

Halogen free and thermal stable novolac derivatives and their properties in epoxy composites

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Abstract

Novel cross-linkable polymer has been developed and successfully used in green PCB laminates with good flame retardancy and thermal stability for recently years. The novel hardener was modified by introducing curable functional groups which can react with epoxy resins under processing, to enhance thermal stability and flame retardancy via the increase of cross-linking density. Some merits of high performance laminates as the novel novolac hardener was used, such as higher glass transition (T_g) due to the highly cross-linking density, and the lower coefficient of thermal expansion (CTE), lower water absorbed by introducing more aromatic units to form rigid and tough chemical structures of laminates. Also the increased flame retardancy due to inflammable gas such as N_2 , CO_2 or other volatile compounds released while fire ignition, without using halogen or phosphorus compounds.

Modified novolac resins (highly aromatic and nitrogen content) were used as flame retardant agent in this study. The cured resins exhibited higher glass transition (T_g) than 180°C , and the char yield at 800°C was increased which elaborates the effectiveness of flame retardancy with evaluated LOI value over 35. This is mainly attributed to the increased crosslink densities and highly aromatic content in modified phenol novolac derivative resins which exhibits the higher thermal degradation energies (E_a). Therefore, the more effective flame retardancy would be expected by the loss of nitrogen and hydrocarbon during combustion. By evaluating the cooperative flame retardancy in organic/inorganic hybrid with char yield and LOI increasing percentage, the effects of filler showed the cooperative flame retardancy only in appropriate addition and difference in crosslinking densities.

Keyword: novolac derivative resins; glass transition (T_g); thermal degradation energies (E_a); flame retardancy

Introduction

Phenolic derivative resins are widely used in industrial applications such as adhesives, coatings, construction, composite matrices and electronic industries. The popularity arises from their good dimensional stability, low cost, high resistant to chemicals, good thermal stability and heat resistant properties [1,2,3]. These rapid growths of phenolic resins' applications have also prompted extensive research to enhance the thermal properties of materials for versatile applications in the electric and electronic industries. Currently, the commercial market is dominated by compounds containing halogens, notably chlorine and bromine, where exceptional flame retarding efficiency is found when these compounds are incorporated as either additives or as reactant. However, they are clearly disadvantageous as toxic and corrosive gases are generated during thermal degradation.

Recent developments in the chemistry of halogen-free flame retardant polymers involve polymers or reactive monomers that are inherently flame retarding such as those containing P, Si, B, N and other miscellaneous elements [4]. Silicon and Phosphorus compounds have been reported to demonstrated effective flame retardancy by forming a foam layer [5,6,7,8,9]. These additives are somewhat toxic and often show adverse affect in other material characteristics such as humidity and heat resistance when applied to epoxy resin compounds. The boric acid and borate salts are also effective flame retardants because impenetrable glass coatings

were formed during thermal degradation to contribute to the intumescent effect. However, these additives have to be used in relatively high concentrations which may affect the physical and mechanical properties of the polymers [10,11,12]. Recently, metal hydrates have been proposed to replace the halogen compounds by water during combustion [13,14]. But the extremely large quantity of additive marred the crosslinking properties of epoxy resin. Nitrogen compounds are widely used as protective coatings due to their transparency, good adhesion, as well as heat and chemical resistance for effective intumesce in fire ignition.

Prior works also attempt to produce flame retarding compounds mainly by restraining the movement of molecular segments in epoxy resin, i.e. stiffening networks at high temperature in order to increase heat resistance, or insert bulky substituent such as aromatic groups into the networks [16]. We present the synthesis of two kinds of epoxy-curable diazo-coupling phenol novolac derivatives which gives rise to high crosslinking densities with reduced free volumes and tie-up the molecular segments and insert bulky substituent such as aromatic groups by nonflammable N element. The synthetic procedure and material characteristics are discussed, and the flame retardancy and thermostability are evaluated and compared against the inorganic filler analogues.

Experimental

Carbonyl phenyl azo novolac resin (CPAN) and Carbonyl phenol-biphenylene azo novolac resin (CPBAN) were prepared which attribute to the two novel phenolic novolac resins. Predetermined amount of CPAN or CPBAN were added to the solution of epoxy/novolac resin/acetone in various weight ratios, respectively. The mixtures were stirred to homogenous, and the acetone solvent removed by

vaporizing in vacuum. The mixed powders were subsequently cured in a mold at 200°C and 5 kg cm⁻² for 2 h and further postcured at 220°C for 3 h to obtain the cured specimens.

ATH filler was added to the mixture of novolac epoxy/novolac resin/CPAN (100/0.5/50) or novolac epoxy/novolac resin/CPBAN (100/0.5/50) in various weight ratios, respectively. And the obtained cured specimens were

followed by same procedures aforementioned.

Results and discussions

Thermal characteristics of cured resins

Thermal degradation was characterized by TGA as shown in Fig. 1. The heating process showed single stage degradation process under nitrogen atmosphere (Fig. 1a and 1b), owing to the high thermostability of increasing crosslink densities and aromatic units. The degradation of blank matrix and Epoxy/PN/CPAN (or Epoxy/PN/CPBAN) cured resins almost overlapping at the temperature around 350°C to 450 °C. Moreover, the diazo-coupling groups generated heat-resistant residues to achieved high char yield at 800°C. While heating under air, the TGA curves are different (Fig. 1c and 1d). The cured

resins showed similar weight loss behaviors below 400°C as that under nitrogen atmosphere. However, a second-stage degradation occurs due to the oxidative reaction at temperature >500°C. As aromatics were reported to exhibit significant char formation under heating with air [17,18,19], the cured resins with diazo-coupling group (Epoxy/PN/CPAN and Epoxy/PN/CPBAN series) incorporated in various content showed an increasing char yield at 800°C. This retardation effect on weight loss was further enhanced related to the diazo-coupling group in the synthesized phenol novolac resin.

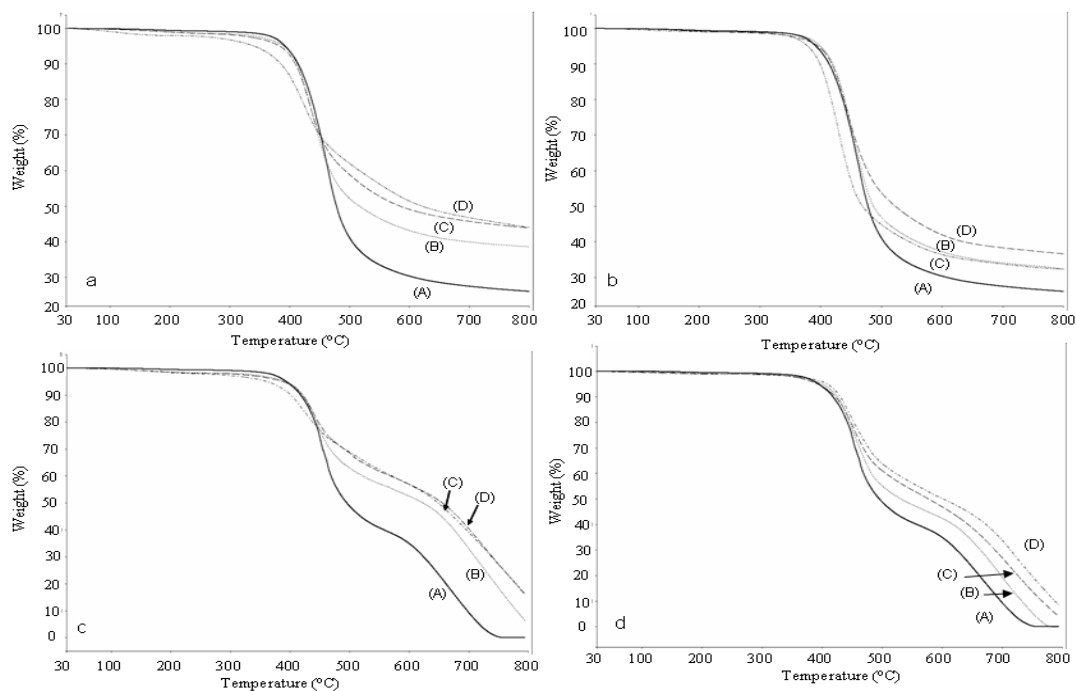


Fig. 1. TGA curves of cured resins: (a) Epoxy resin/PN/CPAN, (b) Epoxy resin/PN/CPBAN, under nitrogen; (c) Epoxy resin/PN/CPAN, (d) Epoxy resin/PN/CPBAN under air. The compositions in all figures: (A) 100/0.5/0, (B) 100/0.5/30, (C) 100/0.5/50 and (D) 100/0.5/100.

The degradation temperatures are summarized in Table 1. The downward shift in T_{onset} , T_d and T_{max} displayed the

same trend, which maybe due to the decomposed azo group at lower temp and they are proportional to the extent

of diazo-coupling. The decrease is more pronounced in CPAN but less so in CPBAN due to the lower extent of diazo-coupling in the phenol-biphenylene structures. All factors play some critical roles in flame retarding polymeric materials through condensed-phase mechanisms and gas-phase mechanisms. In this case, the CPAN and CPBAN advances the temperature (T_{onset} , T_{max} and T_d) due to the nitrogen gas or releasing volatile nitrogen oxidants, through the mechanisms believed to dilute the ambient oxygen gas and decrease heat absorption in heated condition or fire environment. Furthermore, the increased

char yield at 800°C showed the effect of thermostability caused by the non-combustible gas when highly thermostable aromatic products formed.

The limiting oxygen index (LOI) was calculated according to Grack and Long [20] with the equation: $LOI = 16.9 + 0.5 \cdot (\text{char wt. \%})_{800^\circ\text{C in N}_2}$. The addition of CPAN or CPBAN both increased the LOI value from 30 to 40 and from 28 to 36, respectively. These results directly reflected the flame retarding efficiency, the LOI value enhanced in cured resins as well as gradually increased the CPAN and CPBAN contents.

Table 1 Characterizations of cured resins by TGA

	TGA analysis in air (10 °C /min)				TGA analysis in N ₂ (10 °C /min)				LOI
	T _{onset}	T _d ^c	T _{max} ^d	Char yield ^e	T _{onset}	T _d ^c	T _{max} ^d	Char yield ^e	
Epoxy/PN ^a /CPAN ^b									
100/0.5/0	421	393	456	0	417	392	460	25.6	30
100/0.5/30	411	392	442	6.5	405	384	438	38.0	37
100/0.5/50	402	387	438	16.0	400	383	432	43.4	39
100/0.5/100	377	361	427	16.5	372	341	424	44.0	40
Epoxy/PN/CPBAN ^b									
100/0.5/30	421	400	454	0	413	399	454	32.5	33
100/0.5/50	420	392	454	4.2	411	400	453	34.6	34
100/0.5/100	413	409	445	8.6	406	396	443	36.6	36

^a equivalent weight; ^b weight; ^c temperature at the 5 % weight loss; ^d temperature at the maximum weight loss; ^e at 800 °C (%)

Curing behaviors and thermal degradation kinetic

Glass transition temperature (T_g) of the cured resin were determined from DSC (N₂; 10°C/min) showed in fig. 5 and summarized in Table 2. For both epoxy/CPAN and epoxy/CPBAN series, introducing diazo-coupling group to the phenol novolac derivative compounds increases the T_g value, suggesting the incorporated carbonyl group in diazo-coupling group has reacted with epoxy leading to higher crosslinking densities, and raised the T_g .

Thermostability could be further judged from decomposed activation energies (E_a) derived from TGA

measurements using various heating rates (5, 10, 20 and 40°C/min). Two common approaches proposed by Kissinger [21] and Ozawa [22], are employed to derive the activation energies of a thermal degradation reactions. In theory, higher E_a implied higher thermostability. The analysis shows both methods yield similar results where the cured resins containing either the CPAN or CPBAN have all displayed higher thermostability (higher E_a) than the blank resin. This corroborates with the higher crosslinking densities and enriched aromatic amounts. However, an excessive amount of carbonyl group has lead to lower E_a

and lower T_g.

Table 2 Curing behaviors and thermal degradation kinetic

	DSC			TGA	
	Tg (°C)	T _p ^c	ΔH (J/g)	Ea (KJ/mol*K)	Ea (KJ/mol*K)
				Ozawa's method	Kissinger's method
Epoxy/PN ^a /CPAN ^b					
100/0.5/0	115	196	154	177	174
100/0.5/30	189	199	115	200	200
100/0.5/50	195	187	120	196	195
100/0.5/100	173	151	116	194	192
Epoxy/PN/CPBAN ^b					
100/0.5/30	160	202	99	200	198
100/0.5/50	167	198	67	187	185
100/0.5/100	147	194	47	183	181

^a equivalent weight; ^b weight; ^c T_p : maximum reaction temperature.

DSC revealed the enthalpy changes (ΔH) during cross-linking reaction for epoxy resins containing the two types of diazo-coupling agent, CPAN and CPBAN. The results are summarized in Table 2. For both cases, the addition of diazo-coupling agent initiated broader enthalpy change peak. This result suggests the cross-linking reaction occurs across broader temperature range when diazo-coupling agent is present which also implies the diazo-coupling agent mediated the epoxy-phenolic cross-linking. The carboxylic group in the diazo compound seems to display easier cross-linking than that of hydroxyl group with the epoxy group, as suggested by the lower heat change temperature. On the other hand, the additional heat change peak appears less pronounced in the resin

containing CPBAN. This maybe due to the diluted carboxylic group available for cross linking in CPBAN. The heat change (Table 2) in this compound is much lower compared to the case with CPAN and lower cross-linking density is expected. Both the diverseness of reaction and over abundant functional group leads to the increase of residual nonreactive functional group and a increase of free volume. The fact that CPAN showed the lower maximum reaction temperature (T_p) due to higher amounts of diazo-coupling compounds which lead to the higher crosslinking densities when large amount of CPAN is present, and displayed a less increase of Ea while excessive amounts of CPAN are added. The mechanism and structural details are documented in a separated report.

Effects of filler on thermostability

Finally, the effect of filler (3 μ m size Aluminum trihydrate (ATH) particle) in CPAN and CPBAN modified series are examined and the results summarized in Table 3 using the parent polymer Epoxy/PN/CPAN or Epoxy/PN/CPBAN = 100/0.5/50. All char yield and

LOI increasing percentage were evaluated by TGA under air condition using a heating rate of 10°C /min. The LOI was calculated according to Van Krevelen [23] with the equation: $LOI = 17.5 + 0.4 \cdot (\text{char wt. \%})_{850^\circ\text{C in air}}$ and the efficiency brought about by the filler is evaluated from the difference or LOI between the cured resins with filler and

the one without the filler using the following equation:

$$\text{Increasing \%} = \left[\frac{\text{LOI value of individual filler contained cured resin} - \text{LOI value of blank cured resin}}{\text{LOI value of blank cured resin}} \right] \times 100\%$$

Table 3 Characterizations of cured resins with filler

	Filler content ^b	Char yield (%)	LOI	LOI increasing (%)
Epoxy/PN ^a /CPAN ^b				
100/0.5/50 (blank)	0	16.0	24.0	-
100/0.5/50	30	18.6	25.0	4.2
100/0.5/50	50	34.7	31.0	29.1
100/0.5/50	100	37.2	32.0	33.3
Epoxy/PN/CPBAN ^b				
100/0.5/50 (blank)	0	4.2	19.2	-
100/0.5/50	30	29.5	29.3	52.6
100/0.5/50	50	30.0	29.5	53.6
100/0.5/50	100	32.5	30.5	58.9

^a equivalent weight; ^b unit: gram

The char yield all increases with increasing filler, possibly due to the effective oxidation barrier formed by inorganic under high ambient air temperature according to recent studies. Interestingly, the effects of filler are more pronounced in the CPBAN series than that in the CPAN series. However LOI values are tapered off at high filler content for both CPAN and CPAN experiments. The efficiency is saturated at the level of 33.3 % and 58.9 %, respectively for CPBAN and

CPAN, when the filler content reached 100g equivalent weight. It stands to reason that lower crosslinking densities of CPBAN/filler series lead to more pronounced thermal resistant and flame retardant improvement by the filler whereby the oxidation layer can be formed more completely. On the basis of these evidence we can deduced that higher crosslinking densities dominated the thermostability which is characterized by higher thermal degraded activation energies.

Conclusions

The thermostability of epoxy resins containing flame retardant components bearing diazo-coupling functional group in two types of phenol novolac derivative resins were examined by DSC and TGA. The degradation pattern, temperature and rates of the maximum weight loss were all affected by the flame retardant components. Evaluating the LOI value, enthalpy and activation energies concluded the

incorporation of CPAN or CPBAN to epoxy resins can improve the cured resins' thermal properties. Phenol novolac and phenol-biphenylene novolac resins reached higher LOI and char yield by increasing the aromatic amounts and the azo group, which entails better flame retardancy and suggested higher thermostability. However, excessive CPAN or CPBAN leads to increased amount or non-reacted functional group, a reduced T_g and less

increase in degradation activation energy. Further addition of micron size inorganic filler (Aluminum trihydrate; ATH) particle showed the cooperative flame retardant behavior but saturated at certain amount of inorganic addition. This

study concluded the use of highly aromatic content with higher cross linking entities can leads to inflammable and low volatile compounds without the use of halogen or phosphorus elements.

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