

## Synthesis and Thermal Properties of a Novel Nitrogen-containing Epoxy Resin

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**Abstract:** A new nitrogen-containing epoxy resin (XT resin) was synthesized from chain extension of xylenephenolformaldehyde resin (XPF) and triglycidyl isocyanurate (TGIC) in the presence of base catalyst. FT-IR and <sup>1</sup>H-NMR analysis confirmed the chemical structure of XT resin. It was cured with dicyandiamide (DICY) and diaminodiphenyl sulfone (DDS). Dynamic mechanical analysis (DMA) results showed that the introduction of triazine ring provides epoxy polymer with good thermal stability. Furthermore, high char yields at 800°C in thermogravimetric (TGA) analysis indicated that XT resin had potential flame retardance.

**Keywords:** Nitrogen-containing epoxy resin, xylenephenolformaldehyde resin (XPF), triglycidyl isocyanurate (TGIC), thermal stability.

Epoxy resins are extensively investigated and widely used in the electronic/electrical instruments because of their great versatility, good chemical and electrical properties and excellent adherence to many substrates<sup>1</sup>. Now it is required to meet with not only thermal stability but also environmental protection when it is decomposed. The strict environmental protection laws in the world especially in Europe made many electronic/electrical manufacturers have to give up using halogen-containing epoxy resin. This resin has excellent properties but produces toxic gas when it was decomposed<sup>2</sup> and causes serious environmental pollution. As alternatives to halogen-containing epoxy resin, phosphorus-containing epoxy resins<sup>3, 4</sup> have been investigated. Although they exhibit high flame retardance, its industrialization is difficult for its complex synthesis and high cost, as well as debating environmental problems<sup>5</sup>. Nitrogen-containing epoxy resins have excellent thermal stability and good flame retardance and are suitable materials for high-quality electronic/electrical instruments. For example, triglycidyl isocyanurate (TGIC)<sup>6</sup> has excellent thermal properties and self-extinguishability due to high nitrogen content (14.14%) and triazine ring, but it is different to process for electronic/electrical instruments such as the laminate. In this letter, two reactions (**Scheme 1**) are designed to get nitrogen-containing epoxy resins for making the laminate: First, xylenephenol-formaldehyde resin (XPF resin) is synthesized by condensation reaction between xylene formaldehyde resin and phenol. Secondly, XT resin is obtained from one or two ring-opening reaction between XPF resin and TGIC. The

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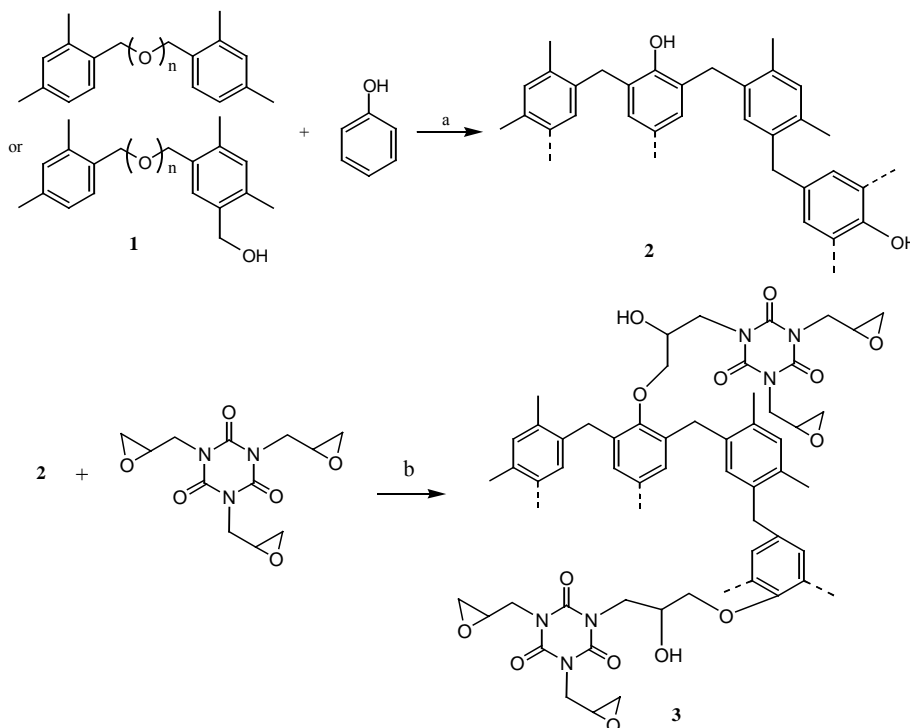
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thermal properties of cured XT resin were characterized by DMA and TGA. The introduction of hydrophobic xylene and triazine ring into XT structure made it with water resistance and good thermal stability, respectively.

General procedure for the preparation of XT resin: A four-necked round bottom flask equipped with a mechanical stirrer, a thermometer and a reflux condenser were charged with XF resin and phenol according to certain formulation and stirred under  $N_2$ . When the temperature reached  $60^\circ C$ , added *p*-toluenesulfonic acid as catalyst, kept the reaction for 6 hours at  $120-125^\circ C$ , then cooled to about  $100^\circ C$ , added TGIC (TGIC : phenol = 3:1, mole ratio), stirred, then added base catalyst after TGIC was dissolved, maintained the temperature at  $140^\circ C$  and continued about 60 min. Finally a clear, yellow solution was obtained and directly used for the next curing reaction. The conversion of TGIC, which was beyond 85%, was monitored by GPC, which is a convenient, exact and quantitative way to trace free phenol content and the synthesis kinetics of XT resin. The epoxy value was 0.32-0.40 mol/100g, which was determined according to hydrochloric acid- pyridine method and varied with the reaction condition.

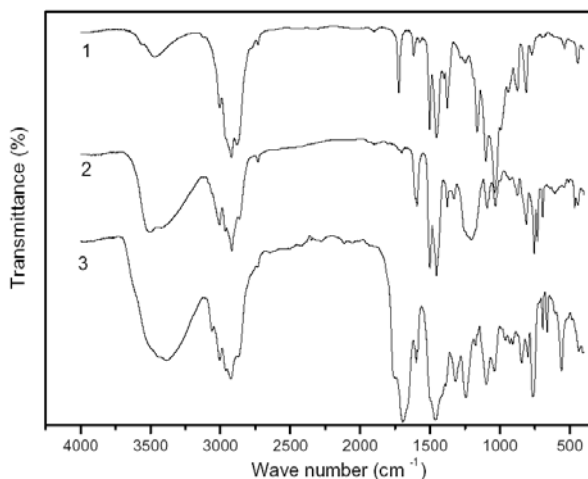
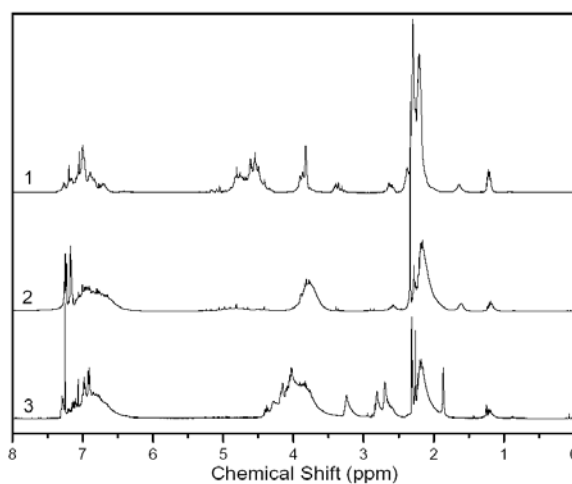
Theoretical amounts of DICY and DDS (equal mole) were added as curing agents and 2-methyl imidazole was used as a curing accelerator for XT resin to get the cured products (XT/DICY and XT/DDS).

**Scheme 1** The synthesis of XPF resin and XT resin (ideal structure).



**1** XF resin; **2** XPF resin; **3** ideal structure of XT resin.

a: *p*-toluenesulfonic acid,  $120^\circ C$ ; b: base catalyst,  $140^\circ C$

**Figure 1** IR spectra of 1, XF; 2, XPF; 3, XT resin.**Figure 2** <sup>1</sup>H-NMR spectra of 1, XF; 2, XPF; 3, XT resin.

VECTOR 22 FTIR spectrophotometer was used for the IR spectroscopy (400-4000  $\text{cm}^{-1}$ ) for the XF resin and products. <sup>1</sup>H-NMR of the XF resin and products were obtained from an Advance DMX 500(500Hz) spectrometer at 35°C using  $\text{CDCl}_3$  as a solvent. From **Figure 1**, IR absorption bands (1160.9, 1099.5 and 1033.8  $\text{cm}^{-1}$ ) of ether linkage (C-O-C) and hydroxymethyl of XF resin disappeared after the reaction, and new absorption bands of phenol (3507 $\text{cm}^{-1}$ ) and stretching vibration of Ph-O (1260-1180  $\text{cm}^{-1}$ ) appeared. Methylene bands (1452, 1375  $\text{cm}^{-1}$ ) had been strengthened for more methylene structures in XPF. IR absorption peaks at 1695 and 916  $\text{cm}^{-1}$  were ascribed to triazine ring and oxirane ring. **Figure 2** shows <sup>1</sup>H-NMR spectra of XF, XPF and XT resin. The chemical shifts of methylene of ether linkage and hydroxymethyl (4.44-4.95

ppm) in XPF resin were absent, and chemical shifts of oxirane group (3.26, 2.83 and 2.70 ppm) appeared, which proved the structures of our products and consisted with the results of IR spectra. From the results of IR and  $^1\text{H-NMR}$  spectra, we concluded that a new nitrogen-containing epoxy resin (XT resin) was synthesized successfully.

DMA and TGA measurements were performed under  $\text{N}_2$  for  $T_g$  data (obtained from the  $\tan\delta$  peak) and the thermal degradation behavior of the cured XT/DICY and XT/DDS (curing condition:  $170^\circ\text{C}/2\text{h}+190^\circ\text{C}/2\text{h}$ ) respectively. From **Table 1**,  $T_g$  of the cured XT/DICY ( $143.1^\circ\text{C}$ ) and XT/DDS ( $176.2^\circ\text{C}$ ) are higher than that of tetrabromo bisphenol A epoxy resin (TBBPAER)/DDS (about  $130^\circ\text{C}$ )<sup>7</sup> because of the introduction of triazine ring (from TGIC) and more aromatic framework (from XF resin) into the cured networks, which indicates that they have a high usage temperature. The temperatures of 5% weight loss of the cured XT/DICY and XT/DDS are  $259.8^\circ\text{C}$  and  $310.9^\circ\text{C}$ , respectively, which shows that they have good thermal performance. Having more aromatic framework, the cured XT/DDS has better thermal performance than the cured XT/DICY. Char yields (**Table 1**) of the cured XT/DICY and XT/DDS indicate that they have potential flame retardance.

The relationship of the structure of XT resin and properties of its thermoset will be further investigated in our laboratory.

**Table 1** The TGA data of the cured resin XT/DICY and XT/DDS.

Cured resin	$T_g$ ( $^\circ\text{C}$ , from DMA)	$T_5$ ( $^\circ\text{C}$ )	$T_{\max 1}$ ( $^\circ\text{C}$ )	$T_{\max 2}$ ( $^\circ\text{C}$ )	$Y_c$ (%)	
					at $500^\circ\text{C}$	in $800^\circ\text{C}$
XT/DICY	143.1	259.8	285.8	409.7	12.87	10.52
XT/DDS	176.2	310.9	335.0	415.4	16.54	13.65

$T_5$ ,  $T_{\max 1}$  and  $T_{\max 2}$  are the temperatures of 5% weight loss, the first and second decomposition peaks, respectively.

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