

# Modification of Polyaralkyl-Phenolic Resin and Its Copolymer with Bismaleimide

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## SYNOPSIS

Polyaralkyl-phenolic resin, whose commercial name is Xylok, is in the class of high-performance resins, but its slow reactivity and brittleness limit its application in modern industry. Many efforts have been made to modify Xylok, but have not satisfactorily resolved these problems. In this paper, the authors employ allylization to improve properties of Xylok. The allyl Xylok can be thermally polymerized by itself or with bismaleimide (BMI) as a good comonomer. The reactivity of the allyl Xylok/BMI resin system was investigated by gel characteristics and differential scanning calorimetry (DSC). The thermal stability of the cured copolymer was evaluated by dynamic thermogravimetric analysis (TGA). No weight loss was observed when the copolymer was heated to 490–500°C in a nitrogen atmosphere. The hot/wet resistance properties of the cured allyl Xylok/BMI resin were investigated by aging it in boiling water. After aging for 100 h, water absorption and heat deflection temperature (HDT) were 2.3% and 280°C, respectively. The properties of the glass fiber reinforced compression molding materials (GCM) based on the copolymer of the allyl Xylok/BMI matrix resin system are also discussed. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

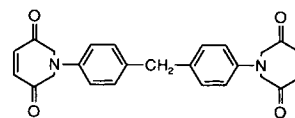
Polyaralkyl-phenolic resin, known commercially as Xylok, is a desirable candidate as a matrix resin for advanced composites. This is primarily because of its excellent insulation, heat resistance, and good processibility.<sup>1</sup> The major disadvantages of Xylok are its slow reactivity and the brittleness of the cured resin; the former due to the aromatic nucleus in its structure and the latter primarily because of its rigid linkage. To overcome this problem, many methods have been developed to modify Xylok, such as hydroxymethylation, epoxidation, olefination, etc., but these methods do not satisfactorily resolve the problems.

After several searches, we found a new method to improve the properties of Xylok by allylization. The allyl Xylok can be thermally polymerized by itself due to the unsaturated double bond in the allyl structure. However, the allyl Xylok is expected to be used by copolymerizing with bismaleimide (BMI) resins to yield a copolymer with excellent heat resistance and good mechanical properties.<sup>2-3</sup>

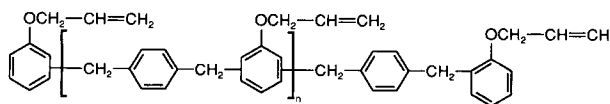
## EXPERIMENTAL

### Materials

4,4'-bismaleimidodiphenyl methane, mp 156–158°C, was obtained from Hu Bei Feng Guang Chemical Plant, China. Polyaralkyl-phenolic resin (mp 60–80°C), whose trade name is Xylok, and allyl chloride (mp 136.4°C, bp 44°C) were obtained from Sicuan Jiang You Insulation Factory, China. Allyl Xylok was prepared by treating Xylok with allyl chloride according to procedures described by Liang Guozheng et al.<sup>4</sup>



4,4'-bismaleimidodiphenyl methane



allyl Xylok

Allyl Xylok (140 g) and 4,4'-bismaleimidodiphenyl methane (100 g) were weighed in a three-necked, round-bottom flask equipped with a me-

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**Table I** Physical Properties of Allyl Xylok and Xylok

	Allyl Xylok	Xylok
Surface appearance (R.T.)	Deep brown solid	Amber solid
Softening point, °C	30–45	60–80
Typical chlorine content, mol/100 g	0.001	/
Typical hydroxyl content, %	0.48	9.7

chanical stirrer and a thermometer. With continuous stirring, the flask was gradually heated in a heating mantle. The temperature was maintained at 110–130°C till a clear homogeneous solution was obtained. After 20–25 min, the resultant solution (prepolymer) was obtained.

Neat resin was prepared by degassing and casting the prepolymer into a glass mold, then curing it according to the desirable cure cycle: 150°C/1 h + 180°C/1 h + 200°C/2 h. After that, it was postcured for 5 h at 230°C and 250°C, successively.

Glass fiber reinforced compression molding materials (GCM) were prepared as follows: adding 30 parts by weight of glass fiber, 35 parts talcum powder, 0.4 parts diisopropylbenzyl peroxide and 0.05 parts imidazole to acetone in which 38 parts of prepolymer was dissolved; kneading thoroughly and drying; then compressing for 30 min at 180°C and postcuring for 8 h at 230°C.

### Measurement of Prepolymer

Differential scanning calorimetry (DSC) was employed with a Du Pont Model 910 at a heating rate of 10°C/min in a nitrogen atmosphere.

The gel time of prepolymer was determined using a hot-plate technique. The prepolymer was spread

over hot plates heated to 120°C, 150°C, 180°C, and 200°C. The time required for the resin to stop stringing and become elastic is called the gel time.

### Measurement of Neat Resin

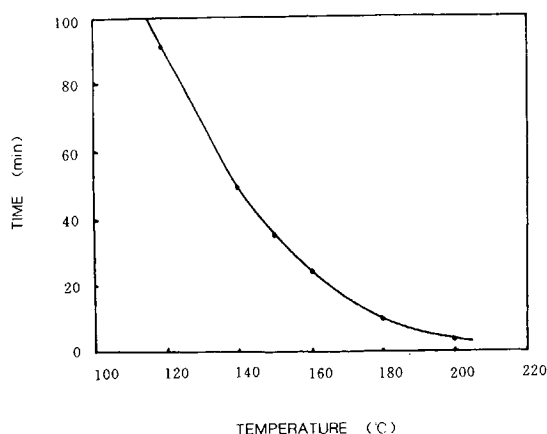
Tensile and flexural data were obtained according to GB 1451–1483 and GB3356–3382, respectively. In addition, fracture toughness by the impact strength and the critical strain energy release rate ( $G_{IC}$ ) was determined by GB 1843–1880. Heat deflection temperature ( $HDT$ ) was obtained by GB 1634–1679 and density by GB 1033–1086.

Thermogravimetric analysis (TGA) was conducted and the glass transition temperature ( $T_g$ ) obtained with a Perkin-Elmer DEL 7A Series TGA7 in a nitrogen atmosphere at a heating rate of 10°C/min.

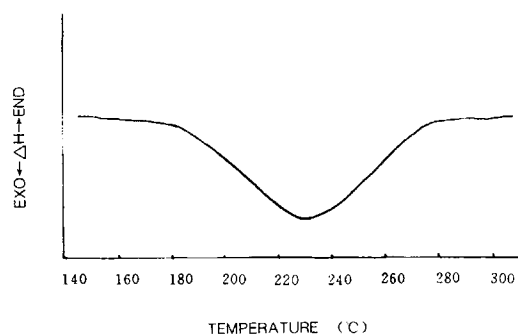
Humidity resistance was measured by placing samples in boiling water and determining the water absorption and  $HDT$  of neat resin samples aged for various lengths of time, testing thermal and mechanical properties of neat resin samples aged for 100 h.

### Measurement of GCM

Composite flexural and impact strengths and Marten's temperature were obtained according to GB 3356–3382, GB 1451–1483, and GB 1035–1070, re-



**Figure 1** Gel time-temperature trace of allyl Xylok/BMI resin system.



**Figure 2** DSC thermogram of allyl Xylok/BMI resin system.

**Table II Cured Allyl Xylok Properties**

Property	Value		Property	Value	
	Dry	Wet <sup>a</sup>		Dry	Wet <sup>a</sup>
Room-temperature tensile			Impact strength, kJ/m <sup>2</sup>	17.6	14
Strength, MPa	78	63	$G_{IC}$ , J/m <sup>2</sup>	169	130
Modulus, GPa	3.9	3.2	HDT, °C	310	280
Elongation, %	2.7	2.2	$T_g$ (DSC), °C	490	478
Flexural strength, MPa			IDT, °C	490	/
Room temperature	114	92	$PDT_{max}$ , °C	530	/
200°C	93	70	$Y_c$ (800°C), %	25	/
250°C	78	55	Density, g/cm <sup>3</sup>	1.23	/

<sup>a</sup> 100 hr in boiling water.

spectively. In addition, dielectric constant and loss tangent were determined by GB 1409–1478. Volume resistance and surface resistance were carried out by GB 1410–1478. Electric strength was measured by GB 1408–1478.

## RESULTS AND DISCUSSION

### Properties of Allyl Xylok

Table I, listing properties of allyl Xylok and Xylok, shows that allyl Xylok has a much lower softening point than Xylok, while both have excellent solubility in ordinary organic solvents such as ether, acetone, toluene, etc.

### Preparation and Properties of Allyl Xylok/BMI

Allyl Xylok can form a homopolymer due to the unsaturated double bonds in its structure, but it is only an oligopolymer. In order to obtain a highly cross-linked network, allyl Xylok must be copolymerized with other resins also having unsaturated bonds or other functional groups. These structures react easily with the allyl Xylok structure.

BMI is a class of high-performance matrix resin for advanced composites,<sup>5-6</sup> which are inherently brittle because of the extensive crosslinking that occurs during polymerization. One of the best ways to reduce brittleness is copolymerization with allyl compounds, so BMI is a desirable comonomer of allyl Xylok.

The BMI employed in this paper is 4,4'-bismaleimidodiphenyl methane. When it is copolymerized with allyl Xylok, the resultant prepolymer has a low softening point (60°C) and can be dissolved in acetone.

Figure 1, a plot of gel time versus temperature for the prepolymer described in this paper, shows that gel time reduces when the temperature increases. At 120°C, it maintains a working life of 90 minutes. When the prepolymer is raised to 150 or 200°C, it will gel in 35 or 2 min, respectively.

Figure 2 presents a typical DSC thermogram of the prepolymer. It shows that the peak exotherm temperature is from 184 to 274°C, onset temperature is 230°C, and polymerization energy is 159 J/g. All values suggest that the prepolymer has good reactivity.

### Property of Neat Resin

Copolymerization between BMI and allyl Xylok belongs to the addition–reaction class. During curing, no byproducts of low molecular weight were generated; the resulting cured structure is compact and has few defects. Table II shows the neat resin properties. Overall, mechanical properties—especially toughness—are outstanding; the cured resin exhibits excellent thermal properties which are primarily due to its highly aromatic characteristics and high crosslinking density. In the case of flexural strength, when tested at 200 and 250°C, 82 and 68% of the original room temperature (R. T.) strength are retained, respectively.

**Table III Postcure Condition vs. HDT of Cured Resin**

Postcure Condition	HDT (°C)
No postcure	246
230°C/8 h	273
240°C/8 h	291
250°C/8 h	310

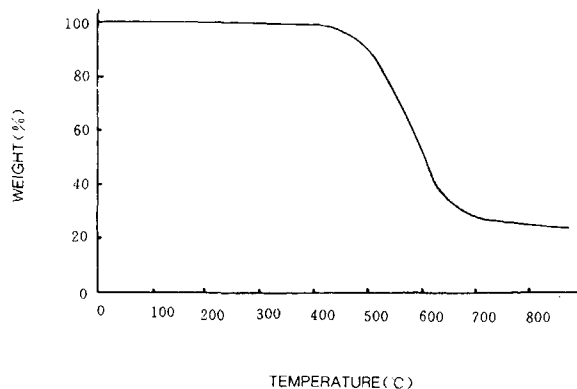


Figure 3 TGA thermogram of cured resin in N<sub>2</sub> atmosphere.

Table III shows the results of various postcure temperatures on *HDT* of neat resin. It suggests that the higher the postcure temperature, the higher the *HDT* is.

In order to obtain some preliminary data on the thermal stability of these materials, thermogravimetric analysis was conducted in a nitrogen atmosphere. The thermogravimetric curve of the neat resin is given in Figure 3. The initial decomposition temperature (*IDT*) is 490°C, maximum decomposition temperature (*PDT<sub>max</sub>*) is around 530°C, and char yield (*Y<sub>c</sub>*) is about 25% at 800°C.

Hot/wet resistance of the neat resin can be reflected by water absorption and the thermal and mechanical properties of the neat resin samples in boiling water for various lengths of time, as shown in Figure 4 and Table II. Aged over 60 h, both the water absorption and *HDT* did not significantly change. After 100 h, equilibrium was almost obtained, the neat resin showed a boiling-water absorption of 2.3% by weight, *HDT* reduced from 310 to 280°C, and the tensile and fracture properties are noted at room temperature with an 81 and 77% retention of room temperature properties, respectively.

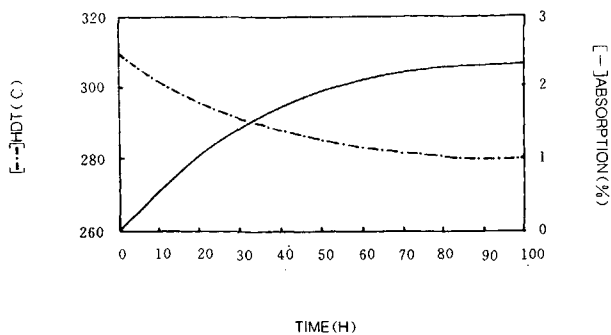


Figure 4 Water absorption-*HDT*-time correlation of cured resin.

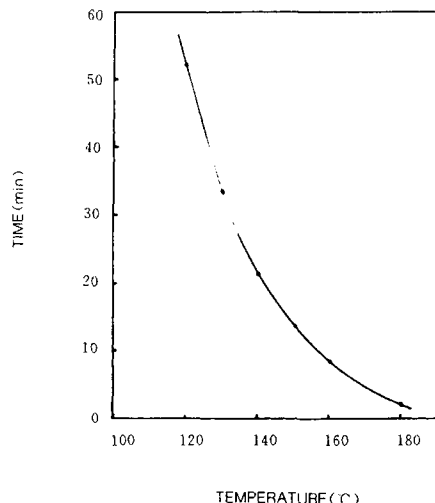


Figure 5 Gel time-temperature curve of allyl Xylok/BMI/accelerators.

In the case of flexural strength, when tested at 200 and 250°C, 75 and 70% of its 200°C and 250°C strength is retained, respectively. All of these data indicate that the neat resin has good hot/wet resistance; this is presumably the result of fewer voids, lower water absorption, and higher crosslinking density in the cured modified networks.

### Preparation and Properties of GCM

As shown above, good reactivity is one characteristic of allyl Xylok/BMI resin, but it is not good

Table IV GCM Properties

Property	Value
Surface appearance	Smooth, no crack, no pit
Density, g/cm <sup>3</sup>	1.98
Flexural strength, MPa	
Room temperature	360
200°C	298
250°C	242
Impact strength, kJ/m <sup>2</sup>	230
Marten's temperature, °C	730
Dielectric constant (10 <sup>6</sup> Hz)	4.8
Dielectric loss tangent (10 <sup>6</sup> Hz)	3.8 × 10 <sup>-2</sup>
Volume resistance, Ω · M	
Room temperature	1.3 × 10 <sup>14</sup>
In water for 24 h	2.6 × 10 <sup>13</sup>
200°C	1.8 × 10 <sup>-2</sup>
Surface resistance, Ω	
Room temperature	1.3 × 10 <sup>12</sup>
In water for 24 h	1.9 × 10 <sup>11</sup>
Electric strength, kV/mm	
Room temperature	17
In water for 24 h	15

enough for the preparation of GCM. In order to improve the resin's reactivity, accelerators are needed. Figure 5 shows gel characteristics of the resin after diisopropylbenzyl peroxide and imidazole are added. At 120°C, gel time is about 52 minutes; when the sample is raised to 150°C and 180°C, the gel time is around 15 and 2 minutes, respectively. All values are lower than those obtained from Figure 1. Press temperature and time are key features of molding in terms of productivity; high press temperature is desired but needs special equipment and molders.

For the GCM properties presented in this paper, the following press cycle was used: press temperature and time were 180°C/30 min and pressure was 45 MPa. After this, postcure was necessary to get reasonable properties of GCM; the selective postcure cycle is 230°C/8 h.

GCM properties for this resin are presented in Table IV. Overall, these properties are very good. In the case of flexural strength, when tested at 200 and 250°C, 83 and 67% retention of the original room temperature flexural strength are obtained, respectively. In addition, GCM shows excellent dielectric properties at R. T. and elevated temperature (200°C), as well as in water for a long time. These data suggest that GCM can also be used as a high-performance insulator.

## CONCLUSIONS

Allylization is a new way to modify polyaralkyl-phenolic (Xylok) resin. The allyl Xylok is a solid with a low softening point and good reactivity. The copolymer of allyl Xylok and BMI exhibits excellent heat resistance with good mechanical properties and hot/wet resistance. In addition, glass fiber reinforced compression molding materials from the allyl Xylok/BMI matrix resin also have very good thermal and mechanical properties as well as outstanding dielectric properties, and can be used as high-performance insulators.

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