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Cresol novolac–epoxy networks: properties and processability

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Abstract

Linear controlled molecular weight *ortho*-cresol novolac oligomers were crosslinked with epoxies to form tough, flame retardant networks with enhanced processability and reduced moisture uptake. At the networks' optimum stoichiometry, the fracture toughness, assessed by the critical stress intensity factor (K_{IC}), was slightly higher for the cresol novolac–epoxy networks (~1.1 MPa $m^{1/2}$) than for similar phenolic novolac–epoxy networks (~0.85 MPa $m^{1/2}$). Cresol novolac–epoxy networks exhibited improved processability under melt conditions relative to phenolic novolac–epoxy materials, and this was attributed to the presence of a methyl group adjacent to the hydroxyl group on cresol repeat units, which reduced the rate of reaction between phenol and epoxy. The use of cresol novolac oligomers also reduced the network equilibrium water absorption, and this was likely due to the presence of the additional methyl on each repeat unit. The equilibrium water absorption for all cresol novolac containing compositions was between 1.7 and 2.1 wt%, comparable to epoxy networks. Cone calorimetry showed that the flame retardance of cresol novolac–epoxy networks was lower than that for the phenolic novolac–epoxy materials, but was far superior to the control epoxy networks. © 2002 Published by Elsevier Science Ltd.

Keywords: Cresol novolac; Novolac; Flame retardant

1. Introduction

Phenolic resins are ideal for structural adhesives and composites since they are flame retardant [1] and cost-effective [2,3]. The major drawback thus far for typical phenolic networks, including both phenolic novolacs cured with hexamethylenetetramine (HMTA) and thermally cured resoles, has been their brittle nature originating from high crosslink densities and high void contents. These typical crosslinking reactions allow little control over network structures and generally lead to highly crosslinked networks. Volatiles such as water and ammonia released during the cure reactions cause the networks to have high void contents.

Curing phenolic novolac resins with epoxies instead of HMTA yields tough, void-free materials. The cure reaction proceeds via nucleophilic addition of the phenolic hydroxyl onto the epoxy group without releasing volatiles [4–6]. These types of materials, in which high compositions of an epoxy component have been cured with phenolic novolacs, have been important in microelectronic packaging applications. However, such materials do not retain the excellent flame properties characteristic of typical phenolic networks since they are mostly comprised of flammable epoxy resins. Previous work from our laboratories has demonstrated that flame retardance, combined with toughness, can be achieved by crosslinking high compositions of relatively high molecular weight novolacs with minor concentrations of diepoxides [7,8]. High phenol to epoxy reagent stoichiometries were utilized to only crosslink the minimum amount of phenols required to achieve low sol fractions, and good toughness and moduli. Hence, relatively high molecular weights between crosslinks (on the phenolic component) in the networks lead to both good mechanical properties and good flame properties.

Commercial phenolic novolacs lack molecular weight control. The phenol monomer is trifunctional, and therefore, branching and even gelation are inevitable as higher molecular weights develop. For example, branching has been shown to occur significantly once the molecular weights reach 900–1000 g/mol [9]. This paper describes properties of related networks with high phenol to epoxy stoichiometries, prepared from linear novolac resins with well-controlled molecular weights [10]. Difunctional

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ortho- or *para*-cresol monomers allow for preparing higher molecular weight linear oligomers without branching. In addition, the presence of a methyl group adjacent to the hydroxy group on *ortho*-cresol was expected to affect the chemistry and the properties of resulting networks. In this study, a 2000 g/mol *ortho*-cresol novolac oligomer was crosslinked with two epoxies, and the network properties and processability were investigated.

2. Experimental

2.1. Materials

Epon 828, a bisphenol-A based diepoxide with an epoxy equivalent weight (EEW) of 187 g/mol was obtained from Shell Chemicals. D.E.N. 438, an epoxidized novolac with a functionality of ~3.5, was supplied by Dow Chemical. A phenolic novolac resin with a molecular weight of ~700 g/mol was donated by Georgia Pacific (Product #GP-2073). *ortho*-Cresol (99 + %), 2,6-dimethylphenol (99%), paraformaldehyde (powder, 95%), formaldehyde (37 wt% solution in water), oxalic acid dihydrate (99%) and triphenylphosphine were obtained from Aldrich. All reagents were used as received.

2.2. Synthesis of a 2000 g/mol ortho-cresol novolac oligomer

The 2000 g/mol *ortho*-cresol novolac oligomer was prepared according to procedures described previously [10]. The M_n of the linear oligomer was controlled by using the Carother's equation to determine the required ratio of the 2,6-dimethylphenol monofunctional endcapping reagent to *o*-cresol. Note that an excess of formaldehyde over the stoichiometric amount was required to achieve good molecular weight control. In a resin kettle equipped with a stainless steel mechanical stirrer and a condensor connected to an outlet, *ortho*-cresol (303.5 g, 2.81 mol) and 2,6-dimethylphenol (47.2 g, 0.39 mol) and paraformaldehyde (94.9 g, 3.0 mol) were added. This mixture, along with oxalic acid dihydrate (2.5 wt% based on the weight of cresol, 7.59 g) was heated for approximately 6 h at 100 °C. An ~10 wt% excess of formaldehyde (37 wt% formaldehyde in water, 27 ml) was then added to the reaction. The reaction was continued for an additional 18 h. It was washed twice with boiling deionized water, then stripped under mild vacuum while being slowly heated to 215 °C.

2.3. Preparation of cresol novolac networks cured with epoxies

A 2000 g/mol *ortho*-cresol novolac resin was cured with a difunctional or a multifunctional epoxy resin using triphenylphosphine as the catalyst. The cresol novolac and ~85% of the required epoxy crosslinking reagent were charged to a three-neck round-bottom flask equipped with a vacuum tight mechanical stirrer and a vacuum adapter. The reactants were heated in an oil bath to 170 °C. Mechanical stirring was begun when the novolac began to soften at ~170 °C. Vacuum was applied incrementally to prevent the material from swelling into the vacuum line. Once full vacuum was achieved (2–5 Torr), the mixture was stirred for about 20 min to degas the blend. During this time, the remaining epoxy with the catalyst (0.1 mol% based on the total concentration of epoxy groups) dissolved in it was degassed in a vacuum oven at ~80 °C. The vacuum was temporarily released to add the remaining epoxy with catalyst. This was stirred for about 4 min under vacuum to fully degas the mixture. The melt was then poured into a mold and placed in a preheated oven. The materials were cured at 200 °C for 2 h and then 220 °C for 2 h.

2.4. Sample preparation for viscosity measurements

Cresol novolac–epoxy mixtures were melt-mixed at 165 °C. The exposure time to heat was maintained less than 3 min to minimize premature curing. The mixed samples were quenched in aluminum pans pre-chilled with dry ice/isopropanol. The samples were ground into powders prior to measurements.

2.5. Formation of a phenolic resole network as a control material for property comparison

A resole resin was cured thermally to form a typical phenolic network (phenolic control). The cure cycle consisted of 70 °C for 4 d, 130 °C for 24 h, then 200 °C for 24 h.

2.6. Sol fraction extraction

The sol and gel fractions of the networks were determined as follows. Film samples of approximately 0.6 g were submerged in ~15 ml acetone for 3 d. The sol fractions were soluble and the gel fractions remained intact. The gel fractions were separated from the sol fractions by filtering the solids from the solutions. The gel fractions were dried in a vacuum oven at 180 °C for 24 h and compared to their initial weights. The acetone in the sol fractions was evaporated at room temperature in a vacuum oven. The sol fractions were also analyzed by ^{1}H NMR to determine their chemical contents.

2.7. Analyses of chemical structures

^{1}H NMR spectra were obtained on a Varian Unity 400 NMR spectrometer. Five millimeter tubes containing approximately 20 mg sample dissolved in DMSO-d_6 were analyzed under ambient conditions. The experimental parameters included a 1.000-s relaxation delay, 23.6°

pulse, and 6744.9 Hz width. Thirty-two repetitions were performed for each sample.

2.8. Thermal and thermo-mechanical properties of cresol novolac–epoxy networks

A Perkin–Elmer dynamic mechanical analyzer (model DMA-7) in a three-point bending mode was used to determine the glass transition temperatures of the cured networks. The T_gs were calculated from the peaks in the tan δ curves. The static force was set to 120 mN and the dynamic force was set to 100 mN. Samples were heated at 5 °C/min from 25 to 200 °C. Two samples of each material were measured and the results were averaged.

One dimension thermal expansion was also measured using a thermal mechanical analyzer equipped with a large quartz parallel plate. The coefficients of thermal expansion (CTE) were determined by calculating the slopes of the expansion curves vs. temperature above and below the glass transition temperatures of the materials.

Room temperature density measurements were conducted using a Mettler-Toledo AG204 balance adapted with a Mettler-Toledo density determination kit for AT/AG and PG/PR balances. Network samples with dimensions of approximately 19 mm × 6.4 mm × 3.2 mm were sanded, then polished, to prevent any trapping of air bubbles in the sample surfaces. Deionized water was degassed in a vacuum oven at room temperature for 30 min prior to use. The weight of the solid in air (A) and the weight of the solid in water (B) were measured. The temperature of the water was controlled to within 0.1 °C and the density of distilled water at that temperature ($\rho(\mathrm{H_2O})$) was obtained from a density table. Room temperature densities were calculated according to Eq. (1).

$$\rho = [A/(A - B)]\rho(\mathrm{H_2O}) \tag{1}$$

The densities at $T_g + 50$ °C were calculated using the densities at room temperature and the CTE below and above the T_g.

2.9. Mechanical properties of cresol novolac–epoxy networks

The critical stress intensity factor, K_{1C}, was used to evaluate the fracture toughness of the phenolic-epoxy networks. The K_{1C} values were obtained from a three-point bend test using an Instron instrument, according to ASTM standard D5045-91. The specimens had a thickness ($b \sim 3.1$ mm) and a width ($w \sim 6.3$ mm). The single edge notched bending method was used. First, a sharp notch was created in the sample by sawing. The sample was placed in a vise, a cold razor blade (which had been immersed in liquid nitrogen) was inserted into the notch and force was applied to initiate a natural crack. The depth of the crack (a) was between 40 and 60% of the width (w). The pre-cracked notched specimen was loaded crack-down in a three-point bend fixture and tested using an Instron model 4204 instrument. The single edge notched bending rig had moving rollers to avoid excess plastic indentation. The three-point bend fixture was set so that the line of action of applied load passed midway between the support roll centers within 1% of the distance between these centers. The crosshead speed was 1.27 mm/min, and the testing was conducted at room temperature. The critical stress intensity factor, K_{IC}, was calculated using the following equation.

$$K_{\mathrm{IC}} = \frac{PS}{bw^{3/2}} \frac{3(x)^{1/2}[1.99 - x(1 - x)(2.15 - 3.93x + 2.7x^2)]}{2(1 + 2x)(1 - x)^{3/2}} \tag{2}$$

where P is the maximum load (kN), S the span (cm), b the specimen thickness (cm), w the specimen depth or width (cm), a the crack length, and x is the ratio of crack length to width of the specimen (a/w).

The rubbery moduli of networks at 50 °C above their glass transition temperatures were determined using creep tests via a Dynastat instrument. Samples with dimensions of 19 mm × 6.3 mm × 3.1 mm were placed in a three-point bend fixture and were heated to 50 °C above T_g. A small load (0.01 kg) was placed on the samples and the displacements at equilibrium were measured. The load was increased by increments of 0.01 kg up to about 0.08 kg while the equilibrium displacement was recorded at each load. The slopes of the load versus displacement curves were used to determine the moduli according to Eq. (3)

$$E = g\left(\frac{P}{\Delta}\right)\left(\frac{L^3}{48I}\right) \tag{3}$$

where g is the gravitational constant = 9.81 m/s^2, P/Δ the slope of load vs. displacement, L the length between supports = 2.54 cm, I is equal to $(1/12)wb^3$, and w and b are the width and height of samples, respectively. The displacement values measured from the Dynastat were accurate to within 0.05 mm.

According to the theory of rubber elasticity, the number average molecular weight between crosslinks (M_x) is inversely proportional to the rubbery modulus

$$M_x = 3RT\rho/E \tag{4}$$

where R is the gas constant, T (K) the experimental temperature ($T_g + 50$ K), ρ the density at $T_g + 50$ K calculated from the room temperature density and the CTE of the samples, and E is the elastic modulus obtained from the Dynastat measurements.

2.10. Equilibrium moisture absorption

To investigate moisture uptake, samples with dimensions of approximately 19 mm × 6.4 mm × 1 mm were dried in a

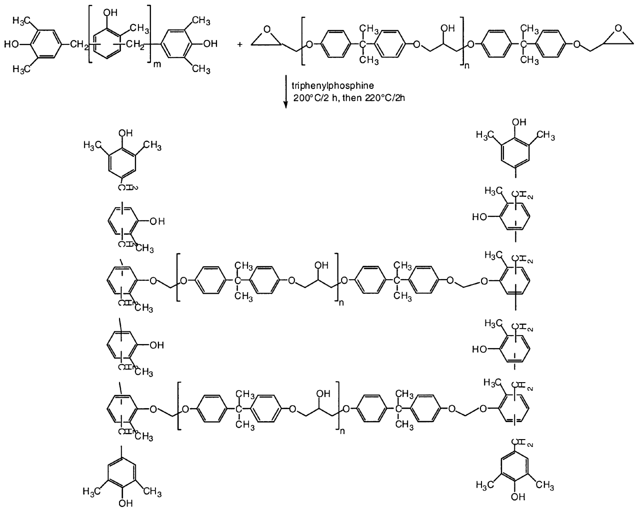

Fig. 1. Cresol novolac–epoxy network formation reaction with high stoichiometric and weight compositions of the flame resistant novolac component.

vacuum oven for 12 h at 150 °C. The initial weight of each sample was recorded. The samples were then submerged in vials containing deionized water. The weight of each sample was measured as a function of time until an equilibrium water uptake was reached. Water absorption at room temperature and at 62 °C were determined.

2.11. Flame properties

Cone calorimetry was used to measure the flame properties of the cresol novolac–epoxy networks. Panels of approximately 6.3 mm thick and a surface area of $10 \times 10\ \mathrm{cm}^2$ were tested in a horizontal orientation with a $50.0\ \mathrm{kW/m^2}$ incident heat flux in a controlled atmosphere cone calorimeter. The ignitability, peak heat release rate, evolution of CO and CO_2, and the time to sustained ignition were recorded.

2.12. Melt processability

Dynamic complex viscosities were measured using a Bohlin Rheometer operating in continuous oscillation mode with a frequency of 1 Hz. Temperature control was accomplished with a Bohlin HTC. The auto-strain was set to maintain the torque at 25% of the maximum torque allowed. The maximum strain for the instrument was 0.25. Approximately 0.7 g of dry powder were pressed into pellets, then placed between the preheated 25 mm diameter parallel plates of the rheometer. The gap was closed to approximately 1 mm and the sides were scraped to remove excess sample before the measurement was begun.

A Brookfield DV-III Programmable Rheometer was used to determine the isothermal viscosities of novolac–epoxy mixtures at the processing temperatures. Approximately 10 g of powdered samples were placed in disposable sample tubes and heated to the test temperatures. A spindle, which was driven through a calibrated spring, was immersed in the test fluid. The viscous drag of the fluid against the spindle was measured by the spring deflection. The torque was used to calculate the viscosities.

3. Results and discussion

Tough, flame retardant, melt processable, phenolic novolac–epoxy networks were previously studied in our laboratories [7,8]. The phenolic novolac resins were prepared from trifunctional phenol and formaldehyde and were thus branched structures. The goal of the present research was to improve the processability and reduce the network moisture absorption of novolac–epoxy networks while maintaining thermal and mechanical properties as well as flame retardance.

A 2000 g/mol *ortho*-cresol novolac oligomer was crosslinked with epoxies to form void-free phenolic networks (Fig. 1). The crosslinking of novolacs with epoxies proceeds via nucleophilic attack of a phenolate ion to ring-open an epoxide. Typical nucleophiles such as triphenylphosphine initiate this curing reaction by first opening an epoxide, thus generating an alkoxide that rapidly abstracts a phenolic proton. The resultant phenolate ion is the active species for epoxy crosslinking. These cresol novolac oligomers differed in both chemistry and properties from the phenolic novolac resins previously studied in our laboratories. The cresol novolac oligomers were linear as opposed to the lightly branched structures typically found in phenolic resins. The 2000 g/mol cresol novolac resin also had a significantly higher molecular weight than the phenolic novolac resins reacted in our previous studies (700–800 g/mol). In addition, the *ortho*-methyl with respect to the hydroxyl group on each cresol repeat unit increased hydrophobicity and reduced reactivity of the hydroxyl groups.

The cresol novolac oligomers were crosslinked with each of two epoxies; a bisphenol-A diepoxide (Epon 828) and an epoxidized novolac (D.E.N. 438, average functionality of 3.5). The diepoxide offered superior processability since it greatly reduced the melt viscosities of the cresol novolac–epoxy resin mixtures.

Properties of the cresol novolac based networks were compared to a series of 'control' thermosets. These included an epoxy control prepared from the difunctional epoxy reagent (Epon 828) crosslinked with a stoichiometric concentration of p,p'-diaminodiphenylsulfone; a phenolic control which was a thermally cured resole network; and a phenolic novolac-Epon 828 epoxy network (65:35 wt/wt ratio) [7]. This latter control composition was chosen because our previous work had demonstrated this to have excellent flame properties combined with good mechanical properties.

Table 1
Compositions and properties of cresol novolac/epoxy networks compared to a series of control thermosets

Epoxy	Novolac (wt%)	OH/epoxy	K_{1C} (MPa m$^{1/2}$)	Sol fraction (wt%)
Epoxy control	–	–	0.62	–
Phenolic control	–	–	0.16	–
Phenolic Nov/Epon 828	63	3.0:1	0.85	12.5
Cresol Nov/Epon 828	80	6.2:1	0.65 ± 0.06	16.7
Cresol Nov/Epon 828	70	3.6:1	1.06 ± 0.04	5.4
Cresol Nov/Epon 828	60	2.3:1	1.20 ± 0.12	7.1
Cresol Nov/D.E.N. 438	80	5.0:1	0.46 ± 0.04	15.6
Cresol Nov/D.E.N. 438	70	2.9:1	1.05 ± 0.09	4.3
Cresol Nov/D.E.N. 438	60	1.9:1	1.08 ± 0.10	11.7

3.1. Network formation and structure

Sol fractions of these networks provided one means for evaluating the extent of crosslinking as a function of weight fractions of the components (Table 1). In general, the 70:30 wt/wt and 60:40 wt/wt novolac–epoxy compositions had low sol fractions, indicating that most oligomers had been incorporated into the networks. The 80:20 wt/wt novolac–epoxy compositions had significantly higher sol fractions. These results indicated that the networks comprised of 80:20 wt/wt cresol novolac-Epon 828 epoxy (6.2 hydroxyls per epoxy) did not form sufficiently well-connected networks. This was surprising since the 2000 g/mol oligomers had an average of 15.5 hydroxyls per chain. ^{1}H NMR of the soluble fractions indicated that only traces of epoxides were in the networks high in novolac (80:20 and 70:30 wt/wt cresol novolac–epoxy networks), suggesting that almost all epoxies had been incorporated (Fig. 2). The sol extracts from the 60:40 wt/wt networks, on the other hand, contained large amounts of unreacted epoxies, even though these had stoichiometric excesses of phenol. 'Post-curing' well above T_g also did not promote further reactions. Thus, it was reasoned that these networks may have been too dense and the lack of molecular mobility probably prevented further cresol hydroxyl-epoxy reactions.

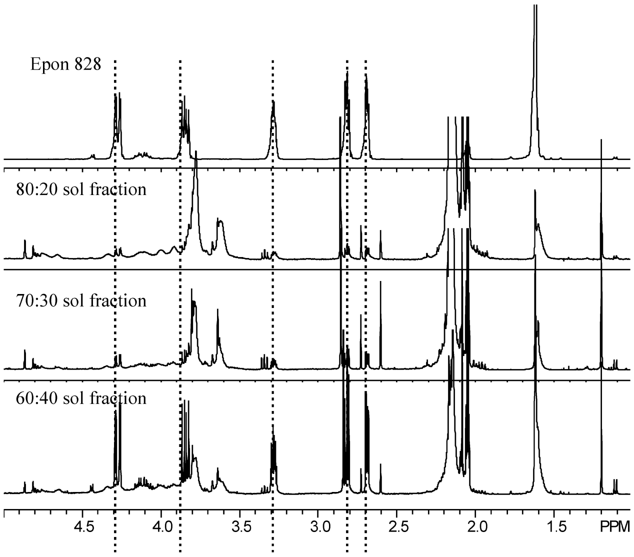

Fig. 2. ^{1}H NMR analyses of the soluble fractions extracted from networks prepared from Epon 828 and the 2000 g/mol cresol novolac oligomer: The sol fraction from the 6:40 wt/wt cresol novolac:diepoxide had significant concentrations of epoxy groups remaining.

To further understand the network structures, the average molecular weights between crosslinks (M_xs) were calculated from rubbery moduli using the theory of rubber elasticity, which inversely relates rubbery modulus and M_x (Eq. (4)). Rubbery moduli were measured in creep tests conducted in a three-point bend configuration at $T_g + 50$ K. An apparent molecular weight between crosslinks was calculated for each network using the density at $T_g + 50$ K and the observed rubbery moduli (Table 2). It should be noted that rubbery moduli are generally measured on extracted networks containing only the gel fractions. However, the rubbery moduli were measured on unextracted networks in these experiments.

For cresol novolac-Epon 828 networks, the 70:30 wt/wt novolac–epoxy composition exhibited the highest rubbery modulus and therefore the lowest apparent M_x. The calculated M_x (1510 g/mol) was reasonable for well-connected networks prepared with a 2000 g/mol oligomer. Of the three compositions studied, the 70:30 wt/wt cresol novolac–epoxy composition (3.6 hydroxyls per epoxy) was considered optimum, where all the epoxy groups were reacted into the networks and the apparent M_x was most reasonable. The rubbery modulus decreased and the corresponding M_x increased at the 80:20 composition. This expected higher M_x was attributed to a looser network formed with less crosslinking agent. When the cresol novolac concentration was decreased to 60 wt%, the rubbery modulus again decreased. According to the ^{1}H NMR analyses of sol fractions, significant epoxy groups remained unreacted in this composition. Thus, the reduced rubbery modulus and concomitant increase in the apparent M_x were attributed to low molecular weight fractions, along with dangling chain ends, which did not contribute mechanically. Similar trends were observed for the D.E.N. 438 epoxy cured cresol novolac networks.

Both the glassy and the rubbery moduli were evaluated from plots of 10-s stress relaxation moduli versus temperature. As expected, the rubbery moduli for both Epon 828 and D.E.N. 438 cured cresol novolac networks increased as the network crosslink density increased (Table 3). For most materials, the same trends are observed for the glassy moduli where higher crosslink densities lead to slightly higher glassy moduli. Interestingly, in the series of cresol novolac networks cured with Epon 828, the glassy modulus for the 80:20 wt/wt composition was significantly higher than those for the 70:30 and 60:40 compositions. This increase in the glassy modulus for the 80:20 composition was most likely due to its ability to form strong hydrogen bonds between unreacted phenolic hydroxyl groups. The hydrogen bond interactions did not

Table 2
Crosslink densities of cresol novolac/epoxy networks

Epoxy	Novolac (wt%)	T_g (°C)	ρ (25 °C)	ρ (T_g + 50 K)	Modulus T_g + 50 K	M_c
Epon 828[a]	65	127	1.23	1.18	9.35×10^6	1413
Epon 828[b]	80	144	1.178	1.163	1.82×10^6	6650
	70	154	1.183	1.168	8.25×10^6	1510
	60	133	1.181	1.168	3.20×10^6	3730
D.E.N. 438[b]	80	145	1.199	1.184	2.63×10^6	4700
	70	152	1.191	1.173	9.12×10^6	1360
	60	142	1.191	1.174	8.02×10^6	1510

[a] Phenolic novolac–epoxy networks.
[b] *o*-Cresol novolac–epoxy networks.

play an important role in the 70:30 and the 60:40 compositions since more hydroxyl groups were reacted with epoxies at these compositions. It is interesting to note that similar trends were previously observed for phenolic novolac-Epon 828 networks [7]. The hydrogen bonding interaction that affected the glassy moduli was not observed for D.E.N. 438 cured cresol novolac networks (Fig. 3). The glassy moduli of all compositions were comparable.

3.2. Thermal and mechanical properties of the networks

The glass transition temperature is a dominating factor in determining the upper use temperatures for polymeric materials. Relationships between network structure and T_g were explored to understand effects of crosslink density, and sol concentration/dangling ends (Table 1). For both series of materials, the T_g was highest for the 70:30 wt/wt cresol novolac–epoxy networks. This was consistent with the low sol fractions and higher crosslink densities calculated from rubbery moduli for these compositions. By contrast, the 60:40 wt/wt cresol novolac–epoxy networks, which contained a significant amount of unreacted epoxy groups, had lower T_gs. The 80:20 compositions also exhibited lower T_gs due to their lower crosslink densities and higher sol fractions. T_gs of the cresol novolac/epoxy networks were significantly higher than those of the phenolic novolac–epoxy networks at comparable compositions and M_x. This may be attributable to the stiffer nature of cresol novolac chains, which results from the 'extra' methyl on each repeat unit.

Table 3
Flame properties of cresol novolac/epoxy networks measured by cone calorimetry

Networks	Phenolic/epoxy (wt/wt)	PHRR (kW/m^2)	Char yield (wt%)
Epoxy control	–	1230	5
Phenolic control	–	116	63
Phenolic Novo/Epon 828	35:65	357	29
Cresol novolac/Epon 828	70:30	448	16
	80:20	391	15
Cresol novolac/D.E.N. 438	60:40	380	17
	70:30	404	18
	80:20	310	18

The network structures were also correlated with their mechanical properties, specifically the fracture toughness, which was measured by the plane-strain stress intensity factor (K_{IC}) (Table 1). Higher K_{IC} values correspond to

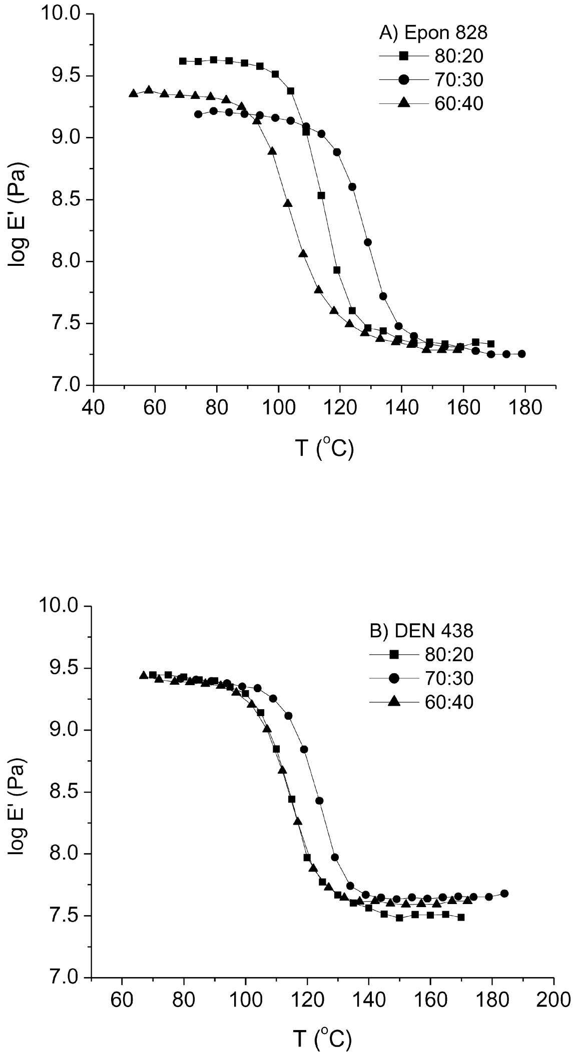

Fig. 3. Ten second relaxation moduli as a function of temperature for (A) cresol novolac-Epon 828 networks and (B) cresol novolac–D.E.N. 438 networks.

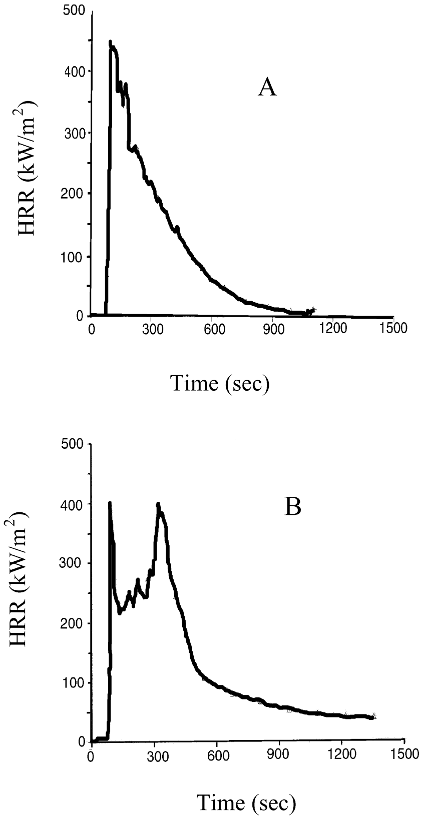

Fig. 4. Cone calorimetry results of (A) cresol novolac-Epon 828 (70:30 wt/wt ratio) and (B) cresol novolac–D.E.N. 438 (70:30 wt/wt ratio).

improved resistance to crack propagation or increased toughness. For both series of networks prepared from the two epoxy reagents, the 60:40 wt/wt cresol novolac–epoxy networks exhibited the highest fracture toughness and this remained relatively high as the novolac composition was increased to 70 wt%. The toughness decreased drastically when the novolac content was increased to 80 wt%. These results confirmed that sufficiently well-connected networks are necessary to achieve good mechanical properties. The residual sol fractions in the 60:40 wt/wt compositions decreased the apparent M_x, but did not result in low fracture toughness. The less crosslinked networks at the 80:20 compositions resulted in brittle materials. Both the 70:30 and 60:40 wt/wt cresol novolac–epoxy networks were tougher than the epoxy control, the phenolic control, and the 65:35 wt/wt phenolic novolac-Epon 828 control.

3.3. Flame results

Flame properties of the cresol novolac–epoxy networks were investigated by cone calorimetry with an incident heat flux of 50 kW/m^2 and 20.9% O_2 (atmospheric oxygen). The heat release rate curves, measured as a function of time, showed different burning profiles for the networks cured with the diepoxide (Epon 828) versus those crosslinked with the multifunctional epoxy reagent (D.E.N. 438) (Fig. 4). The peak heat release rate (PHRR) occurred at the ignition point for networks cured with Epon 828, then the heat release rate decreased rapidly as a function of time. Networks cured with the D.E.N. 438 epoxy showed an initial spike at ignition, but then the heat release rate gradually increased to a maximum followed by a rapid decline. For these networks, the maximum for the bulk heat release rate was recorded as the peak heat release rate. The burning characteristics of the cresol novolac–D.E.N. 438 networks may be more desirable since longer times were required to reach the peaks in the heat release rates, and this is more representative of flame resistant, char-forming materials.

As expected, networks containing higher novolac concentrations exhibited lower peak heat release rates since the novolac contributed to the flame resistance (Table 3). The peak heat release rates of cresol novolac-Epon 828 networks were higher than for the phenolic novolac-Epon 828 networks at similar compositions. The methyl groups on the cresols may have contributed to the higher peak heat release rates by contributing a slightly higher aliphatic content. However, the peak heat release rates of all cresol novolac–epoxy networks (300–450 kW/m^2) were significantly lower than the epoxy control (1230 kW/m^2).

Char formation during burning is desirable because it may form a protective isolation layer at the surface. According to the cone calorimetry results, there were no significant differences in the char yields between the various cresol novolac–epoxy network compositions (15–18 wt% char as described in Table 3). By contrast, the char yields were significantly higher for phenolic novolac-Epon 828 networks (29–33 wt% char) with similar weight compositions. This suggests that increasing the branched structure on the flammable epoxy component does not lead to significant char (this component seems to burn whether one uses difunctional or multifunctional epoxies), whereas increasing the branching capacity of the less flammable novolac component has significant positive impact on char formation during burning. These effects are undoubtedly enhanced by the high novolac to epoxy concentrations also. It is noteworthy that the phenolic network prepared from the resole resin (without any flammable epoxy reagent) produced much more char upon burning relative to the novolac–epoxy networks (~63 wt%) and the epoxy control material (without any more flame resistant novolac or resole) produced only ~5 wt% char. Thus, the positive effect of tailoring the chemistry of materials to achieve flame properties is clear.

3.4. Water absorption

Moisture sorption in composite matrix materials is undesirable because it can cause hydrolytic degradation in both the matrix or at an interface during long-term use. Typical phenolic materials are fairly hydrophilic because each phenolic repeat unit contains a free hydroxyl group [7].

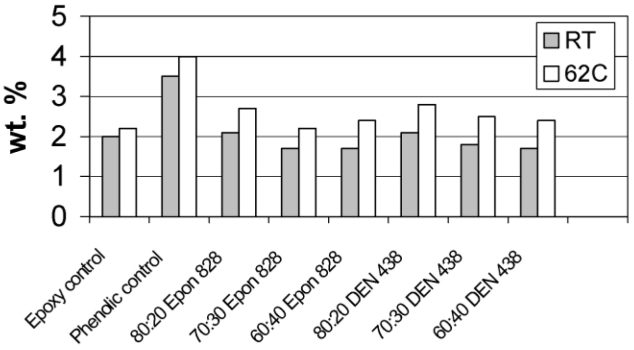

Fig. 5. Water uptake results for *o*-cresol novolac networks at room temperature and 62 °C.

In addition, typical phenolic networks have high void content which further increase the water absorption [2]. Networks comprised of the *o*-cresol novolac oligomers, by contrast, absorbed significantly less moisture, probably as a result of the hydrocarbon methyl substituents in close proximity to the hydroxyl groups (Fig. 5). All of the cresol novolac–epoxy networks showed low equilibrium water uptake (1.8–2.2 wt%) comparable to that of a hydrophobic, control epoxy network (2 wt%).

Equilibrium moisture uptake was studied at both room temperature and 62 °C for a systematic series of *o*-cresol novolac–epoxy networks and direct comparisons were made to analogous materials prepared from phenolic novolac–epoxy resins (Fig. 5). The 62 °C water uptake test was designed as an accelerated protocol, but as expected, the networks also absorbed more water at higher temperatures. All of the cresol novolac based networks had significantly lower equilibrium moisture uptake than similar phenolic novolac materials. For example, at room temperature, the more polar 65:35 wt/wt phenolic novolac-Epon 828 networks absorbed 3.5 wt% water whereas the 70:30 wt/wt cresol novolac-Epon 828 network absorbed only 1.9 wt% water. The water absorption properties of the cresol novolac–epoxy networks were dominated by the cresol novolac component and were found to be relatively unaffected by the structures of the epoxies. As expected, the 80:20 wt/wt cresol novolac–epoxy networks absorbed slightly more water than the 70:30 wt/wt and the 60:40 wt/wt analogues, probably as a result of having higher concentrations of polar phenol groups in the higher novolac compositions. It is also possible that the higher water absorption arises from the looser network structures formed with the 80:20 composition.

3.5. Processability

The novolac–epoxy resin compositions studied in this research were evaluated for their potential use in tough, flame retardant composites. For any composite fabrication method from the melt, the novolac–epoxy resin mixtures must be heated well above their T_gs to obtain sufficiently low processing viscosities (2–10 Pa s). However, novolacs react with epoxies at elevated temperatures even in the absence of an added catalyst; and even a small amount of reaction greatly increases the viscosity. Therefore, it was important to identify the temperature–time limits of a ‘processing window’, wherein the novolac–epoxy mixtures could be melt fabricated into composites.

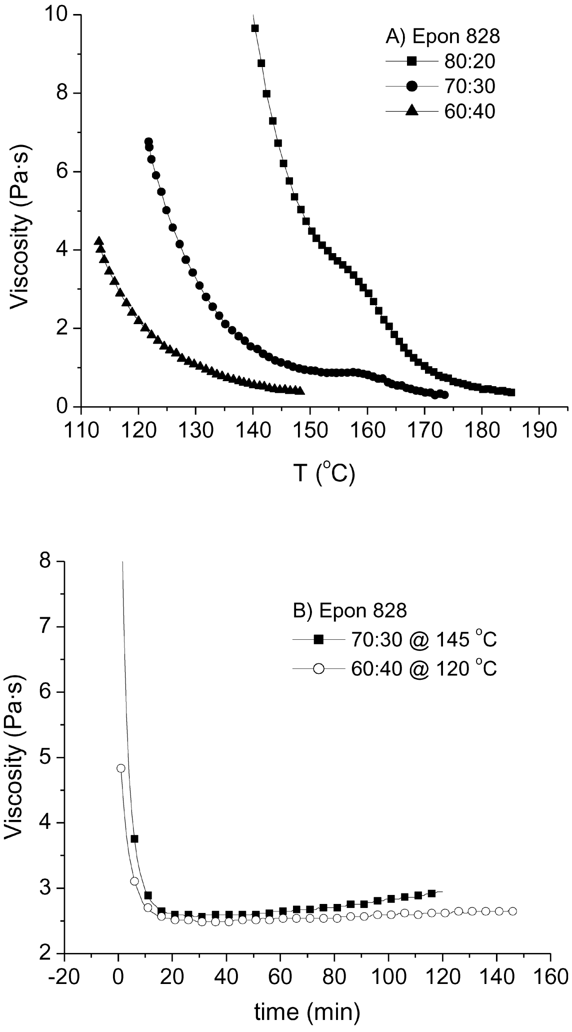

Fig. 6. Viscosity measurements of cresol novolac-Epon 828 mixtures (A) dynamic temperature scans for various compositions and (B) isothermal scan of the 70:30 wt/wt cresol novolac–epoxy composition at 145 °C and the 60:40 composition at 120 °C.

Viscosity measured as a function of temperature for cresol novolac-Epon 828 mixtures showed that increased epoxy content reduced the melt viscosity (Fig. 6(A)), and therefore, the processability was enhanced as the amount of low molecular weight epoxy was increased. From the viscosity measurements as a function of temperature, the temperature at which the viscosity reached approximately 2 Pa s was chosen as the ‘processing temperature’. Higher processing temperatures were necessary for compositions with lower concentrations of epoxies. The isothermal viscosities were evaluated at the processing temperatures of each composition to determine the processing windows (Fig. 6(B)). The 70:30 and 60:40 wt/wt cresol novolac–epoxy

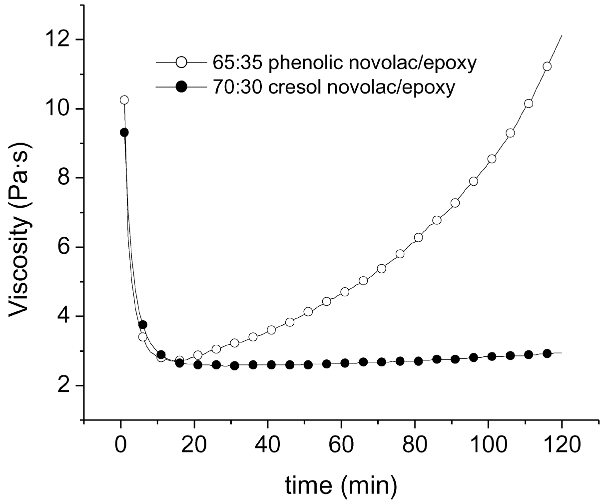

Fig. 7. Isothermal viscosity measurements of a 65:35 wt/wt phenolic novolac-Epon 828 mixture measured at 140 °C and of a 70:30 wt/wt cresol novoalc-Epon 828 mixture measured at 145 °C.

compositions both exhibited excellent viscosity stabilities at their processing temperatures (145 and 120 °C, respectively) with minimal viscosity increase over 150 min.

Isothermal viscosities were measured for the 65:35 wt/wt phenolic novolac-Epon 828 mixture (140 °C) and compared with those of the 70:30 cresol novolac-Epon 828 mixture (145 °C) (Fig. 7). The cresol novolac–epoxy mixture showed only a slight viscosity increase (from 2.5 to 3 Pa s) over a 2 h period, whereas the viscosity of the phenolic novolac–epoxy mixture increased substantially over the same period (3–12 Pa s). Thus, the processing window for the cresol novolac–epoxy mixtures is significantly more desirable than for the phenolic novolac–epoxy mixtures. This enhanced processability was attributed to the slower reactivity of cresol novolac with epoxy groups relative to phenolic novolacs. The methyl group *ortho* to the hydroxyl group probably caused increased steric hindrance of the phenolic hydroxyl-epoxy reactions. It should be noted that this methyl substituent reduced the rate of reaction between the epoxy and novolac components at all temperatures. As expected, a longer time was required to fully cure cresol novolac–epoxy networks relative to the phenolic analogues.

D.E.N. 438 epoxy was not as effective as Epon 828 epoxy in reducing the melt viscosities of the respective mixtures (Fig. 8(A)). At the same novolac–epoxy compositions, higher temperatures were needed to obtain similar viscosities with D.E.N. 438. All cresol novolac–D.E.N. 438 mixtures required at least 160 °C to reach processable viscosities. At these temperatures, the inherent reaction between cresol novolac and epoxies became apparent as the viscosities increased from approximately 1.5 Pa s to approximately 3 Pa s over 100 min (Fig. 8(B)).

A 2000 g/mol *para*-cresol novolac oligomer was also used to form crosslinked networks. However, the melt viscosities of the *para*-cresol novolac resins tended to increase rapidly at elevated temperatures, which prevented homogeneous mixing of the resin components. These processing issues resulted in networks with poor properties.

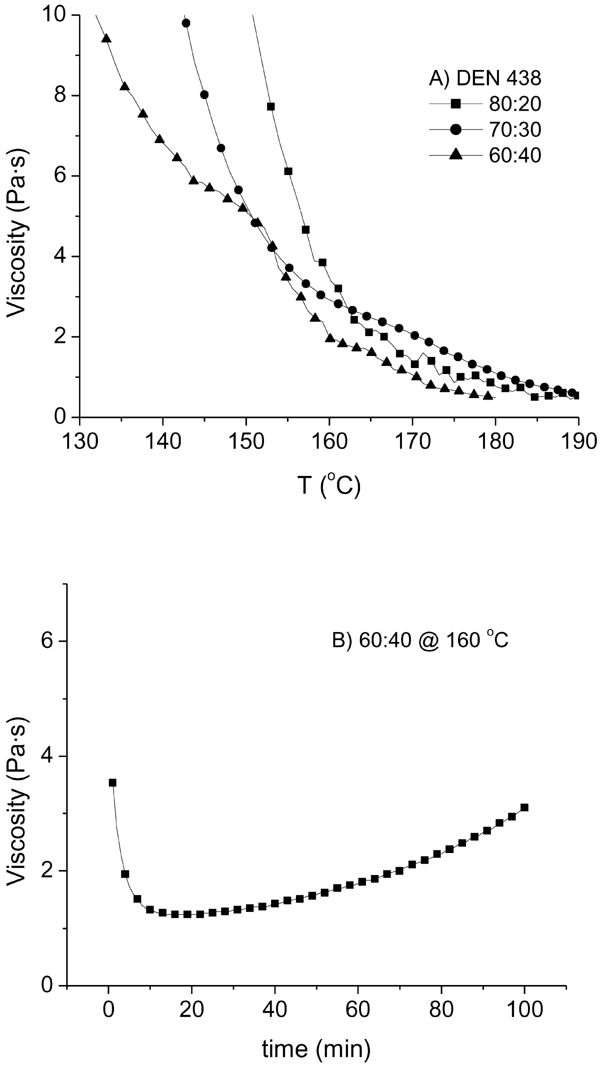

Fig. 8. Viscosity measurements for cresol novolac–D.E.N. 438 mixtures (A) temperature scan and (B) isothermal scan for the 60:40 composition at 160 °C.

4. Conclusions

ortho-Cresol novolac–epoxy networks with high compositions of the novolac component had good toughness, high glass transition temperatures, and low moisture sorption, combined with reasonably good flame properties. The 70:30 and 60:40 wt/wt cresol novolac–epoxy compositions exhibited K_{IC} toughness values >1 MPa m$^{1/2}$ and glass transition temperatures >140 °C. These properties were superior to the epoxy control, the phenolic control and the phenolic novolac–epoxy networks (65:35 wt/wt ratio).

ortho-Cresol novolac–epoxy networks also exhibited significantly lower equilibrium water absorption relative to similar phenolic novolac–epoxy materials. Apparently, the *ortho*-methyl group on each novolac repeat unit inhibited water absorption around the polar hydroxyl groups. Equilibrium water uptake for the cresol based materials was similar to the epoxy control (~2 wt% at room temperature).

The peak heat release rates of cresol novolac–epoxy networks ranged between 300 and 450 kW/m^2 measured by cone calorimetry at an incident heat flux of 50 kW/m^2. The presence of a methyl group on each repeat unit slightly increased the peak heat release rates, and reduced the char yields of cresol novolac networks relative to those of phenolic novolac networks at similar compositions. The flame properties of all novolac–epoxy networks were significantly improved compared to those of the epoxy control, but inferior to that of the phenolic control.

Cresol novolac resins gave rise to longer processing windows when mixed with epoxies at elevated temperatures. This was attributed to the methyl group in close proximity to the hydroxyl group, which sterically hindered the phenolic hydroxyl-epoxy reaction.

Acknowledgements

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