/15 Na	260 °C for 1 h	353	240	260	90
15 Na polymer [15]	260 °C for 1 h	304	240	–	67
CF/epoxy [2, 12]	–	150–261	–	–	⩽ 40
CF/*bis*maleimide [2, 11, 12]	–	250–300	450–500	–	50–70
CF/polyimide [12, 15]	–	230–380	500–600	–	–

^{a}The 1.5% weight loss temperature of composites or the 5% weight loss temperature of resins when subjected to TGA in nitrogen at a heating rate of 20 °C min^{-1}.

^{b}The 3% weight loss temperature after 200 h isothermal ageing in static air.

as a function of temperature from DMA tests were also investigated. Fig. 9 shows the temperature dependence of the CF/15 Na storage moduli which are normalized to the room-temperature storage modulus (G'_{RT}). Even at 260 °C, the CF/15 Na composite cured at 260 °C for 1 h can retain 80% G'_{RT}, i.e. 5.8 GPa, and is expected to be still strong enough for structural applications. The normalized storage modulus of CF/15 Na composite increases significantly as T_{cure} increases from 240 °C to 290 °C, but starts to drop when T_{cure} changes from 290 °C to 316 °C.

3.5. Mechanical properties

Fig. 10 presents typical flexural stress–strain curves of the CF/15 Na composites cured for 1 h at different temperatures. The 260 °C cured CF/15 Na appears to have the highest flexural strength as well as modulus. The interlaminar shear strength (ILSS) and flexural strength of CF/15 Na as a function of cure temperature are shown in Fig. 11. Both strengths remain at a comparable level for the composites cured at 240 and 260 °C, but dramatically drop to below 50% after the T_{cure} increases to 290 and 316 °C. It can be concluded from these results that the CF/15 Na composites start to degrade at a temperature higher than 260 °C, which is in agreement with the thermal characterization discussed before.

The flexural modulus and toughness of CF/15 Na as a function of T_{cure} are drawn in Fig. 12. The toughness decreases to 30% and even 15% when T_{cure} increases to 290 and 316 °C, respectively. Again, the effect of degradation can be obviously observed. On the other hand, the composites cured at different temperatures show nearly constant flexural modulus. This can be explained in that the modulus of polymer matrix composites are generally insensitive to degradation and oxidation [23]. It can be concluded that a good

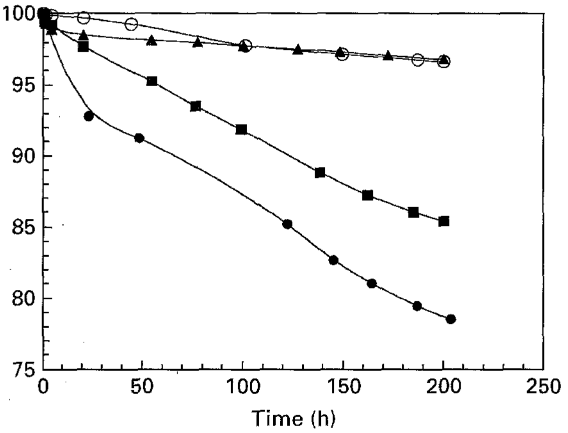


Figure 8 Isothermal weight loss of CF/15 Na composite at (○) 230 °C, (▲) 260 °C, (■) 290 °C, (●) 320 °C.

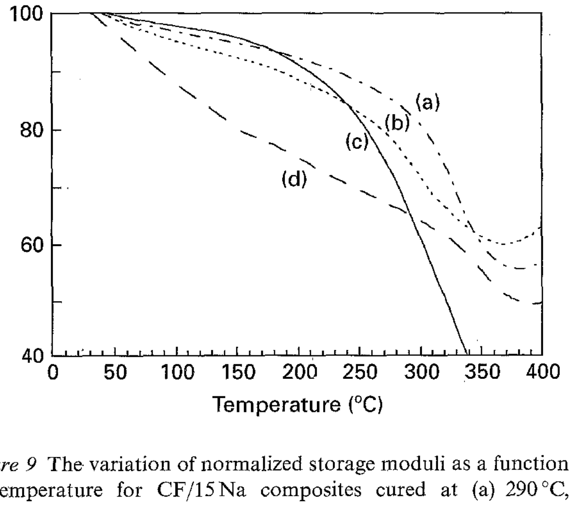


Figure 9 The variation of normalized storage moduli as a function of temperature for CF/15 Na composites cured at (a) 290 °C, (b) 260 °C, (c) 316 °C, and (d) 240 °C. The room-temperature value of G' of each polymer, G'_{RT}, was used as the normalization factor.

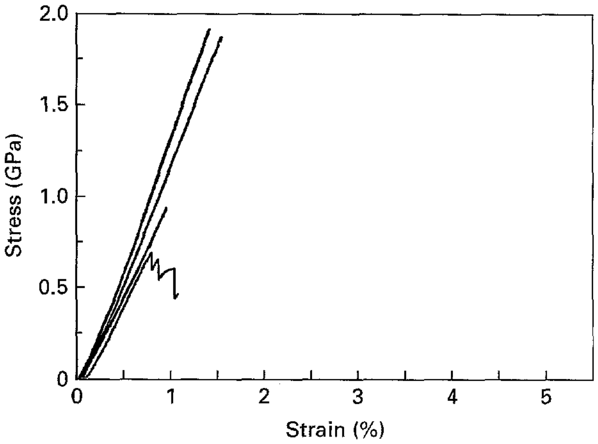


Figure 10 Typical flexural stress–strain diagrams of CF/15 Na composites cured 260, 240, 290, and 316 °C, from left to right.

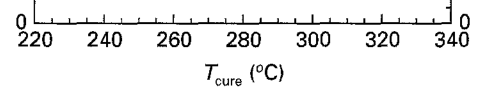


Figure 11 The effect of curing temperature on (○) the interlaminar shear strength (ILSS) and (△) the flexural strength of CF/15 Na composites.

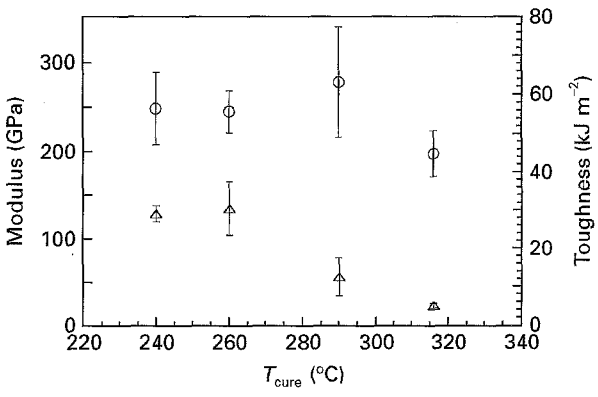


Figure 12 The effect of curing temperature on (○) the flexural modulus and (△) the flexual toughness of CF/15 Na composites.

balance of strength and toughness is achieved in the CF/15 Na composite cured at 260 °C for 1 h.

By summarizing the results of thermal and mechanical studies, the optimized curing conditions of CF/15 Na composite were chosen as 260 °C for 1 h. An estimated maximum service temperature, T_{serv}, of 240 °C was determined.

Scanning electron micrographs of the failure surface of the CF/15 Na composites cured at different temperatures are shown in Fig. 13. Sufficient adhesion was observed between the fibre and the matrix for the composites cured at 240 and 260 °C. The failure modes of both composites are primarily fibre breaking, although some delaminations also exist. However, for the composites cured at 290 and 316 °C, the resin degrades and the fibre/matrix bonding is so low that the failure mode was dominated by delamination. Complete debonding and a clean fibre surface could be seen on the scanning electron micrograph of the 316 °C cured composite.

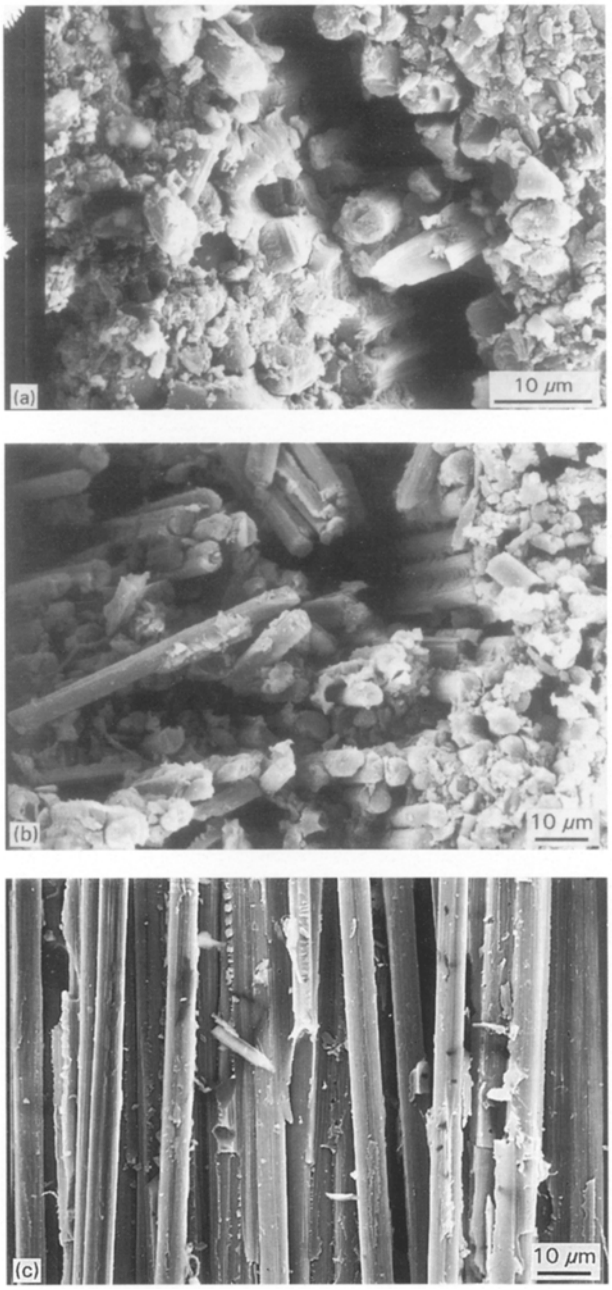


Figure 13 Scanning electron micrographs of the fracture surface from the flexural specimens of CF/15Na composites cured at (a) 240 °C, (b) 260 °C, and (c) 316 °C for 1 h.

4. Conclusion

The carbon fibre-reinforced polynaphthoxazine composite was successfully made through a prepreg process and a compression moulding process. The naphthoxazine monomers were modified to improve the processability in terms of a lower T_m and higher solubility. The void content of the 260 °C cured composite was as low as 4.2%. Because the CF/15 Na composites are cured at different temperatures, the T_g is maintained at 353 °C and is much higher than that of the pure polynaphthoxazines. The CF/15 Na composite exhibits a higher activation enthalpy of the glass transition than its pure polymer. Both the higher T_g and the higher activation enthalpy in the composite can be attributed to the higher crosslink density. The carbon fibre was found to accelerate the curing of polynaphthoxazine.

The optimized curing conditions for CF/15 Na composite are 260 °C for 1 h. The estimated maximum service temperature was assessed to be 260 °C. A high char yield of 90% was obtained for CF/15 Na composite after being carbonized to 800 °C in a nitrogen atmosphere, which will make it to a good candidate for carbon–carbon composites. This composite exhibits good mechanical properties including flexural strength, modulus, toughness, as well as interlaminar shear strength. Based on the ease of the fabrication process, along with good mechanical properties and thermal stabilities, this polynaphthoxazine composite compares favourably with and can even surpass the *bis*maleimide composites.

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