Synthesis and Characterization of Polyfunctional Naphthoxazines and Related Polymers

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SYNOPSIS

In pursuing the new polymers that could provide high mechanical properties and good thermal stabilities, a series of naphthoxazines are synthesized from different hydroxynaphthalenes with aniline and formaldehyde. The molecular structures are confirmed by NMR spectroscopy. After being polymerized in an autoclave, the naphthoxazine derived from 1,5-dihydroxynaphthalene is successfully cured to form the void-free resin. The density and tensile properties of these polynaphthoxazines are measured. Dynamic mechanical tests are performed to determine the T_g, crosslink density, and the activation enthalpy of the glass transition process for the polynaphthoxazines postcured in air at different temperatures. The effect of postcure temperature on the T_gs of the polynaphthzoxazines is investigated and discussed in terms of crosslink density. The polynaphthoxazine shows a T_g higher than the cure temperature. Fourier transform IR spectroscopy is applied for the molecular characterization of the curing systems. Thermal properties of these polynaphthzoxazines are studied in terms of the weight loss after isothermal aging in static air, the decomposition temperature from thermogravimetric analysis, and the change of dynamic storage moduli at high temperatures. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic oxazines were first synthesized in 1944 by Holly and Cope[1] through Mannich reactions from phenols, formaldehyde, and amines. From the 1950s to 1960s, Burke and co-workers synthesized many benzoxazines[2-4] and naphthoxazines[5-7] for the purpose of testing antitumor activity. In addition, benzoxazines were also found as the intermediates in the synthesis of novolac resins.[8]

The oxazine polymers could be deemed as an alternative to traditional phenolics because of the similar main chain structures. A novolac type phenolic resin has the unit, Ar — CH_2 — with some Ph — $CH_2N(R)$ — CH_2 — if hexamethylenetetramine is used as crosslinking agent, whereas polybenzoxazine possess Ph — $CH_2N(R)$ — CH_2 — structure, where Ph denotes phenolic group. They are synthesized by ring-opening polymerization of the aromatic oxazines. The heat-cured polymers

from benzoxazines were first achieved by Scheiber.[9,10] Later, Reiss and co-workers[11] investigated the polymerization of monofunctional benzoxazines with and without phenol as an initiator, resulting in linear polymers with molecular weights under 4000.

In addition to the advantages owned by ordinary phenolics, such as high temperature resistance, dimensional stability, good electrical properties, flame retardance, and low smoke generation, this family of polyoxazines provides tremendous flexibility in molecular design.[12-14] Furthermore, they produce no byproducts during polymerization and require no strong catalysts.[11,15-17]

Recently, polyfunctional benzoxazines were synthesized in our laboratory.[15-19] Phenolic resins cured from such benzoxazines were shown to be crosslinked polymers and exhibit good mechanical properties.[16,17] Some benzoxazine resins were found to have near-zero shrinkage or volumetric expansion on curing. Physical, mechanical, and rheological characterizations were also performed on these polybenzoxazines and their copolymers with epoxies.[17]

The key object of this study is to introduce a new class of polynaphthoxazines with high mechanical properties and thermal stability that can be used as a matrix resin for high-performance composite systems. Three naphthoxazines were derived from the reaction of formaldehyde and aniline with dihydroxynaphthalenes. Another naphthoxazine was made from formaldehyde and p-phenylenediamine with 2-naphthol. The structure of these naphthoxazines were confirmed by NMR spectroscopy. Based on differential scanning calorimetry (DSC) thermograms, specific curing cycles were designed to make polymers from these naphthoxazines. One of the four naphthoxazines was successfully cured to a void-free polymer, and then the density and tensile properties were tested. Dynamic mechanical analysis (DMA) was performed to determine the storage modulus (G'), the loss modulus (G''), glass transition temperature (T_g), and crosslink density (ν) of the polymers with different postcure conditions. Fourier transform infrared (FTIR) spectroscopy was also applied for the molecular characterization of the curing systems. Thermogravimetric analysis (TGA) was used to investigate thermal properties of these polynaphthoxazines. Finally, isothermal aging tests were performed to assess the thermooxidative stability of these polynaphthoxazines.

EXPERIMENTAL

Materials

All the chemicals including formaldehyde (37% in water), aniline (99.5%), 1,5-dihydroxynaphthalene (97%), 2,6-dihydroxynaphthalene (98%), 2,7-dihydroxynaphthalene (97%), 2-naphthol (99%), and p-phenylenediamine (97%), were purchased from Aldrich Chemical Company. They were used without further purification.

Monomer Synthesis and Sample Preparation

Three naphthoxazine monomers, bis(4,5-dihydro-5-phenyl-6H-3,5-oxazinyl)[2,1-a,2′,1′-f] naphthalene (15Na), bis(4,5-dihydro-5-phenyl-6H-3,5-oxazinyl)[1,2-a,1′,2′-f] naphthalene (26Na), bis(4,5-dihydro-5-phenyl-6H-3,5-oxazinyl)[1,2-a,2′,1′-h] naphthalene (27Na), were synthesized according to the scheme shown in Figure 1. The [1,2-a,1′,2′-f] position of the oxazine ring on the naphthalene of the 26Na was confirmed on monofunctional naphthoxazine through reactions of derivatives.[5] The synthesis was performed following the general procedures of aromatic oxazine synthesis.[15] The mixing of 0.4 mol of formaldehyde (37% in water) and 30 mL of dioxane was performed in a 250-mL three-neck flask in an ice bath equipped with a mechanical stirrer. Then 0.2 mol of aniline in 30 mL dioxane were added dropwise with the temperature controlled under 10°C. Additional stirring was continued for 20 min after the addition of aniline. Then, 0.1 mol of the dihydroxynaphthalene in 100 mL dioxane was added, and the system was heated to reflux for 4 hr. The product precipitated from the reaction solution. For N,N-bis(3,4-dihydro-5-phenyl-2H-naphth[1,2-e][1,3]oxazinyl) p-phenylenediamine (2Naa), the synthesis procedures were the same except that the mol ratio of formaldehyde/amine/naphthol was changed from 4/2/1 to 4/1/2.

A homemade autoclave was used to make specimens to minimize the void formation during polymerization. The autoclave consisted of two aluminum parts with a groove inside to place a Teflon O-ring. The autoclave was placed in a compression molder where the heating and temperature control between room temperature and 316°C could be obtained. The temperature fluctuation inside the autoclave was ±2°C. The pressure was applied from a nitrogen cylinder and could be regulated up to a maximum pressure of 1.33 MPa (193 psi). Detailed curing conditions are shown in Figure 2. The cured polybenzoxazines were then postcured at different temperatures to study the influence of postcuring on their T_gs.

Characterization

Proton NMR spectra were taken on a Varian XL-200 operated at 200 MHz. Deuterated chloroform was used as a solvent and tetramethylsilane was added as a standard. A Perkin-Elmer DSC-7 differential scanning calorimeter was used to study the curing parameters of these naphthoxazines in a nonisothermal scanning manner. The temperature sweep was performed from room temperature to 250–290°C with a heating rate of 10°C/min.

FTIR spectra were obtained on a Bomem Michelson MB equipped with a high sensitivity, liquid nitrogen cooled, mercury-cadmium-telluride detector with a frequency range from 5000 to 450 cm^{-1}. The specific detectivity, D^*, of the detector was 1 × 10^{10} cmHz$^{1/2}$/W. The resolution was chosen to be 4 cm^{-1}. The crosslinked polynaphthoxazine samples were prepared as KBr pellets and the naphthoxazine monomers were cast from their tetrahydrofuran solution on KBr plates.
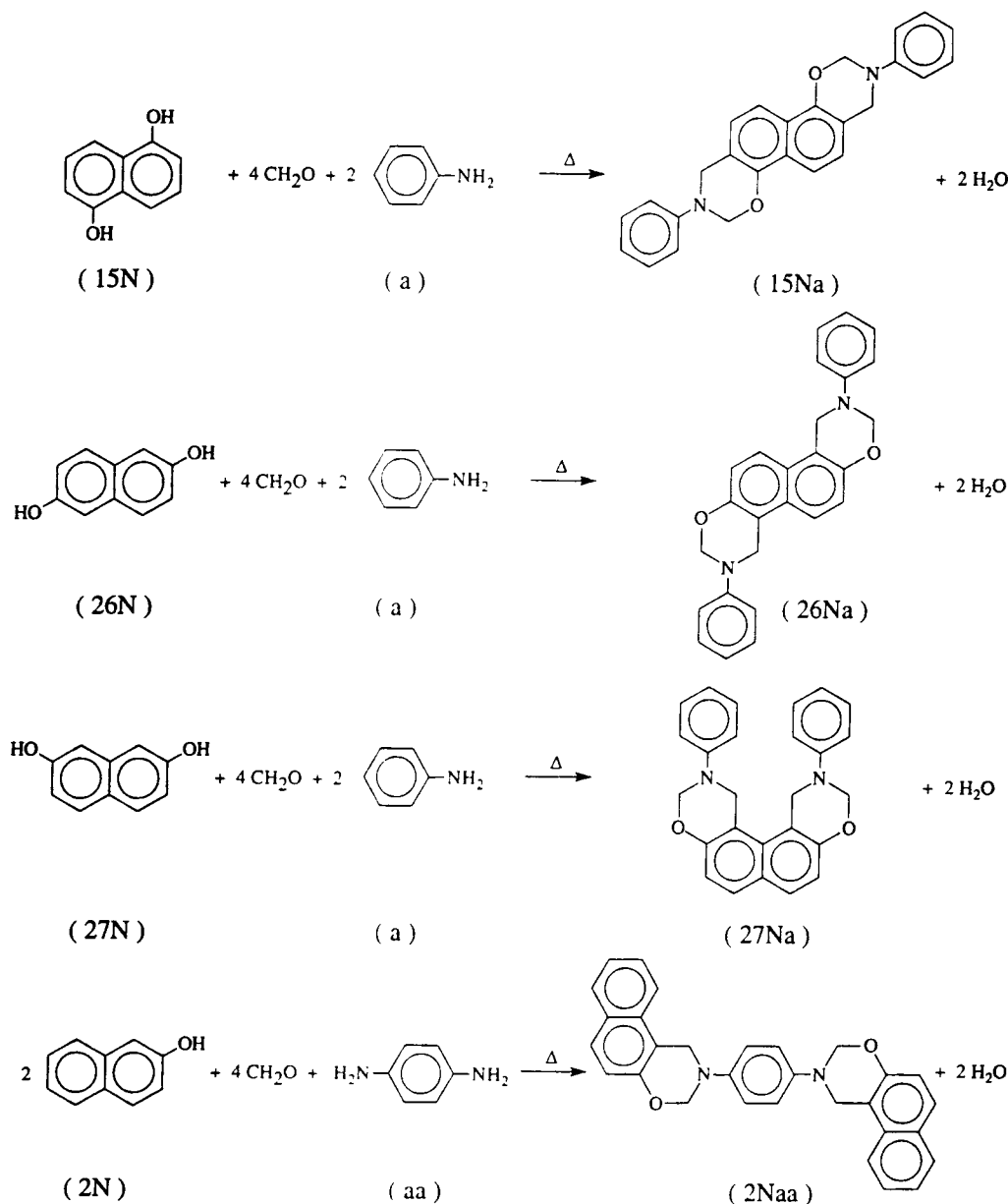
Figure 1   Chemical reactions of the formation of the naphthoxazines.

The density of the 15Na polynaphthoxazines was determined by the water replacement method according to ASTM D792. Tensile measurements were performed in accordance with ASTM D638 using an Instron Model 1125 universal testing apparatus. The room temperature experiments were conducted at a constant crosshead speed of 1.27 mm/min without strain measurement.

TGA was done with the Perkin-Elmer System 4 Model TGS-2 apparatus at a heating rate of 40°C/min in nitrogen atmosphere. Isothermal aging tests were conducted in an oven without air circulation.

The temperature fluctuation in the oven was ±2°C. The specimen dimensions were approximately 40 × 20 × 1 mm. Specimens were predried at 120°C for 1 h and placed in the oven and periodically taken out to measure the weight loss.

Dynamic mechanical tests were performed on a Rheometrics RMS-800 dynamic mechanical spectrometer equipped with a 2000 g-cm force rebalance transducer. Specimens with dimensions of approximately 55 × 12 × 2 mm were tested in a rectangular torsion fixture. A constant strain of 0.15% was applied sinusoidally that was checked in a strain sweep
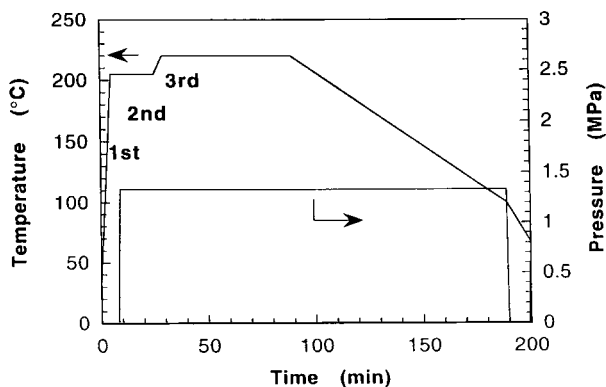
Figure 2 A typical curing cycle for 15Na polynaphthoxazine. The heating rates for the second and third steps are 3.3°C/min and the slow cooling rate is 1.2°C/min down to 100°C.

to ensure that it was in the linear viscoelastic region. The glass transition temperature (T_g) was reported as the maximum point on the curve of the loss modulus (G'') in the temperature sweep test. The test frequency was 1 Hz (6.28 rad/s) for temperature sweep tests. Five frequencies ranging from 0.4 to 60 rad/s were 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 for temperature sweep mode and 0.9°C/min 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.

RESULTS AND DISCUSSION

Synthesis and Characterization of Naphthoxazines

The properties of the synthesized naphthoxazines are shown in table I, including purification method,[15,19] product appearance, yield, melting point, and solubilities of each of the four naphthoxazines. Figure 3 shows the NMR spectra of the four naphthoxazines. The two peaks between 4.5 and 5.5 ppm were assigned to the methylene units, which are characteristic of aromatic oxazines.[15] The peak at 3.6 ppm is correlated to the protons of Mannich base, $-CH_2-NPh-CH_2-$, on the ring-opened oligomers. Such results indicate that only the recrystallization method could give the highest purity, although all the purification methods satisfied the

Table I   The Synthesis Results and Curing Parameters of Naphthoxazines

Materials	Purification Method	Yield (%)	Melting Point (°C)	Appearance	Solvents	Onset of Curing (°C) in DSC Thermogram	Exothermic Peak (°C) in DSC Thermogram
15Na	Wash with EtOH	94	207	Brownish powder	THF, CHCl₃	206	222
26Na	Recrystallization in ethyl acetate	85	219	White needle crystal	THF, CHCl₃	225	245
27Na	Wash with MeOH	90	138	Black powder	THF, CHCl₃	172	208
2Naa	Wash with MeOH	84	230	White powder	THF, CHCl₃; acetone, dioxane	232	248

a THF, tetrahydrofuran.
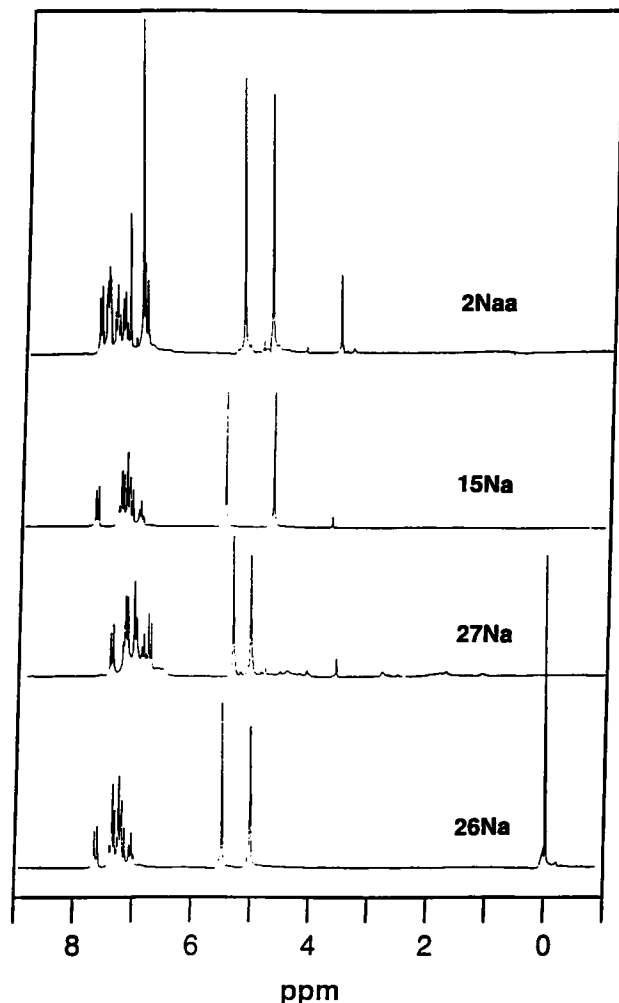
Figure 3 NMR spectra of naphthoxazines.

Figure 4 Nonisothermal DSC scans of naphthoxazines: (a) 15Na, (b) 26Na, (c) 27Na, and (d) 2Naa.

criterion of showing no —OH group at 3300 cm^{-1} in the FTIR spectra.

The nonisothermal DSC thermograms of the four naphthoxazines are presented in Figure 4. All the naphthoxazines except 27Na have high melting points that are very close to their curing temperature (T_{cure}). This means that they will start to polymerize and crosslink as soon as they melt. Such problems can be minimized by processes with higher pressure or reduction of melting point either by mixing with oligomers or other low melting benzoxazines. Fabrications of high performance polymers such as phenolics and polyimides, are sometimes processed under much higher pressure, e.g., 6.9–13.8 MPa (1000–2000 psi).[20,21]

The FTIR spectra of the purified 15Na naphthoxazine, along with the samples thermally cured for 1 h at 220, 240, and 290°C, are presented in Figure 5. The 942-cm^{-1} band could be assigned to the
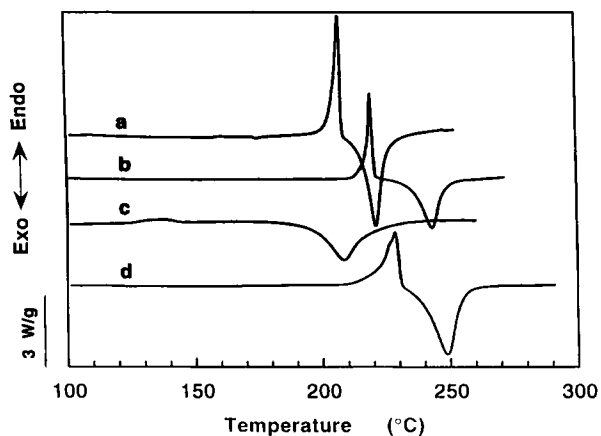
C—H out-of-plane deformation of the α,β-disubstituted naphthalene ring,[22] which indicates the formation of oxazine ring. The FTIR spectrum of 1-bromo-2-naphthol has such a band at 930 cm^{-1} and could be regarded as a model compound for this assignment.[23]

For the FTIR spectra of thermally cured 15Na naphthoxazine, the 942-cm^{-1} band becomes smaller as the curing proceeds, and almost disappears after curing at 260°C for 1 h. On the other hand, the 883 cm^{-1} band that is due to the C—H out-of-plane deformation of 1,2,4-trisubstituted naphthalene arises in the polymerized 15Na.[22] The FTIR spectrum of 2,4-dichloro-1-naphthol has such a band at 863 cm^{-1} and could be considered as a model compound for this assignment.[23] The 942-cm^{-1} band remains in the 15Na cured at 220°C for 1 h, which
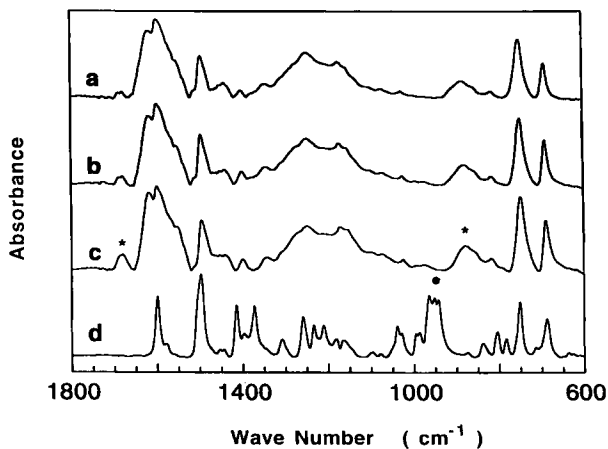

Figure 5 FTIR spectra of the 15Na naphthoxazine cured at different temperatures: (a) 290°C, (b) 260°C, (c) 220°C, and (d) the pure monomer.

Table II The Physical and Mechanical Properties of 15Na Polynaphthoxazine (PNZ) and Other High-Performance Resins

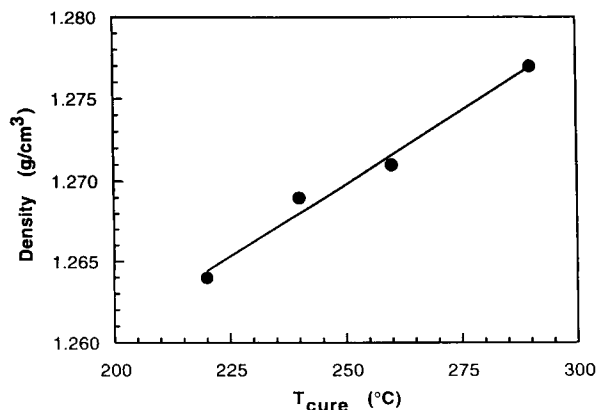| Materials	Tensile Strength (MPa)	Tensile Modulus (GPa)	Storage Modulus at RT G'_{RT} (GPa)	Elongation at Break (%)	Density (g/cm³)	T_g (°C)	Crosslink Density ($\times 10^{-3}$ mol/cm³)
15Na PNZ (cured at 260°C for 1 h)	16	—	1.5	—	1.272	304	7.4
Polybenzoxazines[16,18]	44–64	4.3–5.2	1.8–2.2	1.0–2.4	1.122–1.250	150–260	1.1–10.5
Phenolics[20,24]	35–62	2.7–4.8	—	1.5–2.0	1.24–1.32	~ 175	—
Epoxies[20,24]	28–90	2.4	—	3–6	1.11–1.40	150–261	5.2–10.4
Bismaleimides[20,37]	—	—	—	≤ 2.0	1.35–1.40	250–300	5.1–8.31

ᵃ Cured at 220°C for 1 h.

indicates that the curing reaction is not complete. This incomplete curing results in a low T_g, which is discussed later. The spectra of 15Na cured at 260°C for 1 h and cured at 290°C for 1 h are nearly identical, which implies that 260°C curing can achieve complete curing. Another interesting band shown here is the one at 1674 cm⁻¹, which is tentatively assigned to the C=N stretching from the Schiff base byproduct.[19]

Physical and Mechanical Properties

The physical and mechanical properties of 15Na polynaphthoxazine are presented in Table II. Corresponding data of general epoxies, phenolics, bismaleimides, and polybenzoxazines are listed for reference.[16,18,20,24] The room temperature density (ρ_{RT}) of 15Na naphthoxazines increases with curing temperatures, as shown in Figure 6. The degree of cure for resins would increase at higher curing temperature (T_{cure}) or longer curing time (t_{cure}), which could increase the crosslink density (ν) and restrain molecular motions. Therefore, the resin density would increase as the cure temperature was raised. This phenomenon is similar to most thermosetting polymers. The density of 15Na polynaphthoxazine cured at 260°C for 1 h is 1.272 g/cm³, which is much higher than those of the bisphenol-A-based polybenzoxazines. Additionally, some shrinkage was observed during the curing process whereas polybenzoxazines showed near-zero shrinkage on curing.[18]

The stress–strain curve of 15Na polynaphthoxazine is shown in Figure 7. Its tensile strength is much lower than those of the polybenzoxazines (16 versus 44–64 MPa). However, the real properties might be higher because the resin is very brittle and any tiny defect from specimen preparation, e.g., sanding, could cause premature failure and reduce the strength significantly. From the crosshead strain data, rough estimates of the elongation at break were determined to be 1.0%

Figure 6 The density dependence on curing temperature for the 15Na polynaphthoxazine.
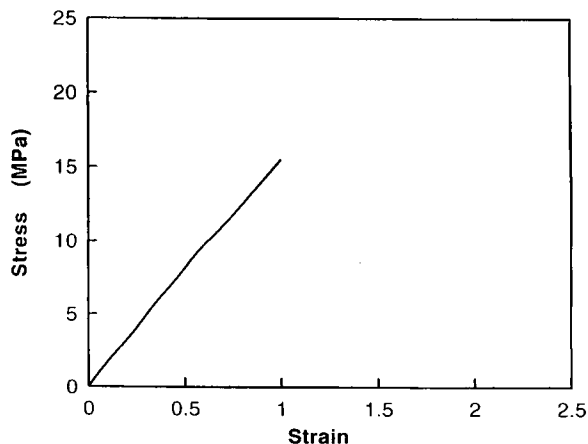
Figure 7 The typical tensile stress–strain diagram the 15Na polynaphthoxazine.
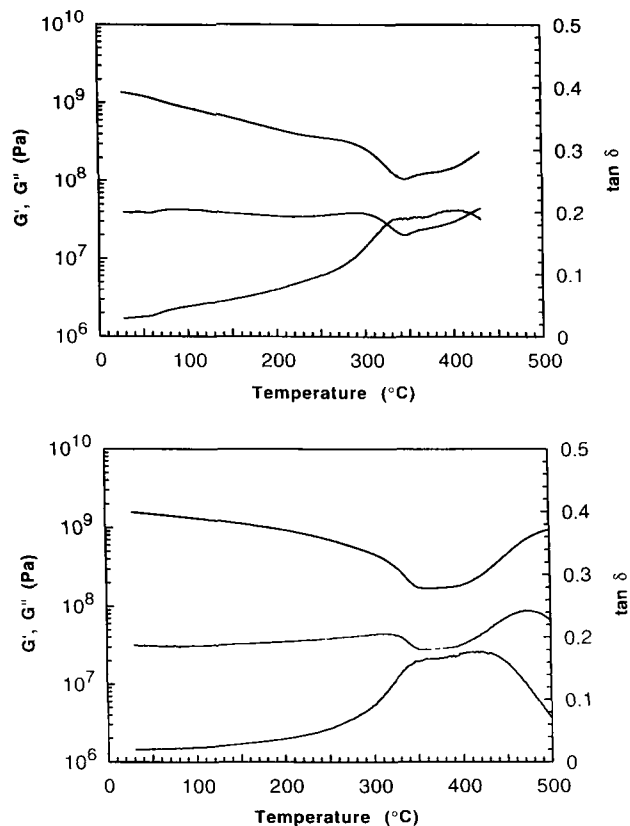
Figure 8 Dynamic mechanical spectra of 15Na polynaphthoxazines cured at (a) 240°C and (b) 290°C for 1 h, in each spectrum from top to bottom: storage modulus G', loss modulus G'', and loss factor tan δ.

for 15Na polynaphthoxazine, which is close to the data of polybenzoxazines (1.0–2.4%).[16,18]

Dynamic Mechanical Analysis

The dynamic mechanical spectra of the 15Na polynaphthoxazine are presented in Figure 8. The increase of G' and G'' after the α transition (T_g) for the 15Na polynaphthoxazine cured at 220°C for 1 h could be an indication of further curing for the incompletely cured polymer, which disappears after postcuring to higher temperatures, i.e., 260°C and above. The increase of G' and G'' after the rubbery plateau for the 15Na cured at 290°C for 1 h might be due to the further crosslinking reactions.[25] This can be supported by the TGA results presented later, which show that a rapid decomposition of 15Na polynaphthoxazine starts at 400–450°C. The minimum postcure temperature to obtain fully cured 15Na polynaphthoxazine is 260°C. The storage moduli at room temperature, G'_{RT}, of 15Na

polynaphthoxazines cured at different conditions are around 1.5 GPa.

The α-transition peaks of the loss factor, tan δ, is associated with the glass transition. The height and area of the α-transition peak could be related to the degree of cure and the crosslink density ν.[26–28] As postcured to higher temperatures, the 15Na polynaphthoxazine continues to achieve higher degrees of cure and crosslink densities that result in lower segmental mobilities, fewer relaxation species, and the shorter and less obvious α-transition peaks.

Figure 9 shows the glass transition temperature of the 15Na polynaphthoxazine as a function of postcure temperature. As the postcure temperatures is raised, the T_gs of 15Na polynaphthoxazines increased without showing a plateau region to achieve the ultimate T_g. It is reasonable to predict that even higher T_gs can be achieved for 15Na polynaphthoxazines if they could be postcured at higher temperatures under higher pressure, i.e., a pressure higher than 1.33 MPa in the autoclave to avoid the problem of void formation.

It is noteworthy that the T_gs of postcured 15Na polynaphthoxazines are always higher than the postcure temperatures applied. This characteristic will be a great advantage for a high-performance polymer because it could be processed at moderate temperature, i.e., 260°C, and still exhibit a high T_g of 305°C. There are only several thermosetting polymers that present such a T_g-higher-than-T_{cure} behavior.[25]

One could attribute such a result to the heat buildup inside the resin during cure because of the exothermic characteristic of benzoxazines.[17,19] Figure 10 presents the 15Na monomer/polymer bulk temperature, which was measured by a thermocouple located inside the resin, as a function of cure time. The 1-cm-thick 15Na monomer was thermally cured
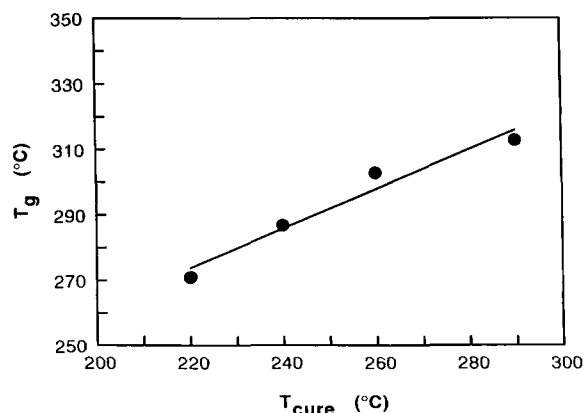
Figure 9 The glass transition temperature (T_g) of 15Na polynaphthoxazine as a function of cure temperature.
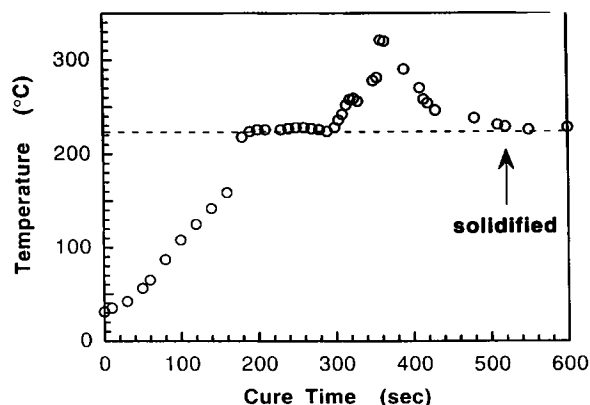
Figure 10 The bulk temperature versus cure time of 15Na naphthoxazine polymerized at the temperature maintained at 222 ± 3°C.

in a small vial that was immersed in an oil bath kept at 222 ± 3°C. Such a curing system was designed to simulate the autoclave process applied to make the DMA test specimens. The 15Na monomer melted and stayed at 223°C between 200 to 300 s and then started to cure and release heat. The temperature of the system raised up to the maximum of 320°C at 380 s and solidified at 520 s. The temperature then came down and stayed at 222°C, which was the same as the external temperature. The product was already crosslinked and could not dissolve in tetrahydrofuran, which is a good solvent for naphthoxazine monomers and uncrosslinked polymers.

As expected, most of the exothermic heat is released in the early stage of curing, and the resin temperature comes down to the environmental temperature after 10 min. This would imply that little or no temperature increase in the postcure stage. Such a result indicates that the heat buildup inside the polymerizing 15Na naphthoxazine can raise the bulk temperature but is not sufficient to explain the high T_g of the postcured product. The T_g-higher-than-T_{cure} behavior might be due to the crosslinking reaction that is not completely quenched in the glassy state when T_g increases and passes over the curing temperature.[25] Furthermore, the high T_g of 15Na polynaphthoxazines could be attributed to its high crosslink density, as can be seen in Table II.

In the frequency/temperature sweep of the DMA tests, different T_gs will be observed at different test frequencies. The activation energy (more accurately, activation enthalpy) of the glass transition can be calculated from the following equation[29]:

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

where ΔH is the activation enthalpy, R is the gas constant, T_{g1}, T_{g2} are the glass transition temperature in Kelvin and related to the test frequencies ω_1 and ω_2, respectively. The Arrhenius plots of 15Na polynaphthoxazines with different T_{cure} are shown in Figure 11. The ΔH remains at the same level, i.e., 155 kcal/mol, for all the curing conditions. This means there is not much change in the relaxation at T_g between polynaphthoxazine molecules with different degree of cure.

From the theory of rubber elasticity, the crosslink density of a cured resin can be determined by the following equation[30]:

$$G = \phi\nu RT = \phi\rho RT/M_c \tag{2}$$

where G is the storage modulus of the cured polymer in the rubbery plateau region above T_g (T_g + 40°C), ϕ is the front factor, R is the gas constant, T is absolute temperature in Kelvin, ρ is polymer density, and M_c is the average molecular weight between crosslinks. The crosslink density ν, also known as concentration of network chains, is the number of network chains per unit volume of the cured polymer. The front factor ϕ is related to the ratio of mean square end-to-end distance between the actual chain and the randomly coiled chain and the ratio of M_c and the average molecular weight before crosslinking. For most crosslinked polymers, the value of ϕ is in the range of 0.5–2.0 and is usually assumed to be unity in most studies in the literature.[28,31-33] It was also treated as unity in this study.

However, eq. (2) stands well only for polymers with low degrees of crosslinking; thus, the results shown here should be regarded only qualitatively
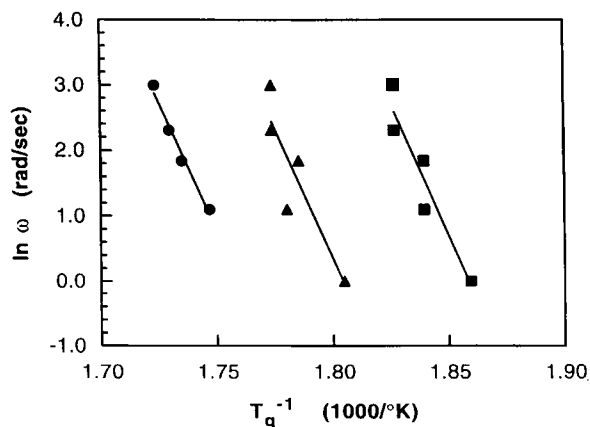
Figure 11 Arrhenius plot of natural logarithmic frequency versus inverse glass transition temperature for 15Na polynaphthoxazines cured at (●) 260°C, (▲) 240°C, and (■) 220°C.
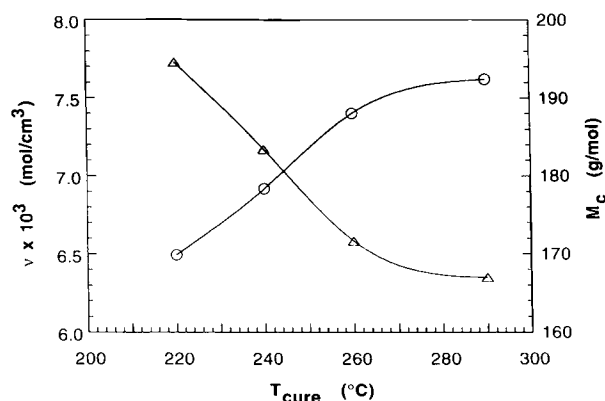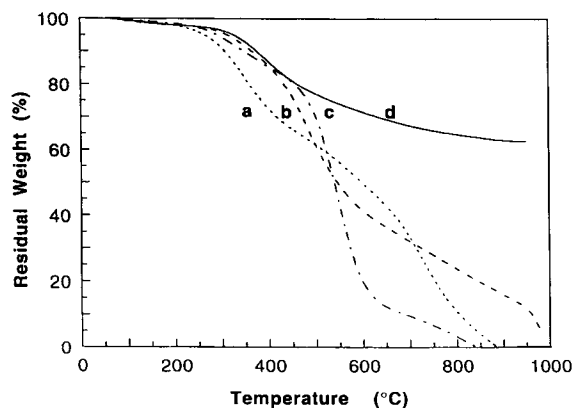
Figure 12   The dependence of crosslink density (○) and the molecular weight between crosslinks (△) on curing temperature for 15Na polynaphthoxazines.

Figure 13   TGA curves of polynaphthoxazines: (a) 2Naa, (b) 26Na, (c) 27Na, and (d) 15Na.

meaningful. By assuming the front factor to be unity, eq. (2) produces the values of M_c for 15Na polynaphthoxazines to be 38–81 g/mol, which are much lower than the real cases. Another semiempirical equation has shown to lead to better agreements between theory and experiments for highly cross-linked systems like epoxies[28,34]:

$$\log_{10}G = 7 + 293\nu = 7 + 293\rho/M_c \qquad (3)$$

where G is in dynes/cm^2, and the valid range is 2 × 10^7 to at least 2 × 10^9 dynes/cm^2.

The ν and M_c calculated from both eq. (3) for 15Na polynaphthoxazine as a function of cure temperature are presented in Figure 12. With the assumption of fully crosslinked and no side reactions, the theoretical molecular weight between crosslinks, $M_{c,t}$, for polymer is 138, which is calculated from the average of two species —C$_{10}$H$_4$O$_2$— and

—CH$_2$(PhN)CH$_2$—. The M_cs of 15Na polymers calculated from eq. (3) were approaching the $M_{c,t}$ (166–194 versus 138) as they were postcured at higher temperatures, which indicates that the crosslinking reactions are nearing completion. As the postcure temperatures increases, 15Na polynaphthoxazines tend to achieve a higher degree of crosslink and level off around a ν of 7.6 mol/cm^3.

Thermal Stability

The thermal properties of 15Na polynaphthoxazine are listed in Table III, including decomposition temperature T_d, defined as the temperature with 5% of weight loss when subjected to TGA test in nitrogen,[35-37] the weight loss after 200 h of isothermal aging in static air, and the char yield from nonisothermal TGA test when subjected to 800°C in nitrogen.

Table III   The Thermal Properties of the 15Na Polynaphthoxazine (PNZ) and Other High-Performance Resins

Materials	T_g (°C)	T_d^a (°C)[34]	10% Wt. Loss Temperature[b] (°C)	Char Yield (%)
15Na PNZ (cured at 260°C for 1 h)	304	325	220	67
Polybenzoxazines[16-18]	150–260	250–400	—	45–65
Phenolics[20,36]	~ 175	—	—	40–50
Epoxies[20,24]	150–261	—	—	≤ 40
Bismaleimides[20,37,39]	250–300	450–500	300–450	50–70

a The temperature at which resin reaches 5% weight loss when subjected to TGA in nitrogen with a heating rate of 20°C/min.
b The temperature at which resin reaches 10% weight loss when subjected to isothermal aging for 200 h in static air.

The TGA curves of the four polynaphthoxazines are presented in Figure 13. These polynaphthoxazines gradually start to decompose from 250 to 300°C. The thermal resistance of 15Na polynaphthoxazine appears to be much better than the other polynaphthoxazines. However, further modification of curing conditions might improve the thermal properties of the other three polynaphthoxazines. The T_d of 15Na polynaphthoxazine cured at 260°C for 1 h is 325°C. The char yield of 15Na polynaphthoxazine after carbonizing to 800°C in nitrogen is 67%, which is quite high in comparison with other polymers. The 15Na polynaphthoxazine could be deemed as a high-char-yield polymer $(\geq 50\%)$[38] and will be a good candidate for the precursor of carbon/carbon composites as well as for fire resistant applications.

To ensure the service temperature of these new resins, the isothermal aging and the stiffness drop at high temperatures in DMA were performed. Figure 14 shows the isothermal weight loss characteristics in static air for 15Na polynaphthoxazines. The temperature at which 10% weight loss occurs for 15Na polynaphthoxazine is 230°C.

After being normalized to the room temperature storage modulus, G'_{RT}, the storage modulus curves of 15Na polynaphthoxazines are presented in Figure 15. These curves show a continuous decrease of stiffness as the temperature is increased. The G' of 15Na polynaphthoxazine increases significantly as the postcure temperature is raised from 240°C to 260°C and remains nearly unchanged as the resin is postcured at 290°C.

By summarizing the results of thermal studies, the estimated maximum service temperature of 15Na polynaphthoxazine was determined to be 200°C. Although the 15Na polynaphthoxazine po-
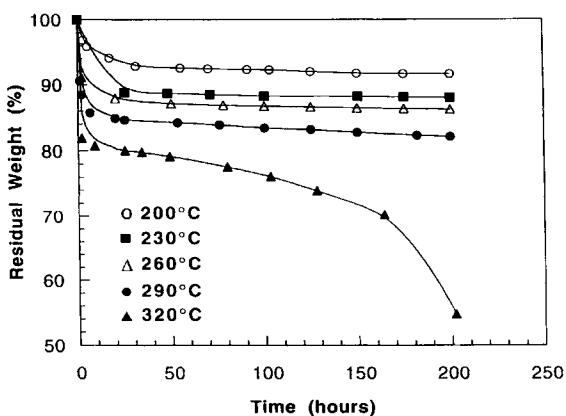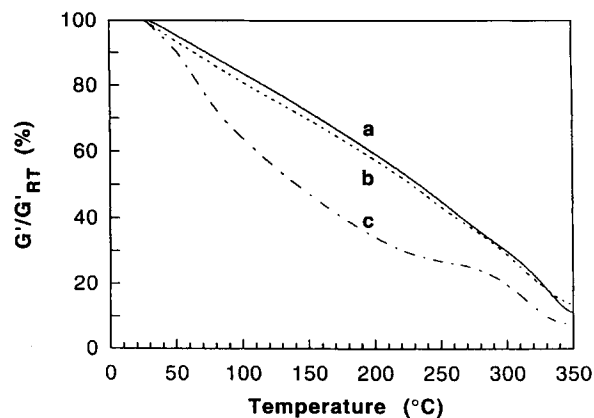

Figure 15 The variation of normalized storage moduli as a function of temperature for 22Pa polybenzoxazines cured at (a) 290°C, (b) 260°C, and (c) 240°C. The room temperature value of G' for each polymer, G'_{RT}, was used as the normalization factor.

stcured at 290°C for 1 h can reach a T_g of 313°C, it starts to lose weight in air from 230°C and the stiffness drop in DMA test shows no improvement as compared with the resin postcured at 260°C for 1 h. Therefore, the postcure temperature for 15Na polynaphthoxazine was chosen as 260°C rather than 290°C.

CONCLUSIONS

Four polyfunctional naphthoxazines, 15Na, 26Na, 27Na, and 2Naa, were synthesized and characterized using NMR. When processed in an autoclave with a maximum pressure of 1.33 MPa, only 15Na was successfully cured to give void-free resin. Further modifications on curing process are needed to obtain useful resins from the other three naphthoxazines.

The room temperature density of 15Na polynaphthoxazine increases with the cure temperature, which could be attributed to the increase of crosslink density after further curing. As postcure temperature increased, the T_g and crosslink density of these polybenzoxazines kept increasing. The maximum T_g achieved for the 15Na polynaphthoxazine is 313°C.

The highly crosslinked 15Na polynaphthoxazine exhibited a T_g-higher-than-T_{cure} characteristic: being capable to process at 260°C and showed a T_g of 304°C. The optimized curing conditions for 15Na polynaphthoxazine is 260°C for 1 h, and the maximum service temperature was determined to be 200°C. The newly developed polynaphthoxazine could exceed epoxies and compete with bismaleimides in terms of mechanical and thermal properties.

Figure 14 Isothermal weight loss of 15Na polynaphthoxazine at different temperatures.

The char yields of the 15Na polynaphthoxazine is 67%, which will make it a good candidate for carbon-carbon composites.

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