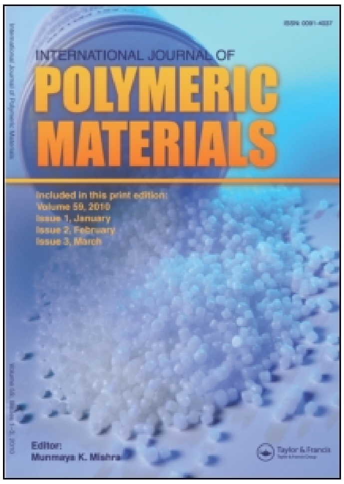

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Liang Guozheng[a]; Gu Aijuan[a]
[a] Department of Chemical Engineering, Northwestern Polytechnical University, Xi'an, P.R. China

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Synthesis and Characteristic of Allyl Novolac and Its Copolymer with Bismaleimide

LIANG GUOZHENG and GU AIJUAN

Department of Chemical Engineering, Northwestern Polytechnical University, Xi'an 710072, Shaanxi, P.R. China

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The main target of the modification of bismaleimide (BMI) is the improvement of the resin's fracture toughness with no, or only minor, reduction in the glass transition temperature (Tg) and the hot/wet environmental stability. In this paper, a new allyl compound modified BMI resin system has been developed for this target. The allyl novolac, coded as AF, was synthesized and characterized. The properties of the modified BMI resin and its composites have been studied in detail. Thermogravimetric analysis (TGA) in nitrogen atmosphere revealed that the modified BMI resin was stable up to 484 °C. The hot/wet properties of the cured copolymer were investigated by aging it in boiling distilled water. After aging for 100 h, water absorption and heat deflection temperature (HDT) were 3.2% and 277 °C, respectively.

Keywords: Allyl Novolacs; Bismaleimide; Copolymers synthesis; Properties

INTRODUCTION

Bismaleimides (BMIs) are primer candidates as matrix resins for advanced composites because of their high temperature resistance, improved hot/wet stability and superior fire, smoke and toxicity properties. However, they do tend to be brittle [1–6]. Many methods have been applied to improve the toughness of BMI, but most of them result in lower thermal properties and hot/wet performance due to dramatic reductions in glass transition temperature. In this paper, a new poly allyl compound-allyl novolac (AF) is synthesized and characterized. The copolymer of BMI and AF are expected to have outstanding thermal properties and hot/wet performance as well as good mechanical properties, laminate properties are also discussed.

EXPERIMENTAL

Reagents and Solvents

4,4'-bismaleimidodiphenyl methane, supplied by Fengguang Chemicals, China, was recrystallization from benzene or ethanol and chloroform. Phenol and allyl chloride were obtained from Xi'an Reagents Chemical Plant, China, and used as supplied.

Preparation of AF

Allyl chloride (12.5 g, 0.16 mol) was added portionwise to a stirred solution of phenol (9.4 g, 0.1 mol) and KOH (8.9 g, 0.13 mol) in water under nitrogen atmosphere. The reaction solution was stirred and refluxed for 2 h. Sodium chloride was separated from the mixture by filtration. Then the filtrated stock was heated to 200°C for 1.5 h to yield 0.095 mol of 2-allylphenol as a pale amber liquid.

To 143 g (1.0 ml) of 2-allylphenol heated at 90°C were added dropwise 64 g (1.6 moles as CH_2O) of formalin (37 % CH_2O) and 3 g (0.08 mole) of oxalic acid over a period of 1h. The reaction was allowed to proceed at 90°C for 8 h. The reaction mixture was cooled to 40°C, separated from the aqueous layer, washed with 30 ml of hot water and then dehydrated under reduced pressure until the temperature reached 160°C to obtain a liquid resin.

Characterization of AF

Infrared (IR) spectra were recorded on a SPECORD-79 spectrometer.

Viscosity determinations were done at 23°C using Brookfild rotating spindle viscometer, Model LVT, accroding to the ASTM D-2393, test method.

Measurement of Prepolymer

A standard laboratory hot-plate equipped with a temperature controller was used to determine the prepolymers gel time at various temperatures. The time required for the resin to stop stinging and become elastic is called the gel time.

Thermal analysis of sample was carried out on a DuPont 990 thermal analyzer unit equipped with a Perkin-Elmer DSCIV differential scanning calorimetric unit. DSC scan were run at 10 °C/min.

Measurement of Neat Resin

Tensile, flexural and impact data of neat resins were obtained according to GB 1451-83, GB 3356-82, and GB 1042-79, respectively. Heat Deflection Temperature (HDT) by ASTM D 648.

Thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer DEL 7A SERIES TGA 7 in a nitrogen atmosphere at a heating rate of 10 °C/min.

Humidity resistance was measured by putting samples into boiling distilled water and determining the water absorption and HDT of neat resin.

Measurement of Composite

Composite tensile, flexural and impact properties were measured by GB 1447-83, 1449-83 and 1042-79, respectively. In addition, short beam shear strength was done by GB 3357-82.

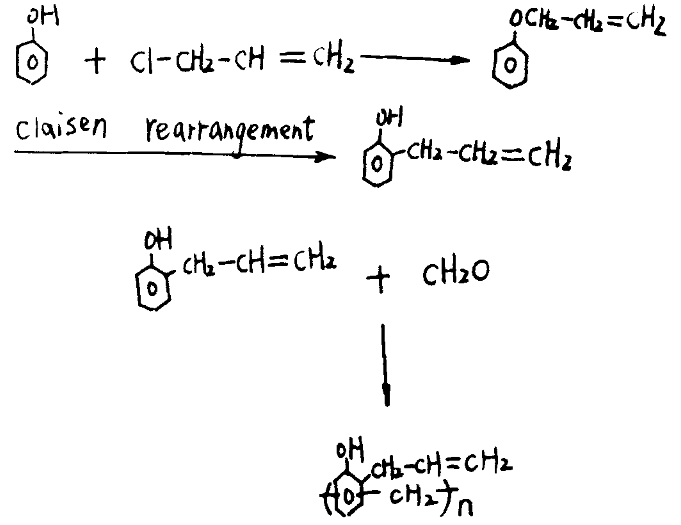
Humidity resistance was measured by putting samples into boiling distilled water and determining the water absorption and SBS strength of composite samples aged for various lengths of time.

RESULTS AND DISCUSSION

Preparation and Characterization of AF

The new functionalized novolac were prepared according to the reaction sequences outlined in Scheme 1.

More particularly, allylphenol reacted with CH_2O to afford the allylized novolac. Allylphenol was prepared from the reaction of phenol and allyl chloride with a strong base followed by Claisen rearrangement. The allylized novolac was prepared by adding portionwise formalin (37% CH_2O) to a stirred solution of allylphenol in the presence of oxalic acid as catalyst.



Scheme 1

Allyl novolac were characterized by IR spectroscopy. Figure 1 presents typical IR spectra of AF. The allyl group could be identified by

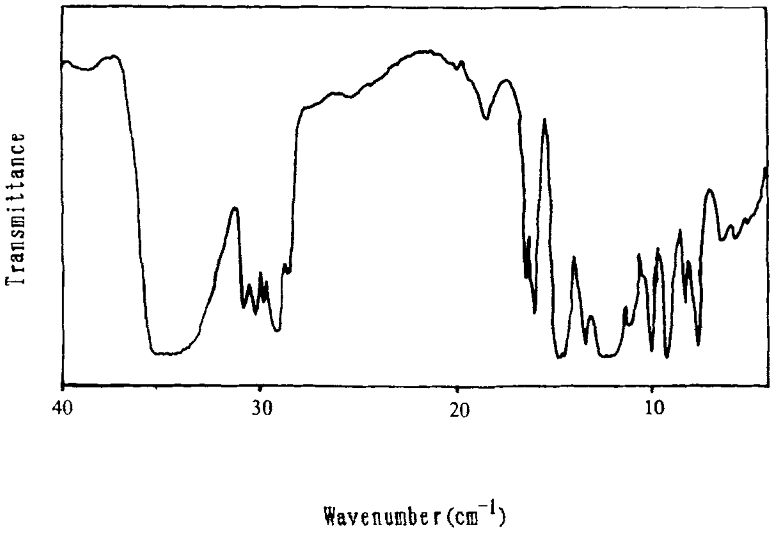


FIGURE 1 Typical IR spectra of AF1.

the absorption bands around 3010,990 and 910 cm^{-1}. A broad and strong absorption around 3495 cm^{-1} associated with the phenolic hydroxyl stretching vibrations. Finally, the absorption band at about 1620 cm^{-1} was assigned to the maleimide olefinic bond.

The typical physical properties are listed in Table I. It can be seen that AF, a red-brown transparent liquid, has a room temperature viscosity between 3.2 and 3.5 Pa.s.

Preparation and Properties of Prepolymer

Formulation

It's well known that the properties of prepolymer, such as softening point, viscosity, solubility in acetone, etc., are associated with the processing cycle of prepolymerization after the formulation has been chosen. The deeper the degree of prepolymerization, such as at high temperature or for long time, the higher the softening point, the poorer the solubility in acetone, the higher the viscosity, the shorter the gel time at the same temperature. On the other hand, when the degree of prepolymerization is too small, the solubility in acetone is also bad. So the degree of prepolymerization must be suitable to the processing technique. Of course, there are no need to continue prepolymerizing when the properties of prepolymers have met the needs of processing technique.

The term prepolymer used following in the paper refers to a homogenous melt obtained by prereacting BMI and AF in different ratio as explained in the experimental section.

Three different formulations were evaluated to see the effect of differing stroichiometries of each component on the processing and performance parameters and also to establish the formulational latitude this system provides.

TABLE I Typical physical properties of prepolymers

Property System	*I*	*II*	*III*
Softening point, °C	35	39	46
solubility in acetone	Good	Good	Poor

The systems were:

System	BMI:AF	
I	1:1	Weight ratio
II	3:2	Weight ratio
III	7:3	Weight ratio

Table II lists the typical properties of prepolymers I ~ III. It can be seen that prepolymer I ~ III are pale brown or brown transparent solid at room temperature with low softening points. The higher the BMI/AF ratio the higher the softening point as well as the worse the solubility and solution stability in acetone. A 50 w/o solution of prepolymers I and II in acetone was prepared. The stability was monitored by checking the change in viscosity with time. The solutions were stored at R.T. for periods of up to a month and periodic viscosity determinations were made. No change in viscosity was observed and no materials settled out of the solution, for the prepolymers I and II. On the other hand, a 50 w/o solution of prepolymer III in acetone was also prepared, but it has poor stability. So prepolymers I and II are particularly suitable for solvent laminating applications, but prepolymer III is not.

Figure 2 gives plots of gel time vs. temperature of prepolymer I, II and III. It can be seen that their gel time are longer than 80 min when the temperature is lower than 100°C, this suggests that all of them have long pot life at room temperature. With the temperature increase, the gel time reduces sharply. When the temperature is 170°C, the gel time is within 3 ~ 12 min.

The relative reactivity of the prepolymer I ~ II could be assessed by comparing the gel times at the same temperatures. From Figure 2 it

TABLE II DSC data of prepolymers

System	*Tdi*, °C	*Tp*, °C	*Tf*, °C
I	168.4	243.7	285.4
II	154.2	240.0	282.7
III	142.9	238.2	279.3

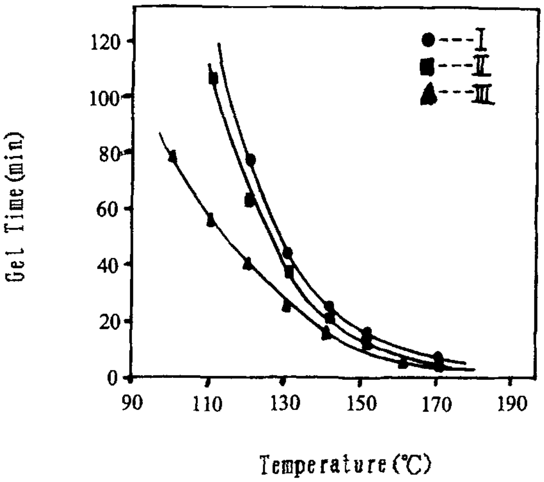


FIGURE 2 Polts of gel time vs. temperature of prepolymers.

can be seen that the relative order of gel time at every same temperature was: I > II > III.

In order to investigate the curing behavior comprehensively, DSC thermograms of I, II, III were recorded in nitrogen. Broad exothermic peaks were observed in the temperature range of 168 ~ 286 °C. These exotherms are believed to be due to thermally induced polymerization reactions because the DSC thermograms of the cured resins did not show exotherms in the same temperature range. The temperature of the first energy release T_1 (start of polymerization), the exothermic peak position T_{exo}, and the temperature of termination of polymerization T_f were determined from the DSC traces and are listed in Table II. It can be seen that temperature of exothermic peak position was affact by the BMI/AF ratio. Thus the T_{exo} of system III was 13 °C lower than that of system I, and the T_{exo} of system II was 5 °C lower than that of system I. The T_1 showed the same trend, but the T_f of them almost equal.

From observing the DSC data, gel characteristics, and softening points of systems I ~ III, it can be seen that their melt temperatures and copolymerization temperatures are very farther, so this suggests that prepolymers have very wide processing windows.

Properties of Neat Resins

For neat resin properties described here, the following curing cycle used: 150 °C/2 h + 180 °C/2 h + 180 °C/2 h + 200 °C/2 h + 230 °C/8 h.

From Table III it can be seen that all the three systems have almost the same and excellent thermal properties, which manifested by high HDT (294 ~ 319 °C, high TGA data, and good strength retentions at an elevated temperature. In the case of flexural strength, when tested at 230 and 250 °C, 80.1 and 71.6% of the original room temperature (R.T.) strength is retained, respectively.

On the other hand, the impact strength and tensile elongation are a function of the BMI/AF ratio. There are an optimum ratio of BMI/AF to get good impact strength and tensile elongation. In this paper, the optimum ratio of BMI/AF is 3:2, and system III give the best integret properties than system I and II.

In order to investigate the hot/wet properties of BMI/AF system, the HDT specimens of system II were immersed in boiling distilled water for 100 h, the moisture absorption and HDT were measured for various lengths of time, as shown in Figure 3. After aged for 100 h, the neat resin shows a boiling water absorption of 3.2 % by weight, HDT reduced from 298 to 277 °C, which was 93% retention of the dry room temperature value. These data suggest that system II has excellent hot/wet resistance.

TABLE III TGA results of polymers

Property/System	*I*	*II*	*III*
R.T. Tensile			
Strength, MPa	85.0	81.4	73.1
Modulus, GPa	3.62	3.68	3.70
Elongation, %	2.7	2.9	2.3
Flexural Strength, MPa			
R.T.	141	147	138
230 °C	113	118	111
250 °C	101	102	102
R.T. Impact Strength, kJ/m^2	7.0	13.1	6.2
HDT, °C	294	298	319

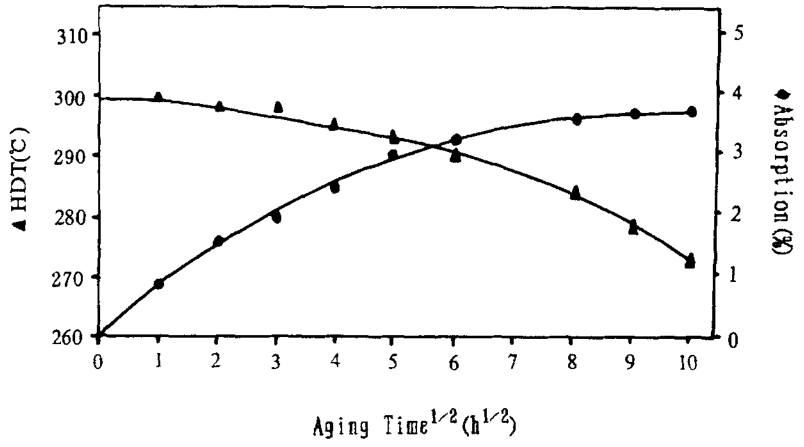


FIGURE 3 Water absorption and HDT vs. aging time of neat resin II.

Properties of Composites

Table IV gives properties of composites based on system II. Overall, these properties are very good, especially the strength at elevated temperature. In the case of SBS strength, when tested at 230 and

TABLE IV Properties of composite II

Property	*Value*
R.T. Tensile	
Strength, MPa	531
Modulus, GPa	34
Elongation, %	2.9
Flexural Strength, MPa	
R.T.	598
230°C	508
250°C	436
SBS Strength, MPa	
R.T.	51
230°C	44
250°C	39
R.T. Impact Strength, kJ/m	203
Resin Content, %	33.3

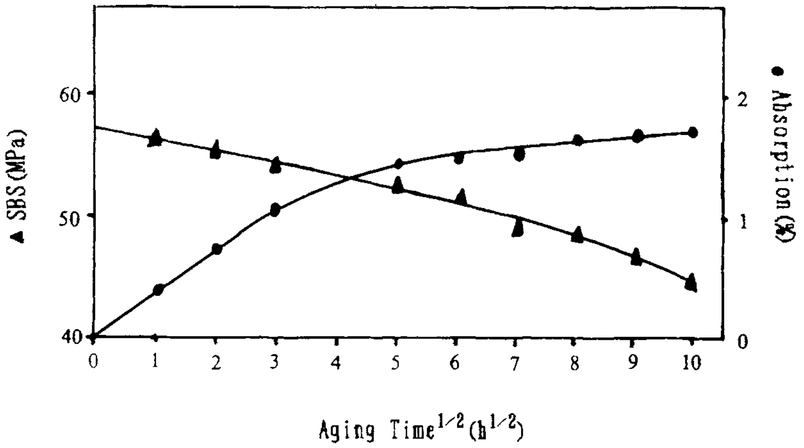


FIGURE 4 Moisture absorptions. SBS vs. aging time of composite II.

250°C, 86.7 and 78% of the original room temperature is retained. A similar type strength retention (84.9 and 72.9%) is noted in the flexural strength.

Figure 4 shows moisture absorption rates and SBS strength of composite based on system II in boiling water. After aged for 100 h, the SBS strength was 45 MPa, which was a 80.4% retention of dry room temperature value. An accompanying water absorption level of 1.7% was observed. So the composite based on system II also shows very good hot/wet properties. These properties suggest that BMI modified by allyl novolac can be used as matrix resin for advanced composites.

CONCLUSIONS

A new poly allyl resin-allyl novolac has been synthesized and used to modify and improve fracture toughness of bismaleimide resins. BMI/AF resin and composite products have excellent high temperature performance expected from a BMI resin along with good impact strength and fine processing characteristics comparable with epoxies. In addition, neat resin and composite show very good hot/wet properties. The characteristics suggest that BMI/AF system is excellent candidates for use in primary structure of advanced military aircraft.

References

[1] Shijin Jin and Albert, F. Yee. (1991). *J. Appl. Polym. Sci.*, **43**, 1849–1858.
[2] Rao, B. S. (1988). *J. Polym. Sci.: Part C: Polym. Lett.*, **26**, 310.
[3] Liu, F. J. Munukuila, S. Levon, K. Tesoro, G. (1992). *J. Polym. Sci.: Part A: Polym. Chem.*, **30**, 157–162.
[4] Mikoryannidis, J. A. and Mellssaris, A. P. (1987). *J. Appl. Polym. Sci.*, **34**, 2657–2672.
[5] Amraham, T. (1988). *J. Polym. Sci.: Polym. Lett.*, **26**(12), 521.
[6] Chaudhari, M., King, J. and Lee, B. (1987). 32nd Inter. SAMPE Symp., April 6–9.