

Novel Nitrogen-Containing Epoxy Resin. I. Synthetic Kinetics

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Received 27 May 2004; accepted 16 October 2004

DOI 10.1002/app.21519

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A novel nitrogen-containing epoxy resin was synthesized by two steps: (1) condensation reaction between xyleneformaldehyde resin and phenol, to obtain thermoplastic xylenephеноlformaldehyde (XPF) resin; and (2) addition reaction between XPF resin and triglycidyl isocyanurate (TGIC). The synthetic kinetics of XPF resin were intensively investigated by gel permeation chromatography (GPC). The results showed that XPF resin, with different molecular weights and low content of free phenol, could be obtained by changing the reaction conditions. The kinetics of reaction between XPF resin and TGIC was monitored by GPC and epoxy value titration. The results showed that the

percentage conversion of TGIC was >85% within 60 min at 140°C and the epoxy value, about 0.3–0.4 mol/100 g, varied with the reaction conditions. This novel epoxy resin exhibited good stability of storage and could be used as a basic resin for making prepreg and laminate. The structures of XPF and XT resins were characterized by IR and ¹H-NMR spectra. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 723–731, 2005

Key words: epoxy resin; synthesis; kinetics (polym.); gel permeation chromatography (GPC); thermoplastics

INTRODUCTION

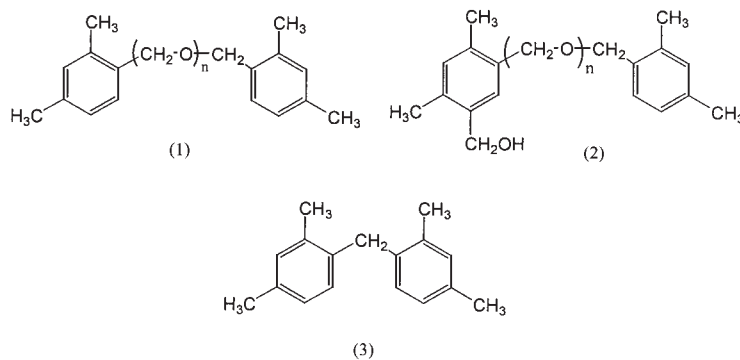
Epoxy resins have excellent overall properties and are widely used as insulation materials. With the rapid development of the electronic/electrical industry, epoxy resins are required not only to strengthen their inherent advantages such as good chemical resistance, low shrinkage, high-grade electrical insulation, and excellent adherence to many substrates, but also to overcome their disadvantages such as brittleness and flammability. Halogen-containing epoxy resins are excellent nonflammable materials and widely used in electronic laminates. However, enactment of strict environmental protection laws worldwide, especially in Europe, have forced many electronic/electrical manufacturers to stop using halogen-containing epoxy resins that, although they have good overall properties, would produce toxic gas and cause serious environmental pollution when decomposed.¹

As alternatives to halogen-containing epoxy resins, phosphorus-containing epoxy resins^{2–8} have been intensively investigated. Although they exhibit high flame resistance, their industrialization is difficult because of complex synthesis processing and high cost, as well as causing debatable environmental problems.⁹ Another kind of substitutes, nitrogen-containing flame retardants, are gradually attracting greater

attention because they are environmentally friendly with less toxicity, no dioxin, and low evolution of smoke during combustion.¹⁰ Some nitrogen-containing epoxy hardeners for improvement of flame retardancy such as melamine–phenol formaldehyde novolac (MPN) resin¹¹ and amino isocyanurate¹² have been reported. Wu et al.¹³ reported organic–inorganic hybrid flame-retardant epoxy resins containing melamine and silicon compounds, although there are few reports on the synthesis of nitrogen-containing epoxy compounds. In this article, we report a new way to synthesize suitable nonflammable epoxy compounds for high-quality prepreg or laminate through modification of triglycidyl isocyanurate (TGIC), which has three epoxy groups in each molecule, and its polymer has excellent thermal stability because of the structure of triazine ring and good self-extinguishments arising from its high nitrogen content (14.14%). However, it is difficult to process because of its insolubility in most organic solvents and its thermoset is brittle for high crosslinking density.

The solvability of TGIC is improved if its molecular symmetry has been broken, and its toughness is increased if the distance between its oxirane rings is increased. A better way to achieve these goals is the introduction of an unsymmetrical structure. We chose phenol-modified xyleneformaldehyde resin, also called xylenephеноlformaldehyde (XPF resin), as a modifier for TGIC because XPF resin has an unsymmetrical molecular structure. Moreover, it has good toughness and good waterproof and dielectric prop-

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Scheme 1 Structures of XF resin.

erties compared to those of other phenol formaldehyde resins because of its hydrophobic xylene structure. Furthermore, XPF resin is very inexpensive in production of electronic/electrical materials.

As a modifier for TGIC, XPF resin should be thermoplastic. Reports on the synthesis of thermoplastic XPF resin have been scarce, and there is a lack of intensive research on the decrease of the content of free phenol, which is toxic in XPF resin. Herein, two steps were designed to obtain a novel nitrogen-containing epoxy resin. First, XPF resin was obtained from a condensation reaction between xyleneformaldehyde resin and phenol, and more efforts were given to thermoplastic XPF resin with different molecular weights and low content of free phenol for the next reaction. Second, a novel nitrogen-containing epoxy resin, XT resin, was synthesized by an addition reaction between XPF resin and TGIC. Ways to improve the percentage conversion of TGIC and to control the epoxy value of the products were studied in detail.

EXPERIMENTAL

Materials

Xyleneformaldehyde resin (XF2602; Suzhou Special Chemicals Co. Ltd., China) contained three main structures (Scheme 1): structure (3) in Scheme 1 is the inert ingredient for no oxygen [acid value < 0.3 mg KOH/g, MW = 300–500, oxygen content is 11 wt % (from elemental analysis)]. Triglycidyl isocyanurate (TGIC) and phenol were used as received. *p*-Toluenesulfonic acid (*p*-TSA) and lithium hydroxide were of reagent grade and used as catalysts for two reactions, respectively. All solvents used were of reagent grade.

Analytical methods

Gel permeation chromatography (GPC) analyses were performed using a Wyatt apparatus (Wyatt Technology, Santa Barbara, CA) with THF at a flow rate of 0.8 mL/min, calibrated by polystyrene standards. The

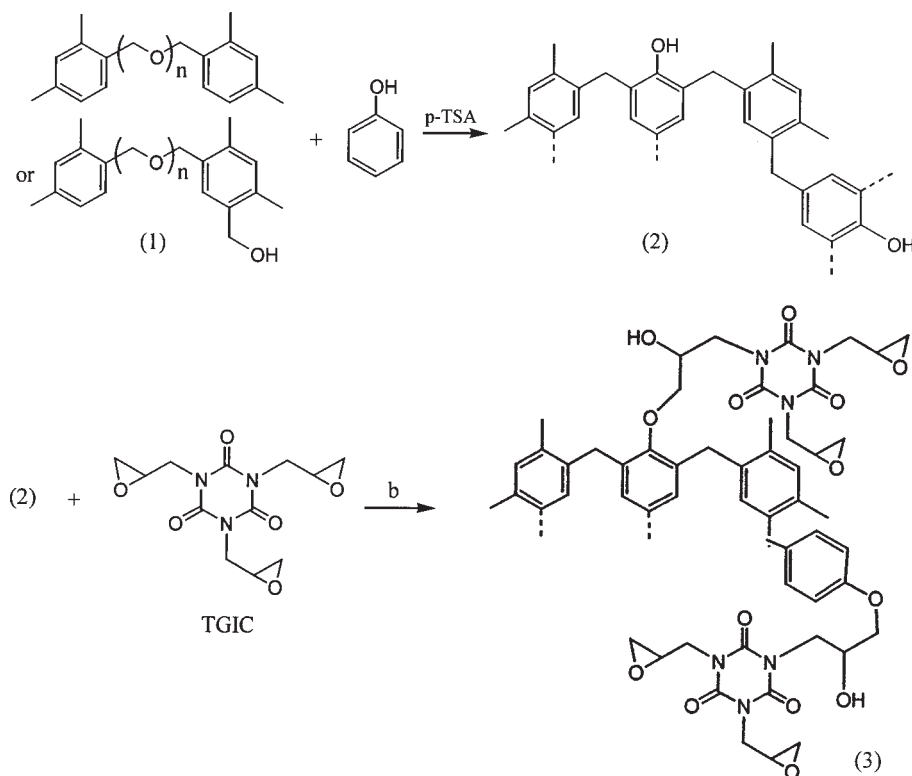
content of free phenol (weight percentage of the unreacted phenol compared to the total weight of product) and conversion of TGIC were calculated from the standard curve, which came from the function of concentration of the phenol/THF or TGIC/THF solution and corresponding elution peak height. The procedure was carried out as follows: a series of exactly prepared solutions of phenol or TGIC/THF (0.1 mg/mL) were injected quantitatively into the GPC system, to obtain the corresponding elution peak heights. Concentration plots of the phenol/THF and TGIC/THF solutions versus elution peak height gave two straight lines. The corresponding linear relative coefficients were 0.9999 and 0.9995 for phenol/THF and TGIC/THF solutions, respectively.

Infrared spectra were recorded by using a Vector 22 FTIR spectrophotometer (400–4000 cm^{-1} , KBr pellet; Vector Laboratories, Burlingame, CA). $^1\text{H-NMR}$ was obtained with an Advance DMX 500 NMR spectrometer (Bruker, Darmstadt, Germany), at 35°C using CDCl_3 as solvent. Elemental analysis (EA) was performed on an F002 Heraeus CHN-O-Rapid elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) using acetanilide as a standard.

Preparation of XPF and XT resin

A general synthetic procedure is described as follows:

A four-neck, round-bottom flask, equipped with a mechanical stirrer, a thermometer, N_2 inlet, a Dean-Stark trap, and a reflux condenser, was charged with 50.0 g XF resin, 36.0 g phenol, and 80 mL toluene. The mixture was stirred under N_2 about 10 min to extrude air out of the solution, after which 0.053 g *p*-TSA was added. The reaction was carried out at the reflux temperature (120–125°C) about 6.0 h. Then a clear, yellow solution was obtained and used for the next reaction without purification. A pale yellow, soft solid product (XPF resin) could be obtained by precipitation with deionized water. TGIC (108.0 g) and DMF (100 mL) were added, and the mixture was stirred at 100°C.



Scheme 2 Synthesis of XPF and XT resin. (1) XF resin; (2) XPF resin; (3) ideal structure of XT resin.

Then 1.0 g 2 wt % lithium hydroxide aqueous solution was added after TGIC was dissolved in the solution. The temperature of the mixture was maintained at 140°C for about 60 min. Then, a clear, yellow solution was obtained. A pale yellow solid product (XT resin) was obtained after being precipitated by deionized water or methanol. The epoxy value, about 0.30–0.40 mol/100 g, varied with the reaction condition, which was determined according to the hydrochloric acid–pyridine method.

IR (cm^{-1}): XPF resin: 3507 ($\nu\text{PhO-H}$), 2879, 2924 (νCH_3), 1452, 1375 (νCH_2), 1260–1180 ($\nu\text{Ph-O}$); XT resin: 3449 ($\nu\text{PhO-H}$), 2879, 2924 (νCH_3), 1695 (triazine ring), 1461 (νCH_2), 916 (oxirane ring).

$^1\text{H-NMR}$ (ppm): XPF resin: 6.43–7.36 (aromatic H), 3.82 (ArCH_2Ar), 2.23, 2.33 (CH_3); XT resin: 6.46–7.31 (aromatic H), 3.50–4.50 (ArCH_2Ar , $-\text{NCH}_2\text{C}<$), 3.26, 2.83, and 2.70 (oxirane ring), 2.23, 2.33 (CH_3).

RESULTS AND DISCUSSION

Synthesis and structural characterization of the XPF and XT resin

XPF resin was prepared by reacting XF resin with phenol by condensation reaction between the *ortho*-H and *para*-H of phenol and carbonium ion from breakage of the ether linkage of XF resin in the presence of acid (Scheme 2). From Figure 1, one can observe that

XF resin had characteristic absorptions at 1034, 1099, and 1161 cm^{-1} for ether linkage (C—O—C) stretching vibration because the benzene ring had a different electronic effect on the C—O—C bond, attributed to the different distance from the C—O—C bond to the benzene ring (or the magnitude of n value), which resulted in multiple peaks in the IR spectrum. The greater the value of n , the smaller the wavelength. As

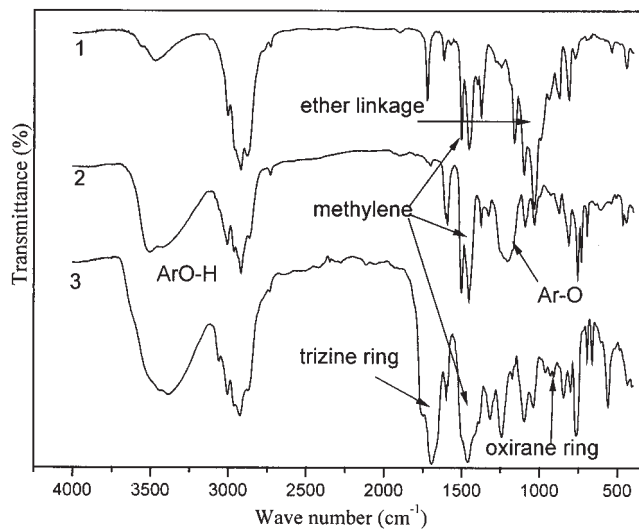


Figure 1 IR spectra: (1) XF; (2) XPF; and (3) XT resins.

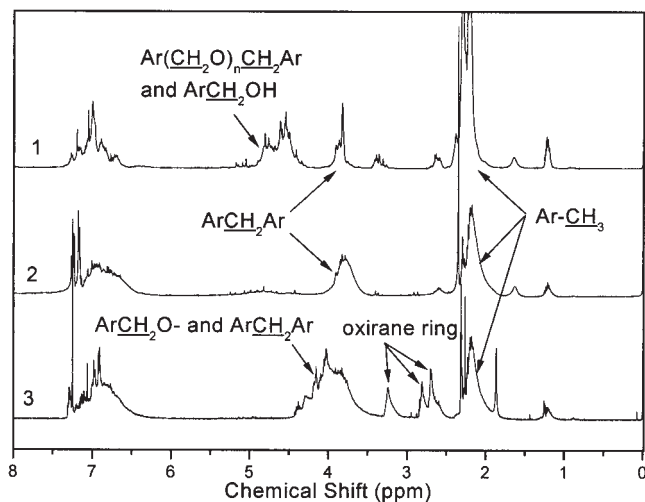


Figure 2 $^1\text{H-NMR}$ spectra: (1) XF; (2) XPF; and (3) XT resins.

the reaction proceeded, these absorptions of ether linkage disappeared, whereas new absorptions of Ar-O-H (3507 cm^{-1}) and stretching vibration of Ar-O ($1260\text{--}1180\text{ cm}^{-1}$) appeared. Methylene linked by benzene ($\text{Ar-CH}_2\text{-Ar}$, $1452, 1375\text{ cm}^{-1}$) had been strengthened for more methylene structures of XPF resin, indicating that phenol had been linked to the backbone of XF resin in the presence of *p*-TSA. XT resin (its ideal structure is shown in Scheme 2) was obtained by a ring-opening reaction between XPF and TGIC. IR absorption peaks at 1695 and 916 cm^{-1} were attributed to the vibrations of the triazine ring and the oxirane ring, respectively, which indicated that the triazine and oxirane rings had been introduced to the molecular structure.

Figure 2 shows the $^1\text{H-NMR}$ spectra of XF, XPF, and XT resins. For different values of n , the methylene of ether linkage of XF resin had different chemical shifts, and had multiple peaks at $4.44\text{--}4.95$ ppm, which contained methylene in hydroxymethyl (ArCH_2OH). Chemical shifts of methylene of ArCH_2Ar appeared about multiple peaks at 3.93 ppm for different chemical environments. There were no chemical shifts of methylene of ether linkage and hydroxymethyl ($4.44\text{--}4.95$ ppm) in the spectrum of XPF resin because of the breakage of ether linkage of XF resin and the completion of condensation reaction in the presence of *p*-TSA. Furthermore, chemical shifts of methylene of ArCH_2Ar were widened because more ArCH_2Ar was generated in the structure of XPF resin. In the $^1\text{H-NMR}$ spectrum of XT resin, the range of chemical shifts of methylene was enlarged because of a new chemical bond produced from the ring-opening reaction of the oxirane ring of TGIC and Ar-OH of XPF resin. Moreover, chemical shifts of the oxirane group ($3.26, 2.83, \text{ and } 2.70$ ppm) appeared. From the results

of IR and $^1\text{H-NMR}$ spectra, we concluded that a new nitrogen-containing epoxy resin (XT resin) was successfully synthesized.

Synthetic kinetics of XPF resin

The oxygen content of XF resin is the measurement of its reactivity to phenol: the higher the oxygen content, the greater the reactivity to phenol. Phenol has three sites (two *ortho* and one *para*) that may react with XF resin. Herein we assumed, on average, that two sites in each phenol could be attacked by carbonium ion, so 50.0 g XF resin should theoretically react with 32.3 g phenol, on the condition that all oxygens of the XF resin were converted to H_2O ($\sim 5.9\text{ g}$). In fact, phenol could not be thoroughly consumed because the carbonium ion was before the reaction with the substituted phenol because of the electron-donating effect and inductive effect of the substituted groups. This meant that the molecular weight (MW) of XPF resin increased but a large portion of unreacted phenols remained in the product. The content of free phenol, defined as the weight percentage of the unreacted phenol against the product, could be used to measure the toxicity of phenolformaldehyde; in our work, free phenol would consume epoxy groups of TGIC in the next reaction without chain propagation and this would decrease the epoxy value of XT resin. So it was necessary to optimize the reaction conditions to obtain XPF resin with low content of free phenol and appropriate MW as a suitable modifier for TGIC.

We monitored the content of free phenol and MW of XPF resin under different reaction conditions by GPC. In this work, the starting retention volume was defined as the point of intersection of the extended line of baseline and tangent of the first peak (see Fig. 3) and denoted the MW of XPF resin.

Figure 3 shows the GPC curves of XPF resin sampled at different reaction times. Figure 4 shows the quantitative relationship of the content of free phenol, and the starting retention volume with reaction time. The value of the first dot in Line 1 of Figure 4 was calculated from the quality of reactants. It was found that the starting retention volume of the product increased slightly at the beginning of the reaction ($0\text{--}1.5$ h). This phenomenon was attributed to the production of monosubstituted phenol with small MW. Moreover, a sharp decrease of the content of free phenol (Line 1, Fig. 4) in this stage supported this conclusion. When the reaction time increased from 1.5 to 6.0 h, the MW of XPF increased with time as a result of the production of multisubstituted phenol, although the content of free phenol decreased slightly because the carbonium ion was before the attack on the substituted phenol. From 6.0 to 11.0 h, MW and the content of free phenol did not undergo any obvious changes,

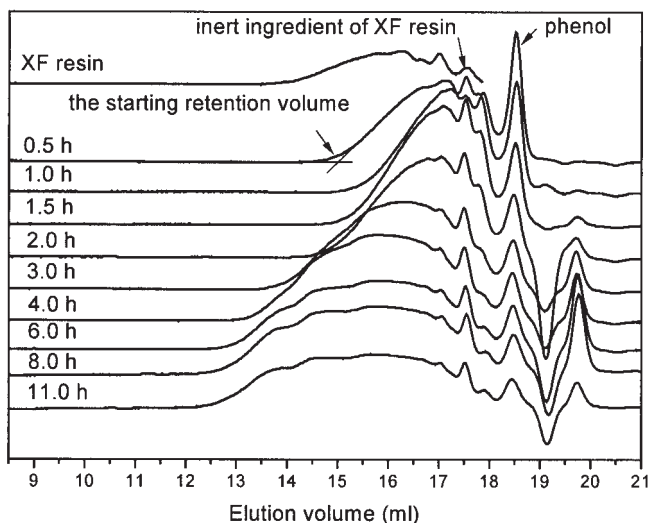


Figure 3 GPC curves of XPF resins sampled at different reaction times. XF/phenol = 2.08 (weight ratio), refluxed in toluene (120–125°C), *p*-TSA (0.062 wt %) as a catalyst.

indicating that the reaction was terminated because oxygen of the XF resin had been consumed.

In the above reaction, toluene was substituted for xylene, so the temperature of reaction was increased (refluxed at about 140–145°C), the rate of reaction was accelerated sharply, and the content of free phenol was obviously decreased. The peak of the unreacted phenol was too low to determinate exactly, and the starting retention volume scarcely changed after 0.5 h.

Figure 5 shows the GPC curves of XPF resin as a function of XF/phenol weight ratio, and Figure 6 shows the quantitative relationships of the content of free phenol and the starting retention volume with XF/phenol weight ratio. The starting retention volume and the content of free phenol decreased with

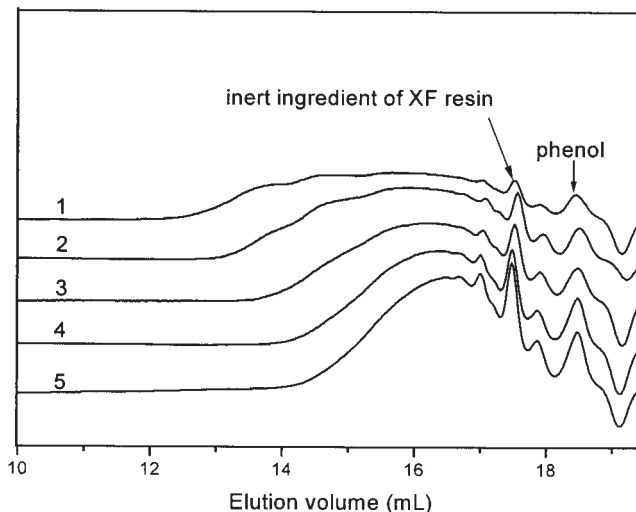


Figure 5 Effect of XF/phenol weight ratios on the GPC curves of XPF resins. XF/phenol: (1) 2.08; (2) 1.79; (3) 1.56; (4) 1.39; and (5) 1.25; refluxed in toluene (120–125°C); *p*-TSA (0.062 wt %) as a catalyst.

increasing XF/phenol weight ratio: that is, the greater the XF/phenol weight ratio, the larger the MW of XPF resin and the less the content of free phenol of XPF resin. XPF resin with larger MW unfavorably reacted with TGIC because of the possible gel effect arising from more Ar—OH in one XPF molecule. Thus a smaller XF/phenol weight ratio may be useful for the synthesis of XPF resin. However, the content of free phenol would be increased sharply when the XF/phenol weight ratio became smaller. Generally, the gel effect may be avoided in the next reaction when the XF/phenol weight ratio is not >1.56. In addition, in our research, to obtain a suitable XPF resin with low content of free phenol, the XF/phenol weight ratio should not be <1.25.

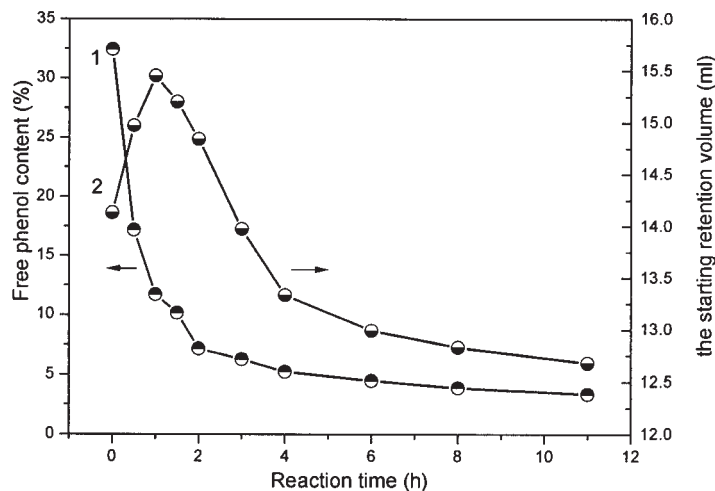


Figure 4 Plots of content of free phenol (line 1) and the starting retention volume (line 2) with reaction time, determined by GPC. XF/phenol = 2.08 (weight ratio), refluxed in toluene (120–125°C), *p*-TSA (0.062 wt %) as a catalyst.

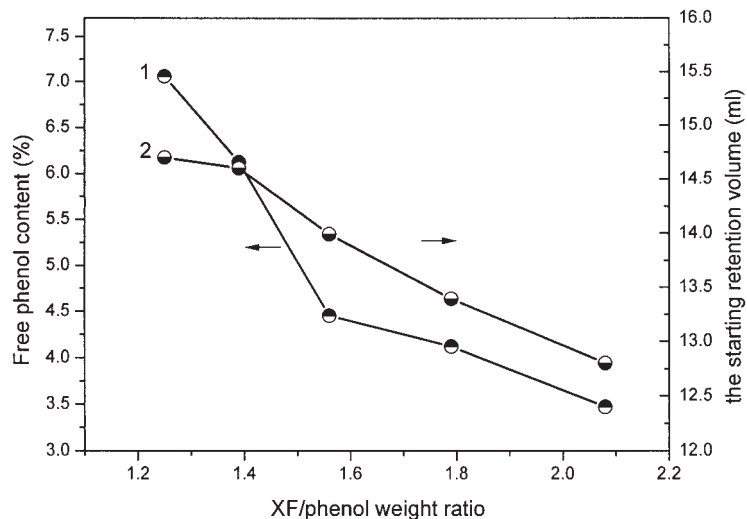


Figure 6 Relationships of free phenol content (line 1) and the starting retention volume (line 2) with different XF/phenol weight ratios, determined by GPC; refluxed in toluene (120–125°C); *p*-TSA (0.062 wt %) as a catalyst.

The amount of *p*-TSA had an obvious effect on the reaction. Figure 7 shows the plots of the content of free phenol and the starting retention volume versus different *p*-TSA concentrations: the greater the amount of *p*-TSA, the less the content of free phenol and the starting retention time. In fact, the reaction rate was accelerated with increasing *p*-TSA, which could be observed from the quick extraction rate of water from the reflux toluene (or xylene). Like the effect of temperature on the kinetics, a greater amount of *p*-TSA (not <0.062 wt %) was conducive to the decrease of free phenol content.

From the preceding results, we identified the reaction conditions that were advantageous in improving the reaction rate and favorable to decreasing the free

phenol content. Thus, the optimum reaction conditions for synthesis of XPF resin were greater amounts of catalyst (not <0.062 wt %), high reaction temperature (in reflux xylene; ~ 140–145°C), and adequate reaction time (~ 6.0 h in toluene and 2.0 h in xylene).

Synthetic kinetics of XT resin

In this step, the goal of introducing the XPF structure to TGIC, by ring-opening reaction between Ar—OH and oxirane ring, was to break the molecular symmetry of TGIC; to decrease the epoxy value properly; and to introduce hydrophobic groups for easy processing, toughness, and insulation properties, respectively.

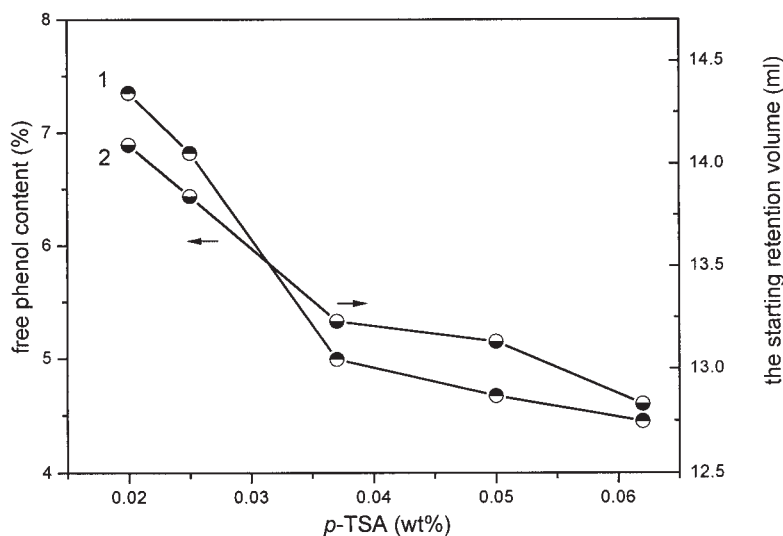


Figure 7 Plots of free phenol content (line 1) and the starting retention volume (line 2) versus different *p*-TSA concentrations. XF/phenol weight ratio is 1.56, refluxed in toluene about 6.0 h, determined by GPC.

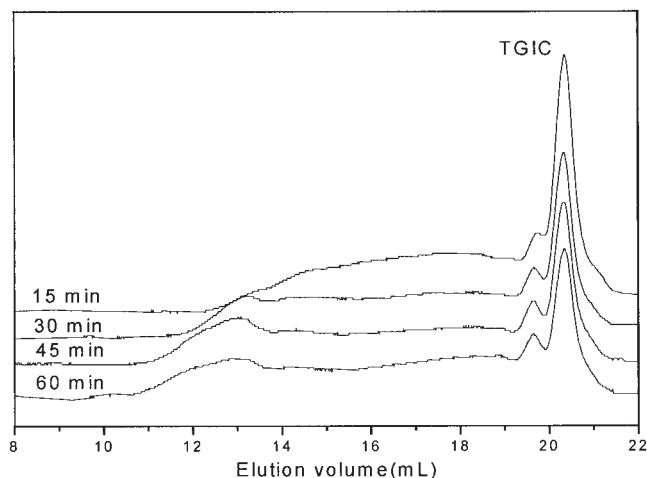


Figure 8 GPC curves of products sampled at different reaction times. XF/phenol = 1.25 (weight ratio), TGIC/phenol = 1 : 1 (mole ratio), refluxed in toluene/xylene within 60 min; catalyst: 2 wt % lithium hydroxide aqueous solution (0.8 wt % of amount TGIC).

To synthesize XT resin characterized by long storage life and good properties, it was the key to improving the percentage conversion of TGIC. It was hoped that only one oxirane ring in each TGIC molecule, on average, would react with XPF resin and, if so, two oxirane rings remained on average in each TGIC molecule. According to this, the theoretical epoxy value could be calculated. For example, when XF, phenol, and TGIC were 50.0, 40.0, and 120.0 g, respectively, the calculated epoxy value was 0.39 mol/100 g. It was observed that the unreacted phenol in XPF resin would react with TGIC, although it did not change the nature of the reaction because the free phenol content was very low compared to excess TGIC in our experiment.

It is well known that Ar—OH readily reacts with the oxirane ring in the presence of base when the reaction temperature is $>100^{\circ}\text{C}$. Many basic catalysts such as triethanolamine, triethylamine, tri-*n*-butylamine, and lithium hydroxide were effective in inducing the ring-opening reaction between Ar—OH and the oxirane ring. The direction of ring opening of the epoxide compound depended on electronic and steric factors and the reaction environment. The side reaction took place between the generated secondary alcohol group of the hydroxyl alkyl products and the unreacted epoxide, and the selectivity of the epoxide phenol reaction had been intensively investigated.¹⁴ We chose lithium hydroxide (2 wt % aqueous solution) as the catalyst for this reaction because of its excellent selectivity¹⁴ and easy removal. The effect of the amount of catalyst was investigated by GPC and observation of stability of products, and it was found that the optimum amount of catalyst (2 wt % LiOH aqueous solution) was 0.5–1.5% with respect to the weight of TGIC.

However, Ar—OH of the XPF resin did not react equally with the oxirane ring because of the electronic effect and steric effect arising from different degrees of substituted phenol. Thus Ar—OH of XPF resin had different reactivity to oxirane ring, which might result in low conversion of TGIC and production of gel. By altering the polarity of the solvent, the percentage conversion of TGIC was improved. The effect of polarity of the solvent on the extent of reaction (especially the percentage conversion of TGIC) is discussed in detail in the following.

Figure 8 and Figure 9 show the GPC curves of XT resin that were sampled at different reaction times in toluene/xylene (volume ratio = 4 : 5) and toluene/DMF (volume ratio = 4 : 5), respectively. Corresponding relationships of the percentage conversion of TGIC, epoxy value, and reaction time are shown in Figure 10.

Figure 10 shows that the epoxy value of the product in toluene/xylene was equal to that in toluene/DMF in the early stage (15 min), but the percentage conversion of TGIC in toluene/xylene was much lower than that in toluene/DMF. A lower percentage conversion of TGIC in toluene/xylene meant that each TGIC molecule had more than one oxirane ring that reacted with Ar—OH, leading to two results: (1) the increase of MW of XT resin (the starting retention volume of the product in 60 min was about 11.0 mL in Fig. 8) and occurrence of the gel effect if the reaction continued; (2) a majority of TGIC was retained in the product. This was because toluene/xylene was a nonpolar system for XPF and TGIC compared to that of toluene/

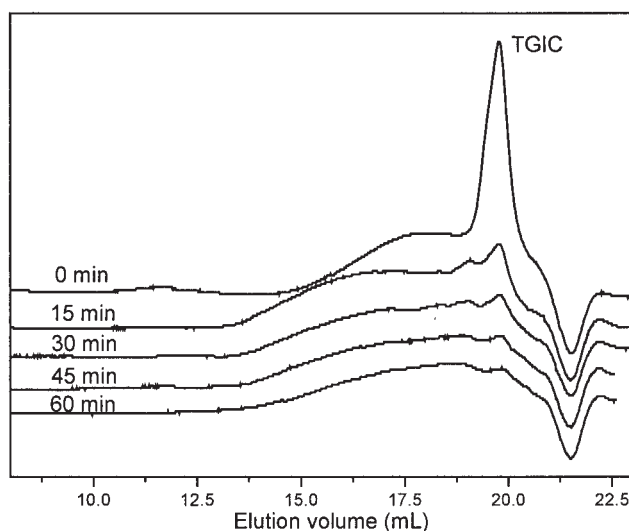


Figure 9 GPC curves of products sampled at different reaction times. XF/phenol = 1.25 (weight ratio), TGIC/phenol = 1 : 1 (mole ratio), refluxed in toluene/DMF within 60 min; catalyst: 2 wt % lithium hydroxide aqueous solution (0.8 wt % of amount TGIC).

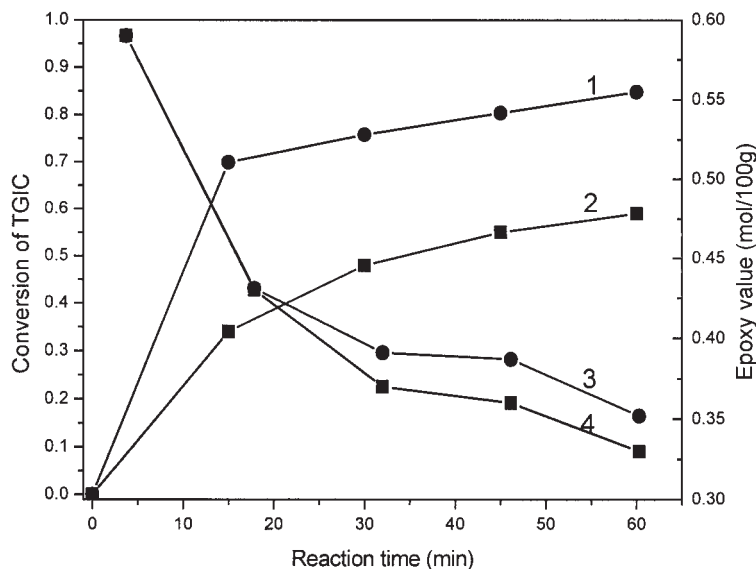


Figure 10 Relationships of TGIC conversion, epoxy value, and reaction time in toluene/xylene and toluene/DMF. Catalyst: 2 wt % lithium hydroxide aqueous solution (0.8 wt % of amount TGIC). Line (1): TGIC conversion in toluene/DMF; line (2): TGIC conversion in toluene/xylene; line (3): epoxy value in toluene/DMF; line (4): epoxy value in toluene/xylene.

DMF; therefore, XPF resin was embedded in toluene/xylene, and Ar—OH of the XPF resin assumed unequal reactivity to TGIC because of the steric effect and electronic effect arising from different substituted groups and different chemical environments. At the same time, TGIC was difficult to dissolve entirely, even if it melted in the reaction temperature. Because Ar—OH was prone to react with dissolved TGIC, each dissolved TGIC had more than one oxirane ring that reacted, and so the gel effect readily occurred. Moreover, a large portion of the unreacted TGIC would quickly precipitate from the solution. These results made the product inhomogeneous and useless for manufacturing prepreg or laminate. If the xylene was substituted by DMF, TGIC could be dissolved entirely because the polarity of the solvent improved and XPF molecules were more widely distributed, which caused the steric effect to decrease; thus a majority of TGIC reacted with the XPF resin in a short time and thus the MW of XT resin did not obviously increase (Fig. 9).

The final percentage conversions of TGIC in toluene/xylene and toluene/DMF were about 60 and 85%, respectively, and the corresponding epoxy values of product in toluene/xylene and toluene/DMF were 0.32 and 0.35 mol/100 g, respectively. These results showed that a polar solvent (toluene/DMF) favored the synthesis of XT resin. XT resin from toluene/DMF was a stable, clear solution, which had about 8% nitrogen content (in solid content, from elemental analysis) and could be reserved about half a year without precipitation.

CONCLUSIONS

A novel nitrogen-containing epoxy resin was synthesized by an addition reaction between triglycidyl isocyanurate (TGIC) and XPF resin that was prepared by a condensation reaction between xylene formaldehyde resin and phenol. The structures of XPF resin and XT resin were identified by IR and $^1\text{H-NMR}$ spectra. The synthetic kinetics of XPF was intensively investigated by gel permeation chromatography (GPC). The optimum reaction conditions for synthesis of thermoplastic XPF resin, with different molecular weights and low content of free phenol, included higher amounts of catalyst (not <0.062 wt %) and reaction temperature (refluxed xylene; ~ 140 – 145°C) and a longer reaction time (~ 6.0 h in toluene and 2.0 h in xylene). The reaction kinetics of XPF resin and TGIC was monitored by GPC and epoxy value titration. The results showed that the conversion of TGIC was $>85\%$ and the epoxy value was 0.35 mol/100 g within 60 min at 140°C . A stable, clear XT solution (nitrogen content was about 8% in solid) was obtained and could be reserved about half a year without precipitation. Further research on XT resin will be continued in our laboratory.

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