polymer

Flame retardant novolac–bisphthalonitrile structural thermosets

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Abstract

Void-free, thermoset networks prepared from phenolic novolacs cured with bisphthalonitrile (BPh) reagents display attractive mechanical, thermal, and fire characteristics. The network properties depend strongly on the novolac–BPh composition. Networks containing 15 wt% BPh or greater had T_gs above 180 °C and good fracture toughness ($K_{1c} \sim 0.8$ MPa m$^{1/2}$). Cone calorimetry results for an 80:20 (wt/wt) novolac/BPh network, at an incident heat flux of 50 kW/m^2, demonstrated a peak heat release rate of 137 kW/m^2 and char yields $> 50\%$. These excellent flame properties are similar to those of phenolic resole networks, which are brittle but known to be flame retardant.

The cure reaction between the novolac and BPh was monitored by the disappearance of the nitrile peak at 2200 cm^{-1} in the FTIR. The nitrile was $\approx 90\%$ consumed after 1 h at 200 °C and ~ 20 min at 220 °C.

The molecular structure of a novolac–BPh crosslink was studied in model reactions using monofunctional phenols. 2-Hydroxydiphenylmethane was reacted with BPh in the melt at 200 °C for 3 h using a 25:1 molar ratio (6.1:1 eq. ratio) of 2-hydroxydiphenylmethane/BPh. FTIR and ^{1}H NMR suggested that the product generated from the model melt reaction contained a diiminoisoindoline structure. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Phenolic networks have found many industrial applications ranging from aerospace to electronics and consumer goods since Baekeland patented the first processing technique for the production of phenol–formaldehyde resins in 1907 [1]. These materials have as their principal attributes the combination of good flame performance and low cost. The flame resistance of these networks is attributed to their highly aromatic character, and possibly also to the inhibiting effect of the phenol groups against oxidative degradation [2,3]. They form large amounts of char upon burning, which causes slow burning rates and incomplete combustion. These performance characteristics make phenolic networks good matrix candidates for light-weight composites used in civil structures and transportation vehicles. In the interest of public safety, materials used in enclosed civil structures must have low combustibility and smoke toxicity. The limiting factor for most organic matrix composites is their lack of thermo-oxidative stability under intense heat such as fire.

Conventional curing reactions for novolac resins require a formaldehyde source, which is often hexamethylenetetramine (HMTA) [3,4]. These curing reactions, however, generate volatile side products such as formaldehyde, ammonia and organic amines [2], which in turn lead to voids in the networks or composites, and which compromise the strengths of the materials. Resoles can cure thermally without added crosslinking reagents, but these reactions also eliminate volatiles (e.g. water, formaldehyde) which cause voids. Therefore, most current phenolic resole or novolac networks have limited utility in structural applications due to poor mechanical properties.

Recent research has focused on curing novolac resins with reagents that do not generate volatiles upon cure to improve the toughness of phenolic networks. Indeed important products exist based on epoxy-cured phenolics where the epoxy reagent is the major component [5]. In some cases these materials comprise the base resins for semiconductor packaging because they have better hydrophobicity when compared to amine cured epoxies. These materials display good toughness but the high epoxy concentration undesirably increases their flammability [5].

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More recently, workers in our laboratories have studied novolac–epoxy compositions with high novolac weight fractions and high phenol/epoxy offset stoichiometries [6–8]. These networks had greatly improved combinations of mechanical and flame properties. For example, K_{1c} toughness values of >1 MPa m$^{1/2}$ were obtained with this approach as opposed to $K_{1c} \approx 0.16$ for a conventional resole network. The flame properties on the neat networks (i.e. no reinforcing fiber) measured by cone calorimetry at 50 kW/m^2 incident heat flux indicated peak heat release rates of about 250–300 kW/m^2. This was far better than analogous values for epoxy networks (~ 1250 kW/m^2) but not as low as those measured for neat (but brittle) resole networks (~ 100 kW/m^2).

There is continuing interest in high temperature thermosetting matrix resins for advanced composites. Keller et al. [9–21] demonstrated that networks from bisphthalonitrile reagents cured with small amounts (1–3 mol%) of an aromatic diamine (Fig. 1) were highly resistant to thermo-oxidative degradation, and some that were postcured at 375 °C had T_gs in excess of 450 °C. Fire testing demonstrated their outstanding characteristics in composites [22]. The thermo-oxidative resistance of these networks was attributed to a high level of aromaticity and the proposed formation of heterocyclic crosslinks in the networks (Fig. 1). Networks from reactive oligomers with phenylethynyl, maleimide, or nitrile functionalities cured at elevated temperatures (>200 °C) have also been shown to have good thermo-oxidative stability [15,23–25].

The focus of this research has been to cure phenolic novolac resins with reagents that produce non-flammable crosslink structures. We have discovered that phenolic novolac resins react with bisphthalonitrile reagents to produce void-free networks with attractive structural and fire characteristics. Importantly, the major components of these resins are the economical and commercially available novolacs. It has been demonstrated that nucleophilic phenol groups readily react with the nitrile groups of phthalonitriles.
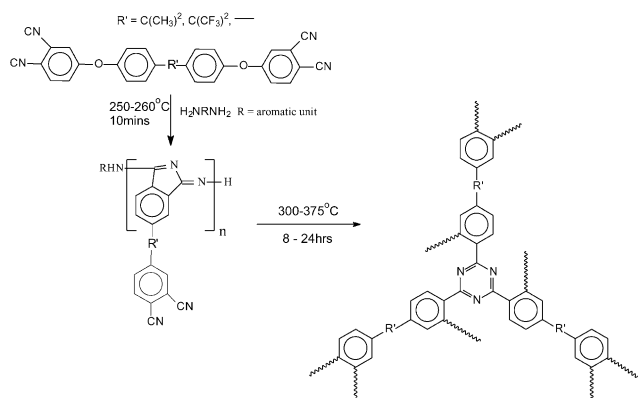

Fig. 1. Proposed bisphthalonitrile oligomer reaction with a small amount of an aromatic amine to form a 'B-staged resin', and subsequent network formation [15].

The molecular structure of the novolac–BPh crosslink has been studied in model reactions in an effort to better understand the chemical nature of novolac–BPh networks. An excess of a monofunctional phenol and BPh were reacted to form a soluble model material, which was characterized using ^{1}H NMR and FTIR. Results suggest that the molecular structure of the novolac–BPh crosslink is heterocyclic.

2. Experimental

2.1. Materials

The commercial phenol–formaldehyde novolac resin with an average phenol functionality of 7.1 (GP-2073) was kindly provided by Georgia-Pacific. 4,4′-Bis-(3,4-dicyanophenoxy)biphenyl (BPh) was generously provided by Eikos Incorporation. General aspects of its molecular structure were reported previously (Fig. 2) [26]. Both reagents were used as received. 2-Hydroxydiphenylmethane was purchased from Aldrich and used as received.

2.2. Methods

2.2.1. Network formation from the novolac resin and 4,4′-bis-(3,4-dicyanophenoxy)biphenyl

Systematically varied amounts of BPh and the novolac resin were charged to a three-neck, round bottom flask equipped with a vacuum tight mechanical stirrer and vacuum adapter. The novolac was melted at approximately 200 °C, was degassed for 10–15 min at 2–5 Torr, then the required amount of BPh was added resulting in a black, viscous melt. The melt absorbs light strongly and it is very difficult to observe whether it is completely homogeneous. The solution was stirred and further degassed for approximately 5 min, then poured into a pre-heated polysiloxane mold. Each molded sample was cured for 1 h at 200 °C and 3 h at 220 °C in air, then cooled to room temperature.

2.2.2. Melt reaction between 2-hydroxydiphenylmethane and BPh

2-Hydroxydiphenylmethane (10 g) was charged to a one-neck round bottom flask equipped with a reflux condenser and magnetic stir bar. The reagent was heated to 200 °C and maintained at this temperature for approximately 30 min. BPh (0.97 g) was blended into the melt to establish a 25:1 molar ratio (6.1:1 OH/CN eq. ratio) between 2-hydroxydiphenylmethane and BPh. (*Note*: the 6.1:1 equivalence ratio was the same as that used to prepare the 85:15 (wt/wt)
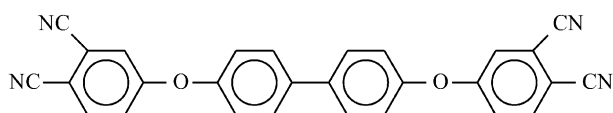

Fig. 2. Molecular structure of 4,4′-bis-(3,4-dicyanophenoxy)biphenyl.

novolac–BPh networks.) The melt mixture was reacted for 3 h at 200 °C at which point the mixture turned dark green. The product from the reaction was isolated by precipitation in dichloromethane, followed by decantation of the dichloromethane. The product was purified by dissolving it in THF and reprecipitating it in dichloromethane. The THF/dichloromethane mixture was decanted and the product was air dried for 12 h, then vacuum dried at 40 °C overnight.

2.3. Measurements

Dynamic mechanical analysis (DMA) in a three-point-bend mode was used to determine the T_gs and force versus displacement curves in the rubbery regions. These measurements were performed using a Perkin–Elmer dynamic mechanical analyzer, Model DMA-7. The samples were heated from 25 to 220 °C at 5 °C/min with the peak in the tan δ curve signifying the T_g. To measure force versus displacement in the rubbery regions, each sample was heated to approximately 60 °C above its T_g and was deformed at a rate of 20 mN/min until 250 mN was reached. The slopes of the force versus displacement curves were used in Eq. (1) to determine the rubbery moduli, E, for the samples. P/Δ is the slope of the force versus displacement curve

$$E = p(P/\Delta)(L^3/48I) \tag{1}$$

where L is the instrument span (20 mm), p is the gravitational force (9.81 m/s^2), and I is $(1/12)wb^3$, w is the width of the sample (6.35 mm) and b is the height of the sample (2.00 mm). The values of E from Eq. (1) were used with the theory of rubber elasticity to calculate the molecular weights between crosslinks (M_c) for the networks

$$M_c = 3RT\rho/E \tag{2}$$

where M_c is the molecular weight between crosslinks, E is the rubbery modulus, R is the gas constant (8.314 J/K/mol), T is the temperature in Kelvin at 60 above the T_g of the sample, and ρ is the density of the sample 60 K above its T_g.

Scanning electron microscopy (SEM) was used at 500 × magnification to view fractured surfaces of the thermosets, to confirm that voids were not being produced in the networks. The stress intensity factors (K_{1c}) or fracture toughness were measured using an Instron in the three-point-bend mode using a modified form of ASTM standard D 5045-91. The specimens were 3.12 mm thick × 6.28 mm wide × 38.1 mm long. A small crack was initiated in each sample using a liquid nitrogen cooled razor blade. The crack spanned approximately 30–70% of the sample thickness. The crosshead speed was applied at 1.27 mm/min and the stress at break was recorded. It should be noted that these thermosets were 'dark greenish-black' and it was not possible to measure the crack lengths before breaking the samples. Thus, the crack length was measured after the

samples were broken by observing the 'pre-cracked' as opposed to the fractured region.

Sol-fractions of the networks were measured by placing 30–50 mg of each sample into 20 ml of tetrahydrofuran (THF). The samples were extracted in THF for 72 h, then the solvent was removed by air drying for 24 h and vacuum drying at ~40 °C for 24 h. The remaining mass was weighed as the sol. The sol-fractions and gel-fractions were calculated by dividing the weights of the sols by the initial sample weights. Three measurements were made on each network and an average was taken.

Network formation was monitored by FTIR using a Nicolet Impact 400 spectrometer coupled with a thermostatically controlled IR cell. The percent conversion of the nitrile groups was monitored by measuring the disappearance of the nitrile peak at approximately 2200 cm^{-1}. FTIR was also used to help determine the structure of the product isolated from the model melt reaction by monitoring characteristic stretches in the 3000–3300 cm^{-1} region and the 1600–1700 cm^{-1} region.

^{1}H NMR was collected on a Varian Unity 400 MHz instrument with a frequency of 399.954 MHz. A 22° pulse angle was used with an acquisition time of 3.7 s and a recycle delay of 1 s. d$_6$-DMSO was used as the NMR solvent.

Flame and thermal properties were measured using cone calorimetry and TGA. The cone calorimetry samples were 4 in. in length × 4 in. wide × 0.25 in. thick. The samples were heated in a horizontal orientation in a cone calorimeter at 50 kW/m^2 incident heat flux. Char yields, smoke toxicity, peak heat release rates, total heat released, and times to ignition were measured. Using a Perkin–Elmer model TGA 7 thermogravimetric analyzer, 8–12 mg of samples in the form of small solid particles were heated from 25 to 900 °C at a heating rate of 10 °C/min. The final char yields, and the temperatures at which 5% weight loss occurred were recorded for each sample under inert (N$_2$) and atmospheric conditions.

3. Results and discussion

3.1. Network synthesis

An ~700 g/mol novolac oligomer from phenol and formaldehyde with an average functionality of 7.1 was cured for 1 h at 200 °C and 3 h at 220 °C with 5, 10, 15, 20 and 25 wt% BPh. Although the curing reaction is not well understood, it is hypothesized that the nucleophilic phenol can attack the electrophilic carbon of a nitrile to form a phenoxy substituted imine. The imine may then propagate further by attacking another nitrile, either intramolecularly in the *ortho* position to form an isoindoline type structure or intermolecularly to form a diimine containing conjugated structure. The rate of disappearance of the nitrile infrared absorbance at 2200 cm^{-1} was one metric used to monitor

progress in these reactions. It must be noted, however, that since the fully cured network structure is not yet well understood, disappearance of the nitrile functional group may not signify full cure. The areas under the nitrile FTIR peaks for mixtures of 90:10 and 80:20 (wt/wt) ratios of novolac/BPh decreased by 90% upon curing for 1 h at 200 °C and 20 min at 220 °C (Fig. 3). Curing beyond this time or temperature did not reduce these areas further in either case.

3.2. Model study—melt reaction of 2-hydroxydiphenylmethane and BPh

The chemical structures of the novolac–BPh networks synthesized with high concentrations of phenol relative to phthalonitrile are not clear. In this study we attempted to clarify the molecular structure of the novolac–BPh networks by characterizing the product(s) formed from the melt reaction of a monofunctional phenol (which had a similar chemical structure to the novolac) with BPh. 2-Hydroxydiphenylmethane was reacted with BPh using the same OH/CN equivalence ratio used to synthesize the 85 wt% novolac–15 wt% BPh networks (Fig. 4). This corresponded to a 25:1 molar ratio of 2-hydroxydiphenylmethane/BPh (6.1 hydroxyls per nitrile). The reaction was conducted in the melt at 200 °C for 3 h which was similar to the curing cycle for the novolac–BPh networks. The green crude mixture formed as a result of the reaction was added slowly to dichloromethane to remove unreacted phenols and to precipitate the product(s) generated from the reaction. After purifying the product(s), their molecular structure was characterized using ^{1}H NMR and FTIR (Figs. 5 and 6).

The ^{1}H NMR spectra of the compound isolated and purified from the melt reaction of 2-hydroxydiphenylmethane with BPh showed three broad proton signals at 3.9–4.1, 6.5–8, and 9–9.3 ppm (Fig. 5). The proton signals between 3.9 and 4.1 ppm correspond to the methylene protons of 2-hydroxydiphenylmethane. These C–H methylene absorptions also appear in the FTIR spectra as a doublet stretch at ~3000 cm^{-1}. The proton signals between 6.5 and 8 ppm correspond to the aromatic protons of both 2-hydroxydiphenylmethane and BPh. The protons resonating between 9 and 9.3 ppm are characteristic of N–H protons. These can be attributed to isoindoline type protons formed from intramolecular imine attack on a nitrile, or also to
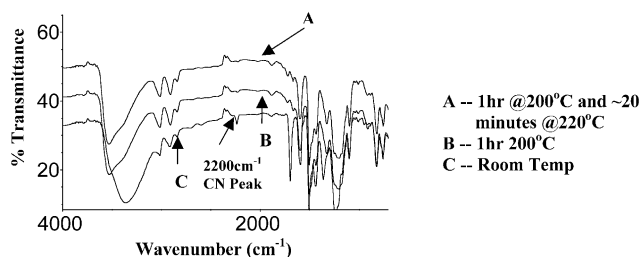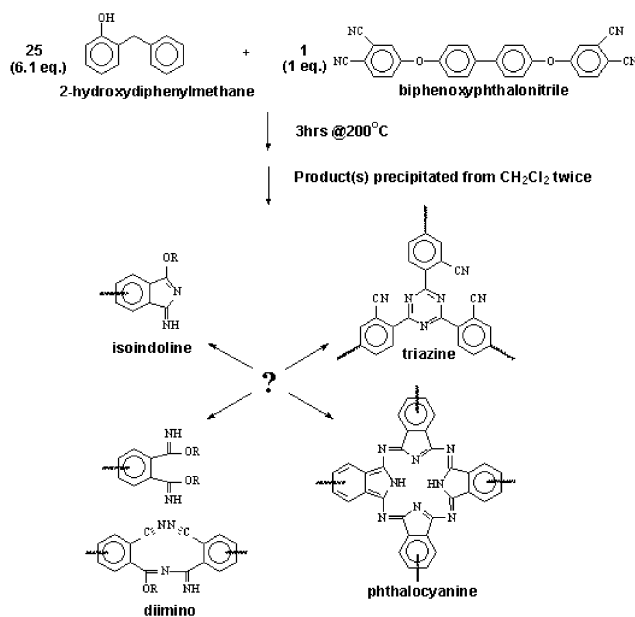

Fig. 4. Possible reaction products of the model melt reaction between 2-hydroxydiphenylmethane and a bisphthalonitrile.

diimine structures resulting from intermolecular imine attack on a nitrile. It is expected that intramolecular reactions would be favored due to the formation of the 5-membered heterocyclic ring. Unfortunately, these imine resonances are broad which makes quantification very difficult. The absorption bands in the FTIR spectra occurring at 1600 cm^{-1} (C=N) and 3300 cm^{-1} (N–H) provide support for these structures within its molecular framework (Fig. 6) [27,28]. Peaks at upfield chemical shifts between −8 and −9 ppm indicative of phthalocyanines were not observed. Also, a sharp doublet at ≈9 ppm characteristic of triazine rings was not observed [29]. Integration of the three groups of proton resonances in the ^{1}H NMR spectra yields a ratio of 3.8:56:2.8 of aliphatic/aromatic/N–H protons on isoindoles and diimines (Fig. 5). This ratio along with FTIR data suggests that the product has approximately one phenol fragment per four nitriles (Fig. 6).

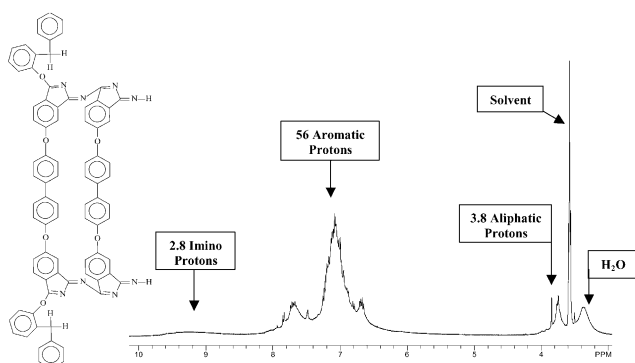It is important to point out that the molecular structures

Fig. 3. FTIR spectra of a 90:10 (wt/wt) novolac/BPh network cured for 1 h at 200 °C, then 20 min at 220 °C.

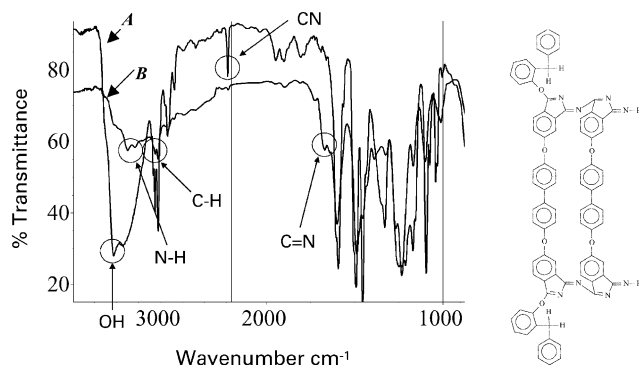Fig. 5. ^{1}H NMR of the product isolated from the 2-hydroxydiphenylmethane–BPh model reaction.

Fig. 6. FTIR spectrum: (A) 25:1 molar ratio (6.1:1 eq. ratio) of a melt mixture of 2-hydroxydiphenylmethane and BPh before reaction. (B) Product generated after 3 h at 20 °C.

of the novolac–BPh crosslinks may differ with higher concentrations of BPh relative to nucleophilic phenols in the networks. Determining the molecular structure of the crosslinks in other compositions of novolac–BPh networks is currently under investigation.

3.3. Network properties

Gel-fraction measurements were completed to investigate the level of cure in the novolac–BPh network materials. Networks with 15, 20 and 25 wt% BPh had gel-fractions greater than 0.9 (Fig. 7). The gel-fractions, coupled with the FTIR data, suggest that the novolac–BPh resins undergo high levels of crosslinking during the designated cure procedure.

We analyzed fracture surfaces of the networks with SEM to ensure that no volatiles were generated during the curing cycle. Network compositions with 85:15 and 80:20 (wt/wt) novolac/BPh were analyzed at 500 × magnification (Fig. 8), and no voids, which would appear as large dark craters, were observed. Voids promote crack propagation, which reduces the fracture toughness of glassy network materials. Thus, the absence of voids in the novolac–BPh networks helps to explain the good toughness of these materials ($K_{1c} \approx 0.8$ MPa m$^{1/2}$) as discussed later in this paper.

Rubbery moduli were measured on the novolac–BPh networks and used to estimate M_c (Fig. 9). The equivalence ratio of phenol/nitrile (i.e. OH/CN) in the initial thermosetting mixtures decreased from 19.6:1 at 5 wt% BPh to 3.1:1 at 25 wt% BPh. Thus, it was expected that more crosslinks
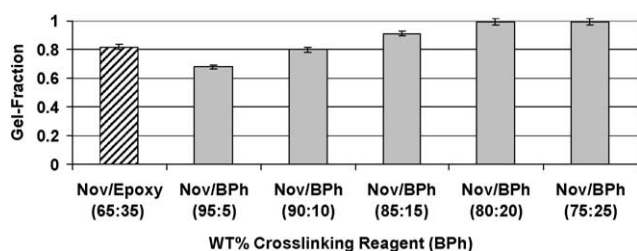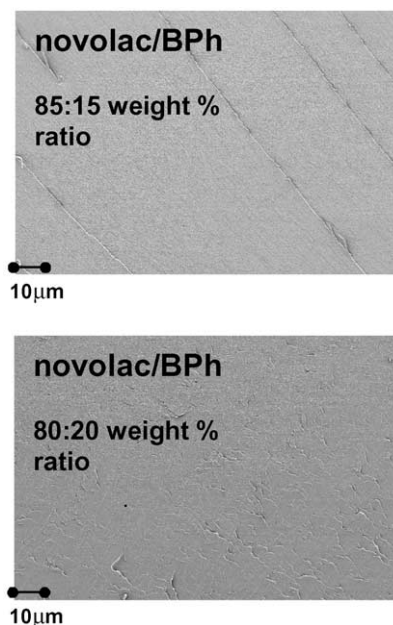

Fig. 8. SEMs at 500 × of 85:15 and 80:20 (wt/wt) ratios of novolac–BPh networks.

would result as the level of BPh was increased along this series (i.e. more phenol groups would react). Consistent with this premise, the rubbery moduli increased significantly as the concentration of BPh in the networks increased, suggesting that BPh efficiently cures the novolac resin. Corresponding substantial decreases in calculated M_c values followed from this data (Fig. 9).

The 85:15 (wt/wt) novolac–BPh network had calculated M_c values similar to a 65:35 (wt/wt) novolac–diepoxide network (control). The 65:35 (wt/wt) novolac–diepoxide network was elected as the control in this experiment because it had been previously demonstrated in our labs that this network had a high T_g, good toughness, and good flame retardance [7,8]. Therefore this material served as an excellent benchmark for any new network materials prepared from high compositions of novolacs crosslinked with minor compositions of different crosslinking reagents. Increasing the BPh concentration in the networks beyond 15 wt% resulted in significantly higher rubbery moduli and correspondingly lower M_c values (Fig. 9). Based on a rubbery modulus of the 25 wt% BPh–75 wt% novolac network, the M_c was calculated to be approximately 400 g/mol.

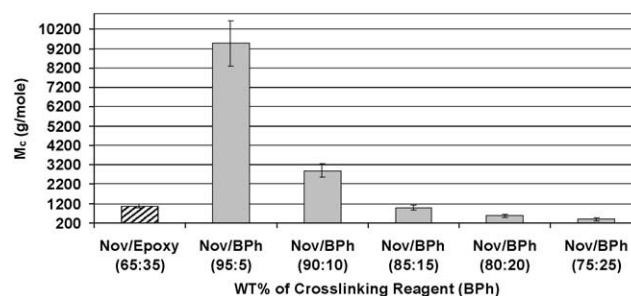Fig. 7. Gel-fractions versus novolac–BPh composition.

Fig. 9. M_c versus novolac–BPh composition (wt%).

The low M_c value (high rubbery modulus) suggests that the reaction between BPh and the novolac resin produced a highly crosslinked network. The high level of crosslinking helps to explain the good toughness observed in these materials using considerably less crosslinking reagent as compared to novolacs crosslinked with epoxy components [7,8,30]. Also, the low M_c values for the novolac–BPh networks correlate well with the high percent conversion of nitrile groups determined by FTIR and the high gel-fractions measured for these materials.

Novolac oligomers cured with 15, 20, and 25 wt% BPh had T_gs in excess of 180 °C (as demonstrated with DMA), which is well into the range desirable for electronic applications (and maybe even aerospace) (Fig. 10). This is significantly higher than T_gs observed for networks prepared with the same novolac resin cured with diepoxides (from bisphenol-A and epichlorohydrin) [7,8,30]. For example, a 65:35 (wt/wt) novolac–bisphenol-A diepoxide network (which had the most desirable mechanical properties of this compositional series) prepared from the same novolac oligomer had a T_g of ≈120 °C. Novolac oligomers cured with only 5 wt% BPh had a T_g of ≈120 °C, whereas the neat novolac oligomer had a T_g of 90 °C. The elevation of the glass transition temperature to 120 °C indicated that even low levels of BPh significantly cure the novolac oligomer. The decreases in M_c values with increasing concentration of BPh correlated well with the increases in T_g.

3.4. Network thermo-oxidative stability

The thermo-oxidative characteristics of the novolac–BPh networks were excellent, as measured by both TGA and cone calorimetry. The weight loss profiles of the materials were analyzed as a function of temperature by TGA in both inert (nitrogen) and air (20% oxygen) environments at a heating rate of 10 °C/min. All of the networks yielded approximately 50 wt% char after burning in the cone calorimeter (under atmospheric conditions). TGA indicated a slow degradation in air beginning at about 500 °C and extending to 750–800 °C. This slow degradation rate may be attributable to the high concentration of novolac in these networks, which may protect against degradation even at these very high temperatures. The degradation profiles by TGA for these materials was similar in air and nitrogen, with between 60 and 80 wt% char remaining at
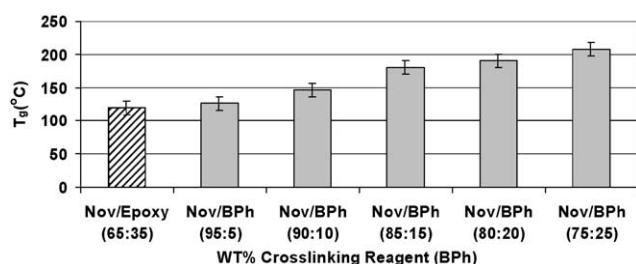
700 °C. Polyarylene ethers as well as polyimides, which are noted for their thermo-oxidative resistance, show little or no char yields at this temperature in air and about 20–50 wt% in nitrogen [31–40]. As would be expected based on the higher crosslink densities of the higher composition BPh networks, the TGA study indicated that networks cured with higher compositions of the BPh reagent had higher char yields (Fig. 11). The weight loss measurements also showed that under atmospheric conditions the 5% weight loss temperature for each novolac–BPh network did not occur until 480–500 °C, which is comparable to polyimides and polyarylene ethers [31–38]. Under nitrogen, the 5% weight loss temperatures and char yields for the novolac–BPh networks were approximately equivalent to those observed under atmospheric conditions. This suggests that oxygen does not play a significant role in the thermal degradation of novolac–BPh networks.

The primary interests for material applications of bisphthalonitrile resins have been in the fields of marine and aerospace technologies. The marine industry depends on glass or carbon fiber reinforced polymer composites to provide good mechanical properties at significantly reduced weight when compared to certain metals. Typical polymers used for these applications are unsaturated polyesters, vinyl esters, and epoxy resins. However, these materials are highly flammable and do not pass the US Navy's extremely stringent MIL-STD-2031. The MIL-STD-2031 is a flammability specification issued by the Navy in 1991 concerning materials to be used aboard submarines [41]. This specification contains test methods and requirements for cone calorimeter flammability performance such as peak heat release rates, ignitability, and combustion gas generation. The cone calorimeter is an instrument which applies a given radiant heat flux, such as 50 kW/m^2, to the surface of a 4 in. × 4 in. sample. The surface of the sample is continually sparked until it ignites, then the sample is allowed to burn. The cone calorimeter records such flammability characteristics as peak heat release rates, total heat released, and char yield following the burning process.

The MIL-STD-2031 specification has been in place for the last decade. However, the bisphthalonitrile composites are one class of a few organic materials which have met the specifications without surface treatment [18–20]. Therefore these materials have been of significant interest to the Navy

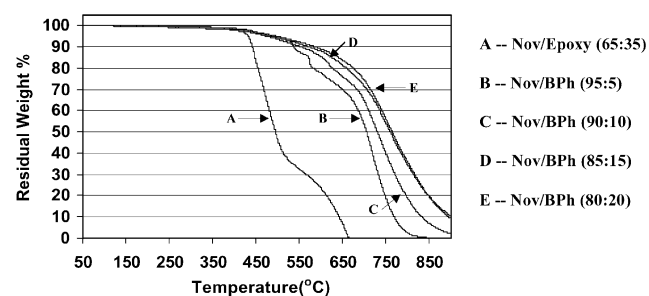Fig. 10. T_g versus novolac–BPh composition.

Fig. 11. Residual weight of novolac–BPh networks by TGA in air.

for materials aboard submarines as well as naval vessels. However, the greatest drawbacks against these materials have been their high cost and lack of availability.

Our approach, which involved curing the low cost novolac with relatively low weight percentages of BPh, has enabled us to produce materials with the combined properties of superior flame resistance and ductile, structural mechanical properties. Cone calorimetry results demonstrated that the rates of burning for the novolac–BPh networks were slow as compared to almost any other flame retardant networks or linear polymers (Table 1) [31,32,36, 39]. The peak heat release rate represents the maximum burning rate during the experiment. For example, at an incident heat flux of 50 kW/m^2, the peak heat release rate of an 80 wt% novolac–20 wt% bisphthalonitrile neat network (i.e. no reinforcing fibers) was 137 kW/m^2, almost as low as the resole control material with a value of 116 kW/m^2 (recall that the resoles are known to be flame resistant but are quite brittle). This can be compared to a typical peak heat release rate of 1250 kW/m^2 for aromatic epoxy networks measured under the same conditions [7]. Upon increasing the network concentration of BPh from 10 to 20 wt%, the total heat released and peak heat release rate decreased while the time to ignition increased. This is most likely a result of a higher level of crosslinking in the 80:20 network, which improved the thermo-oxidative resistance. The char yields for both networks after burning (from the cone calorimetry measurements, Table 1) were similar.

3.5. Network fracture toughness

Critical stress intensity factors (K_{1c}) were measured to determine toughness and relate this to the chemical compositions. The 85:15, 80:20, and 75:25 novolac–BPh (wt/wt) networks all had good toughness ranging from 0.8 to >1 MPa m$^{1/2}$ (Fig. 12). Such values mean that these materials fall into the range of epoxy networks, and are a tremendous improvement over the analogous K_{1c} value of 0.16 MPa m$^{1/2}$ recorded for the resole control network. It is also significant that although the novolac–BPh networks had much higher levels of crosslinking as related to the
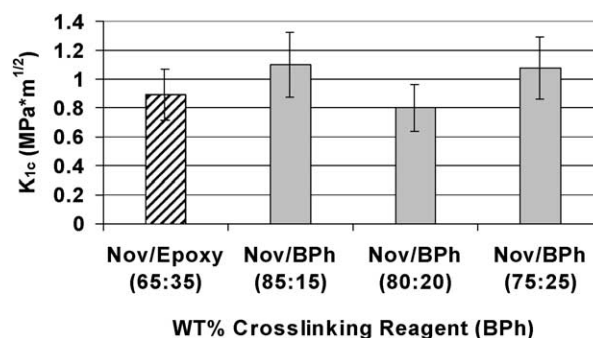

Fig. 12. K_{1c} versus novolac–BPh composition.

phenolic-epoxy networks previously evaluated in our laboratories [6–8], this did not diminish their toughness.

4. Conclusions

We have discovered that high compositions of phenolic novolac oligomers can be readily cured with 15–20 wt% of bisphthalonitriles to form tough, high T_g, extremely flame resistant thermosets. Studies of soluble model compounds suggest that the molecular structures of the novolac–BPh crosslinks are isoindole and diimine structures. Current focus is on elucidating the molecular structures of other novolac–BPh compositions, on understanding the evolution of such structures during burning, and on developing economical methods for synthesizing the bisphthalonitrile monomers.

Table 1
Cone calorimetry results measured at an incident heat flux of 50 kW/m^2 for 90:10 and 80:20 (wt/wt) novolac–BPh networks as compared to selected aromatic linear polymers

Material	Time to ignition	Total heat release (MJ/m^2)	Peak heat release rate (kW/m^2)	CO/CO$_2$ (kg/kg)	Char yield (%)
Novolac/bis-A epoxy (65:35)	74	156	263	0.02	26
Commercial resol network (control)	–	–	116	0.011	65
Polyetherimide[a]	70	128	128	0.08	79
Polysulfone[a]	67	297	431	0.06	56
Fluorine and phosphorus containing polyether[a]	91	87	120	5.0	19
Novolac/BPh (90:10)	73	85	212	0.015	53
Novolac/BPh (80:20)	102	49	137	0.019	54

[a] From Ref. [39].

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