

Acetyl-Capped Paraformaldehyde as Crosslinking Agent for BMI-Modified Novolac Resin for Resin Transfer Molding

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ABSTRACT: Paraformaldehyde was end-capped with acetyl groups and was applied as a crosslinking agent for a bismaleimide (BMI)-modified novolac resin system. The processibility of the resin system containing 5 wt % crosslinking agent still met the need for resin transfer molding (RTM), whereas the thermomechanical properties of crosslinked resin improved significantly. The composites based on the resin system and woven glass fabric showed

better flexural strength, modulus, and higher retention rates at 200 and 300°C than that based on a resin system without acetyl-capped paraformaldehyde. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1265–1271, 2002

Key words: acetyl-capped paraformaldehyde; BMI-modified novolac resin; resin transfer molding; processibility; heat resistance

INTRODUCTION

Phenolic resins, notwithstanding their centurial long history, still attract a great deal of research interest. Based on the high aromatic content and very high crosslinking density in the structure, phenolic resins show unique properties such as high dimensional stability, good strength retention at high temperatures, high char yield, and flame retardation. Therefore, they play an especially important role in the modern vehicle and construction.

Phenolic resins are usually cured through condensation reactions. For matrix of composites, volatile release upon curing becomes the major disadvantage of phenolic resins. To avoid the volatile releasing, alternative curing mechanisms were studied. A successful approach was to introduce allyl groups into the phenolics, and the resins were cured with bismaleimides,^{1–3} through the “Ene” reaction and the Diels–Alder reaction.^{4–6}

A modified novolac resin system for resin transfer molding (RTM) was developed recently.⁷ In this novel system, the novolac resin was allylated and a bismaleimide (BMI) was incorporated to cure the resin. In the BMI-modified novolac resins for RTM, the degree of allylation and the content of BMI were limited by

the requirement of the low viscosity for processing.⁷ Consequently, quite a portion of the reactive sites in the novolac structure remained unused. Hence, it is interesting to study the utilization of these reactive sites for making additional crosslinking, and thus, improving the heat resistance of the cured resin.

Although hexamethylenetetramine (HMTA) and paraformaldehyde are the most commonly used crosslinking agents for novolac resins, they are not suitable for the purpose of the present work because the decomposition temperatures of these compounds are too low. Polyacetal has been used to cure novolac resins at a temperature of ~ 200°C,⁸ but it is not soluble in the BMI-modified novolac resin system. It is known that the stability of paraformaldehyde can be improved by capping the hydroxyl end groups through esterification⁹ or through etherification.^{10–12} Accordingly, we use acetyl-capped paraformaldehyde (ACPF) as crosslinking agent for improving the BMI-modified novolac resin system for RTM. In the present study, the effects of ACPF on the processing properties of the BMI-modified novolac resin system are investigated, and the thermomechanical properties of the cured resin and the composites are studied.

EXPERIMENTAL

Materials

Phenol and formaldehyde (37% aqueous solution) were chemical reagents acquired from Beijing Organic

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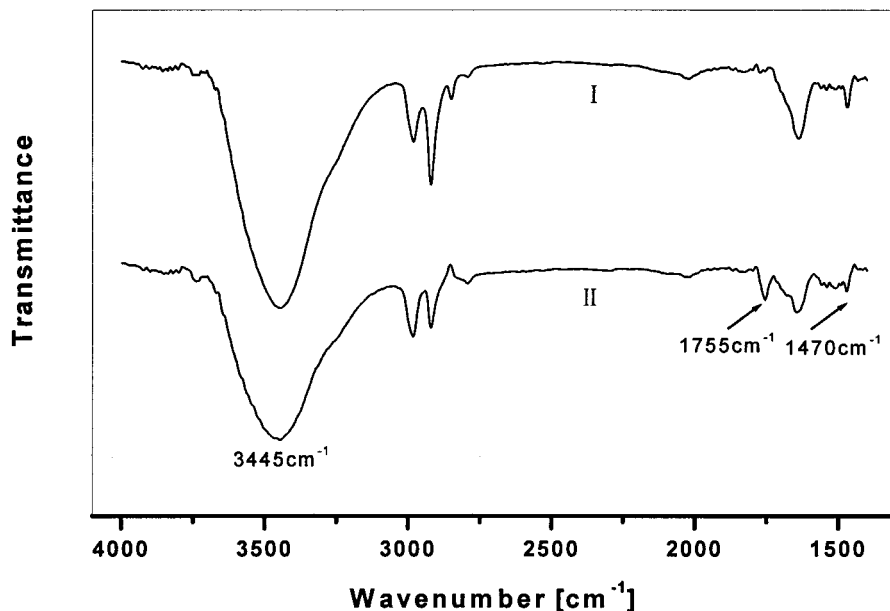


Figure 1 FTIR spectra of paraformaldehyde (I) and ACPF (II).

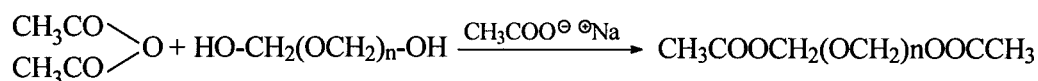
Chemicals Factory (Beijing, China) and were used as supplied. Allyl chloride was obtained from Qilu Petrochemical Co. (Zibo, China) and used after distillation. 4,4'-Bismaleimidodiphenyl methane (BMI) was purchased from Fenguang Chemical Co., Ltd. (Honghu, China). It was a crystalline substance with a melting temperature of $\sim 172^\circ\text{C}$ and a molecular weight of 286. Allyl phenyl ether was synthesized in this laboratory. It was a clear liquid with a boiling point of 220°C and viscosity of 0.01 Pa s at 25°C .

Paraformaldehyde, acetic anhydride, sodium acetate, and HMTA were chemical reagents from Beijing Yili Chemicals Co. (Beijing, China).

Synthesis and preparation

Preparation of ACPF

Acetyl-capped paraformaldehyde was prepared according to the following reaction⁹:



Paraformaldehyde, acetic anhydride, and sodium acetate, in a weight ratio of 1 : 10 : 0.016, were added to a three-necked flask equipped with a mechanical stirrer and a thermometer. The mixture was refluxed at 140°C for 2 h in a nitrogen atmosphere. The product was filtered and thoroughly washed with methanol and then with acetone. The resulting white powder was dried *in vacuo* at 50°C .

The product was characterized by FTIR.¹³ The esterification number (d) was estimated according to the change of the hydroxyl band at 3445 cm^{-1} :

$$d = \frac{A'_{3445}|A_{1470} - A''_{3445}|A_{1470}}{A'_{3445}|A_{1470}}$$

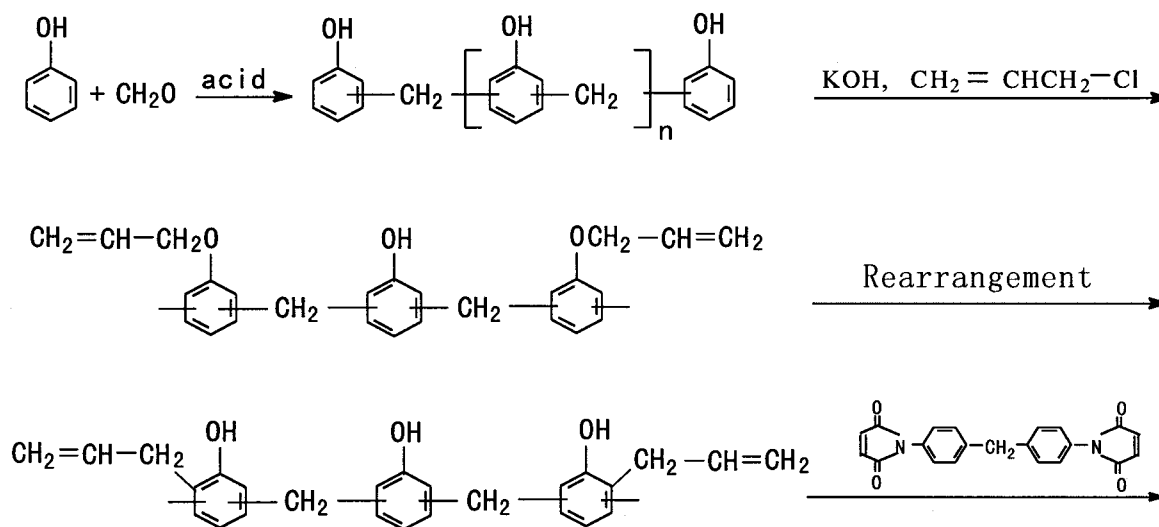
The band at 1470 cm^{-1} for the oxymethylene units was used as reference for the calculation (Fig. 1). Because paraformaldehyde was a crystalline powder, the es-

terification was not complete. Here, the value of d was 0.54 for ACPF.

Synthesis of the BMI-modified novolac resin

A BMI-modified novolac resin was prepared in the following steps: (1) synthesis of novolac resin; (2) allylation of the novolac resin; (3) rearrangement of the allyl groups; and (4) prepolymerization of the allylated novolac resin with BMI (see Scheme 1).

The novolac resin was prepared by oxalic acid catalyzed condensation, with a molar ratio of phenol to formaldehyde of 1 : 0.9. The allylation reaction of novolac resin was carried out at 80°C for 5 h in butanol solution, with a molar ratio of phenol group of novolac resin to KOH to allyl chloride of 1 : 0.5 : 0.5. Number-average molecular weight and allyl content of novolac resin were 454 and 48.34%, respectively, calculated according to the $^1\text{H-NMR}$ data.¹⁴



Prepolymer

Scheme 1 Synthesis of BMI-modified novolak resin.

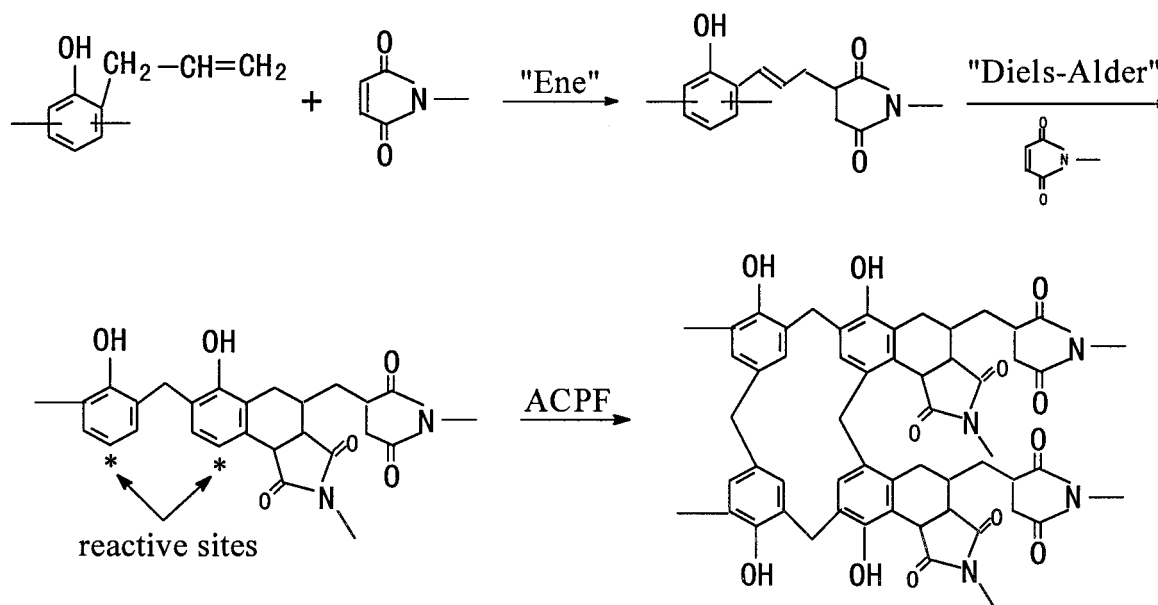
For the prepolymerization, the allylated novolak resin and BMI, with a molar ratio of allyl groups to BMI 1:0.5, were added into a three-necked flask equipped with a mechanical stirrer, a thermometer, and a condenser. Allyl phenol, 5 wt % of the allylated novolak resin, was also added. The prepolymerization was effected by continuously stirring at 115°C for 40 min. After that, a clear homogenous resin was obtained.

Blending of ACPF with the BMI-modified novolak resin

ACPF and BMI-modified novolak resin were blended at 115°C for 15 min.

Preparation of the cured resin

The resin mixture was degassed in a vacuum oven at 100°C for 4 h and then poured into a rectangular mold.



Scheme 2 ACPF is incorporated to make cross-linking by using the unused reactive sites in the novolak structure.

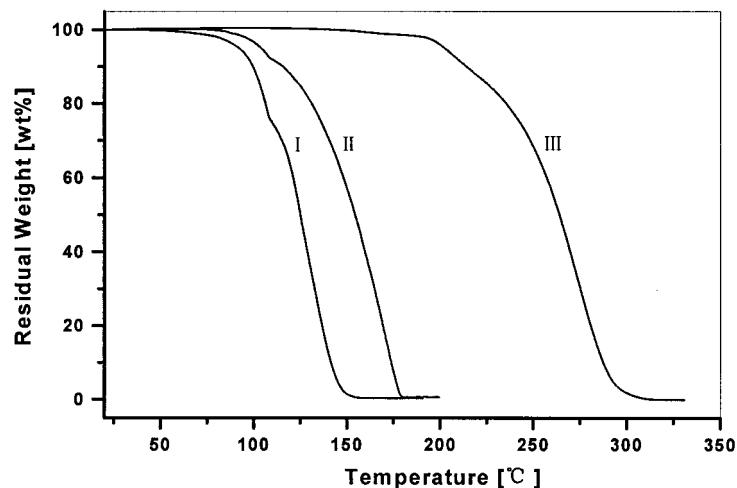


Figure 2 TGA thermograms for paraformaldehyde (I), HMTA (II), and ACPF (III) at a rate of 5°C/min in N₂.

The cure cycle was 170°C/2 h + 200°C/6 h, and the postcure procedure was 250°C/6 h.

Fabrication of composites via RTM

Composites were fabricated in a homemade RTM setup. The rectangular mold with woven glass reinforcement was preheated to 100°C. The resin was heated to 100°C and injected into the mold with the assist of a vacuum. The cure cycle was 170°C/2 h + 200°C/6 h, and the postcure was effected at 250°C/6 h. The composites were machined into specimens for flexural testing.

Characterization and measurements

FTIR spectra were obtained on a Bruker EQUINOX55 spectrometer. The viscosity was determined on a NDJ-79 viscometer. The gel time was measured in a controlled temperature instrument. Thermal analysis of the resin system was performed on a Perkin–Elmer

7 DSC at a heating rate of 10°C/min in a nitrogen atmosphere.

The thermal stability of the cured resin was studied on a Perkin–Elmer 7 TGA analyzer, at a heating rate of 5 or 20°C/min in a nitrogen atmosphere.

Heat distortion temperature (HDT), water absorption, and flexural tests were conducted according to the standard GB-1634-79, GB1034-86, and GB1042-79, respectively. The flexural tests for the composites were carried out according to the standard GB1449-83.

RESULTS AND DISCUSSION

Choice of the crosslinking agent

The curing of the BMI-modified novolac resin takes place through the Ene reaction and the Diels–Alder reaction. As indicated in Scheme 2, free reactive sites on the phenol ring remain after these reactions. They can be used for making additional crosslinking if a crosslinking agent of the novolac resin is incorporated.

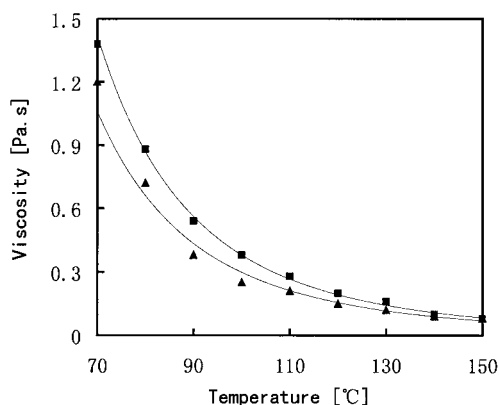


Figure 3 Viscosity–temperature curve of the resin systems: (■) resin system containing 5 wt % ACPF; (▲) resin system without ACPF.

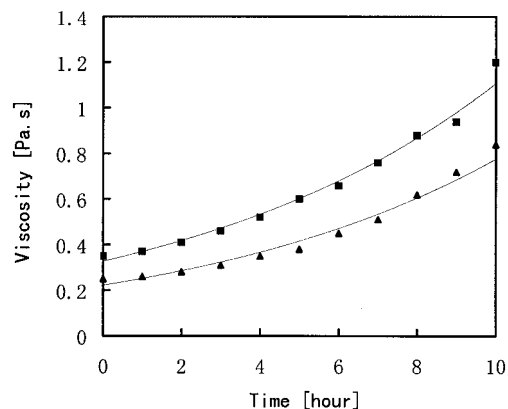


Figure 4 Change of viscosity of the resin systems with time at 100°C: (■) resin system containing 5 wt % ACPF; (▲) resin system without ACPF.

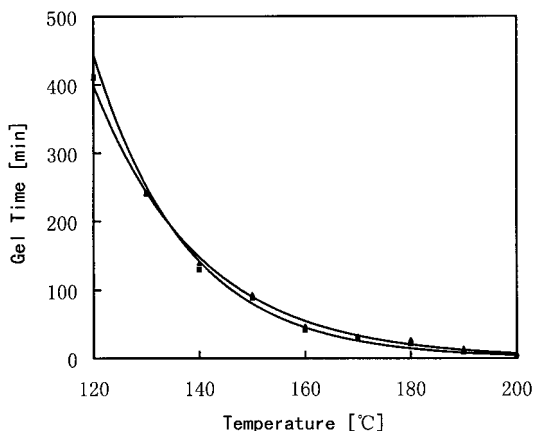


Figure 5 Gel time–temperature correlation of the resin systems: (■) resin system containing 5 wt % ACPF; (▲) resin system without ACPF.

Because the reactions at the phenol ring are condensed, strategically, to avoid porous development, these reactions for increasing the crosslinking density should be subsequent to the Ene reaction and the Diels–Alder reaction.

HMTA is the most commonly used crosslinking agent for the novolac resin. Paraformaldehyde was also used as curing agent. However, decomposition temperatures of these compounds are too low for the purpose of this work. It was reported that onset temperature in the DSC thermogram was 140°C for the curing of a novolac resin with paraformaldehyde,¹⁵ whereas the onset temperature for the curing of the BMI-modified novolac resin was ~ 160°C.⁷ The potlife will be reduced substantially and porous materials will be resulted if they are incorporated in the resin.

As the terminal hydroxyl groups of paraformaldehyde are responsible for the low decomposition temperature, the stability can be improved greatly by end-capping.⁹ ACPF prepared by us showed an onset temperature of 195°C in the TGA curve (Fig. 2). For comparison, the onset temperatures in TGA curves for HMTA and paraformaldehyde were 129 and 108°C, respectively. Therefore, ACPF was chosen as the crosslinking agent for the BMI-modified novolac resin.

Effects of ACPF on the processibility

The BMI-modified novolac resin was used for RTM. It is important to study the effect of ACPF on the processibility of the resin system. ACPF of 5 wt % based on the novolac resin was dissolved in the resin system at 100°C. The viscosity–temperature curves and viscosity–time curves at 100°C for the resin systems are given in Figures 3 and 4, respectively. It is seen that a slight increase in the viscosity of the resin system was caused by incorporation of the crosslinking agent. The viscosity at 100°C was increased from 0.25 to 0.40 Pa s as 5 wt % of ACPF was incorporated. After 4 h at 100°C, the viscosity of the resin system containing crosslinking agent was still < 0.5 Pa s. That is to say, the resin system had a potlife sufficiently long for RTM.¹⁶

Gel time, the time needed for the resin to reach the gel state at a given temperature, depends on the reactivity of the resin system. Figure 5 shows the temperature dependence of the gel time of the resin systems. The difference in gel times for the resin systems with or without ACPF at a given temperature was insignificant. The results indicated that ACPF did not take part in the reaction at the early stage of curing.

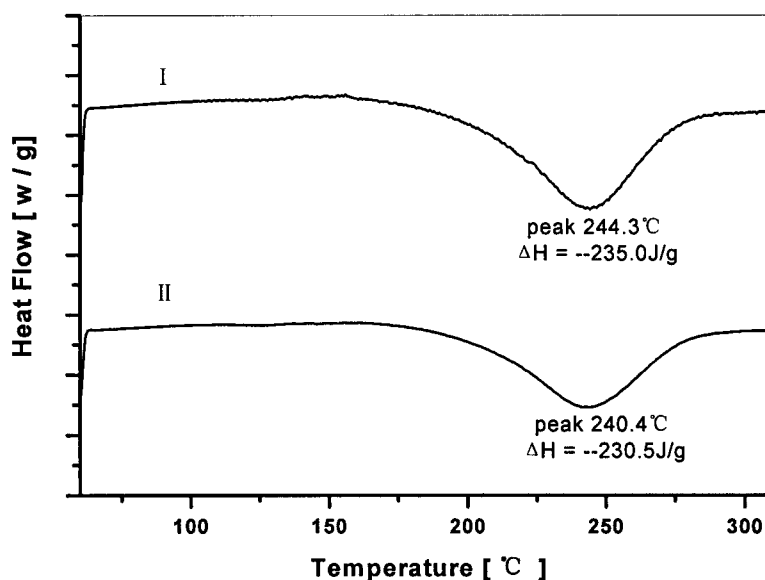


Figure 6 DSC curves of sample containing 5 wt % ACPF (I) and sample without ACPF (II) at a rate of 10°C/min in N₂.

TABLE I
Properties of the Cured Resins

Properties	Neat resin	Resin containing 5 wt % ACPF	Resin containing 8 wt % ACPF
Flexural strength (MPa)	122.4	131.6	133.0
Flexural modulus (GPa)	3.53	3.85	3.90
Water absorption (%)	4.50	4.45	4.45
HDT (°C)	273	291	295
T_g (°C)	288	322	325
Density (g/cm ³)	1.31	1.33	1.34

The difference in DSC thermograms for the resins with or without ACPF was marginal (see Fig. 6). The sample containing ACPF had a slightly higher peak temperature and larger enthalpy. Therefore, incorporation of the crosslinking agent did not require a change in the curing regime.

Thermomechanical properties

The effect of the crosslinking agent ACPF on the properties of the cured resins was significant. It is seen in Table I that incorporation of 5 wt % of ACPF gave rise to enhancement of HDT for 18°C and glass transition temperature (T_g) for 34°C, and a remarkable improvement in flexural properties, too. As the incorporation of ACPF was 8 wt %, further improvement in HDT, T_g , and flexural properties was insignificant compared with that containing 5 wt % of ACPF; however, the processibility became worse, such that the viscosity at 100°C was 0.60 Pa s and >1.0 Pa s after 3 h. In addition, the density of the cured resins containing ACPF was increased slightly, and there was a little improvement in water absorption. The physical improvement of the cured resin could be attributed to the

formation of a more perfect network. With the incorporation of ACPF, the free reactive sites on the phenol ring after Ene and Diels–Alder reactions were used for making additional crosslinking and no porosities were developed during the curing process.

Thermal stability of the crosslinked resins was studied by thermogravimetric analysis (TGA). It is seen in Figure 7 that the onset temperature of decomposition was increased from 402 to 416°C with the incorporation of 5 wt % of ACPF, and the temperature for 10% weight loss was increased from 445 to 458°C. The char yield at 700°C was increased for ~5%. It is clear that the thermal resistance of the resin was improved by incorporation of ACPF.

Void-free composites based on the BMI-modified novolac containing 5 wt % ACPF can be fabricated by RTM process. Properties of woven glass composites are given in Table II. It is seen that the flexural strength and modulus of the composite based on the resin containing the crosslinking agent were comparable to that of the control. As expected, the retention rates of the strength and modulus at 200 and 300°C were improved significantly by the incorporation of the crosslinking agent.

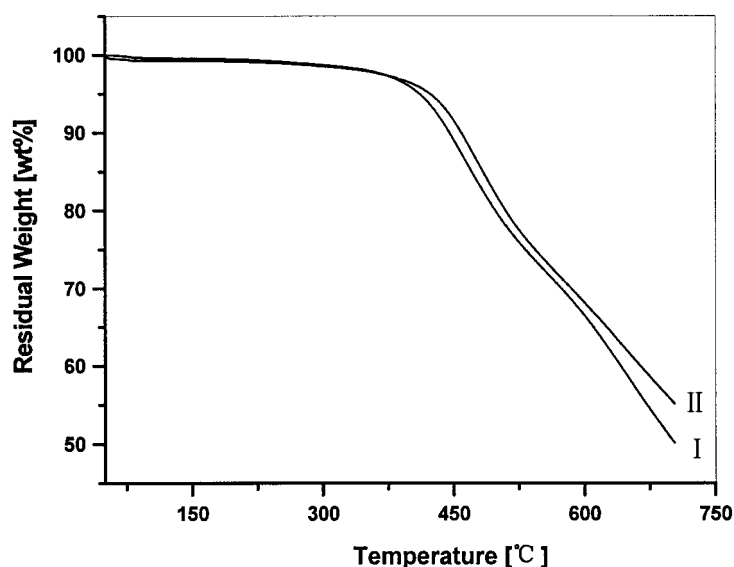


Figure 7 TGA curves of the cured resins at a rate of 20°C/min in N₂ (I) resin without ACPF; (II) resin containing 5 wt % ACPF.

TABLE II
Properties of the Composites Based on BMI-Modified
Novolak and Woven Glass Cloth Fabricated
by RTM Process

	Composite I		Composite II	
	Value	Retention rate	Value	Retention rate
Resin content (wt)	33		34	
Flexural strength (MPa)				
23°C	413	—	408	—
200°C	371	90%	382	94%
300°C	267	65%	330	81%
Flexural modulus (GPa)				
23°C	27.7	—	27.6	—
200°C	25.3	91%	26.1	94%
300°C	21.5	78%	23.0	83%

Composite I, The resin Without ACPF; composite II, the resin containing 5 wt % ACPF.

CONCLUSION

In the BMI-modified novolac resin, there are unused reactive sites in the novolac structure. They can be utilized for making additional crosslinking by incorporation of a crosslinking agent of high decomposition temperature. The resin system containing 5 wt % ACPF showed good processibility for RTM. The cured resin containing ACPF displayed improved thermal

resistance. The void-free composites were prepared by RTM process based on the resin system and woven glass cloth. By virtue of the crosslinking agent, the strength retention at high temperatures was improved significantly.

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