Thermal and Physical Properties of Allyl PPO and Its Composite

Lihua Wang,[1] Qingyu Xu,[2] Donghua Chen,[1] Yuhong Yuan,[1] Wanjun Tang,[1] Laoli Wang[2]

[1]*Hubei Key Laboratory for Catalysis and Materials Science, College of Chemistry and Materials Science, South-Central University for Nationalities, Wuhan, People's Republic of China 430074*
[2]*Hubei Institute of Chemistry, Wuhan, People's Republic of China 430074*

ABSTRACT: The thermal behavior of allyl PPO and its cured resin were investigated. In the allyl PPO curing process, the specific temperatures were $T_{gel} = 173.6°C$, $T_{cure} = 225.4°C$, and $T_{treat} = 237.7°C$, and the activation energy (E_a) was 122 kJ/mol. The average number of PPO molecular units between two crosslinking points was about 20. In the degradation process of cured allyl PPO resin, the temperature at which mass loss equaled 1% was much higher than 300°C. The E_a for degradation was calculated as 125 kJ/mol, with a degradation fraction (α) in the range of 0.15–0.65, or 117 kJ/ mol with an α of 0.10–0.90. The most probable mechanism function of decomposition of the cured allyl PPO resin was $f(\alpha) = 2(1 - \alpha)^{3/2}$ or $g(\alpha) = (1 - \alpha)^{-1/2} - 1$. The thermocompressed laminate of the allyl PPO blending with an additive resin (made from BDM and DP) exhibited the desired properties. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4111–4115, 2006

Key words: poly(phenylene oxide); curing of polymers; thermosets; thermal properties; degradation

INTRODUCTION

Thermosetting poly(phenylene oxide) (PPO), referred to chemically as poly(2,6-dimethyl-1,4-phenylene oxide), the most attractive dielectric substrate in recent years, is more and more popular in manufacturing superlaminating printed circuit boards (PCBs) for mounting high-frequency mobile electronic communication devices, high-speed information processors, and high-frequency radio communication equipment. This modified material inherits the valuable properties of PPO, such as a very low dielectric constant, a very low dielectric dissipation factor, a very high glass-transition temperature (T_g), and good resistance to acids, alkalis, and hot water. Moreover, after cure processing as the thermoset material, it also has good resistance to aromatic hydrocarbons and halohydrocarbons, as well as good dimension stability at high temperatures, both of which are very important for PCB substrates, as they usually encounters organic solvent washing and high temperature in soldering in whole device manufacture.

Allyl PPO, as the basic derivative of thermosetting PPO, with crosslinkable allyl groups in its macromolecular units, was early disclosed by Tsuchida et al.,[1,2] in 1981, and many efforts to modify it have been reported in the literature.[3] The present study was mainly concerned with the characteristics of kinetics in its curing reaction and the thermal degradation right afterward. Some physical properties of a set of thermocompressed plates and a desired composition were also explored.

EXPERIMENTAL

Instrumental

The TG spectra were reported using a Perkin-Elmer (Boston, MA) Thermo Gravimetric Analyzer, TGS-2, at heating rates of 5, 10, 15, 20, and 25 K/min under a nitrogen flow of about 80 mL/min. Mass was close to 3 mg for all runs. Differential scanning calorimetry (DSC) was performed using a Mettler-Toledo DSC822^e (Greinfensee, Switzerland) differential scanning calorimetric analyzer. The heating rates were 2.5, 5.0, 10, 15, 20, and 25 K/min, and the nitrogen flow was about 50 mL/min. A sample (about 10 mg) was placed in aluminum pan with a pierced lid, and an empty aluminum pan served as a reference. The dielectric constant (ε) and dielectric dissipation factor (tan δ) were measured according to National Standard of China GB/T4722-92 by a high-frequency Q-meter from Shanghai Electrical Instrument (Shanghai, China), under an ambient dry temperature of 23.0°C and a wet temperature of 21.5°C (relative humidity 85%).

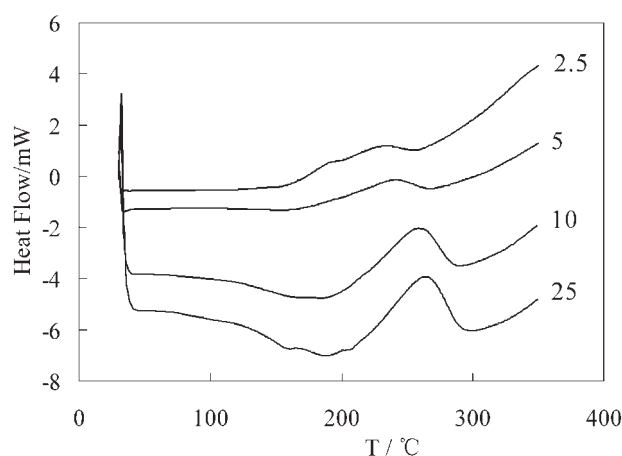*Correspondence to:* L. Wang (longwangrx@mail.scuec. edu.cn).

Figure 1 DSC curing curves of ally PPO at different heating rates.

Sample preparation

Starting material

The PPO was a commercial product from General Electric Plastics (Pittsfield, MA), in scale marked for PPO 857, with the following chemical criteria: $\overline{Mw}$, 6300; $\overline{Mn}$, 2350; T_g, 160°C; soft point, 210°C; density, 1.02; dielectric constant (ε), 2.54.

According to Katayose and Oda,[3] an average of 15% of the molecular units were substituted with allyl groups.

Thermocompressed plates

The neat PPO and allyl PPO plates were powdery materials formed by a thermocompressor at 220°C for 2.5 h without initiator.

The PPO and allyl PPO composite plates were 80% the above neat material and 20% an additive crosslinkable resin. The additive resin was a mixture of o,o'-diallyl bisphenol A (DP) and 4,4'-bismaleimidediphenylmethane (BDM) and their copolymerized oligomer. All the materials (including 4% initiator vs. weight of additive resin) were well mixed using chloroform as the solvent. After the solvent was evaporated, the materials were granulated into powder and formed in a shape according to above the thermocompression procedure.

To make the glass-fiber-reinforced allyl PPO composite plate, glass fiber was steeped in an allyl PPO composite chloroform solution and the solvent evaporated. The operation was repeated until the weight of the allyl PPO composite was equal to the glass fiber and following the thermocompression treatment.

Additional tests

The water absorption tests were carried out according to National Standard GB1034-86 of China. In the solvent resistance test, 10 g of the thermocompressed

plate sample was immersed in 1000 mL of boiling trichloroethylene for 5 min. In the extraction tests thermocompressed plates were cut into small pieces and extracted in boiling trichloroethylene for 24 h.

RESULTS AND DISCUSSION

Heat and kinetics of allyl PPO cure reaction

DSC scans of allyl PPO in cure reaction at different heating rates are shown in Figure 1. The cure reaction onset temperature, T_{onset}, the peak exothermic temperature, that is, the maximum reaction rate, T_{peak} or T_p, and the reaction end temperature, T_{end}, at different heating rates are listed in Table I. The reaction heat values, calculated from the area under the DSC curve, are also shown in Table I.

The specific temperatures of allyl PPO in curing can be deduced from the intercept of T versus β, shown in Figure 2. To minimize the heating rate effect, extrapolation of T_{onset}, T_{peak}, and T_{end} to $\beta = 0$ can yield the gel, curing, and heat treatment temperatures. In our operation T_{gel} was 173.6°C, T_{cure} was 225.4°C, and T_{treat} was 237.7°C, all of which were used as references in other operations.

With the reaction heat ($-\Delta H$) we were able to estimate the approximate length of a segment of the cured allyl PPO resin chain that contained a crosslinking point. Theoretically, when a double bond converts to two single bonds in polymerization, the reaction heat is about 83.6 kJ/mol.[4] The quotient from this value divided by the average reaction heat in cure reaction is the formula for the molecular weight of the segment, for example, 83,600/34.5 = 2423. This indicates that the average number of PPO units ($M_w = 121$) in the segment was about 20, and the conversion of the allyl groups in the cure reaction was not high compared with the average degree of substitution of 15%.

Under nonisothermal conditions, the rate of reaction, $d\alpha/dt$, is dependent on temperature, T, and the extent of conversion, α, and can be expressed as:

$$\frac{da}{dT} = \frac{A}{\beta} e^{-E_a/RT} f(\alpha)$$

where R is the gas constant, β is the heating rate, $\beta = dT/dt$ and $f(\alpha)$ is the kinetic function. Given that $f'(a_p)$ is approximately 1 at the peak temperature, T_p,

TABLE I
Parameters of Curing Reaction at Different Heating Rates

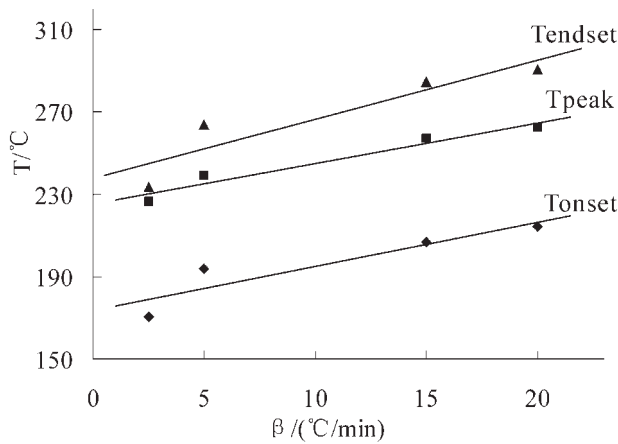| β (°C/min)	T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	ΔH (J/g)
2.5	170.4	226.5	233.4	38.1
5.0	194.0	239.0	264.0	31.8
15.0	206.8	257.1	284.6	34.9
20.0	214.3	262.4	290.6	33.0

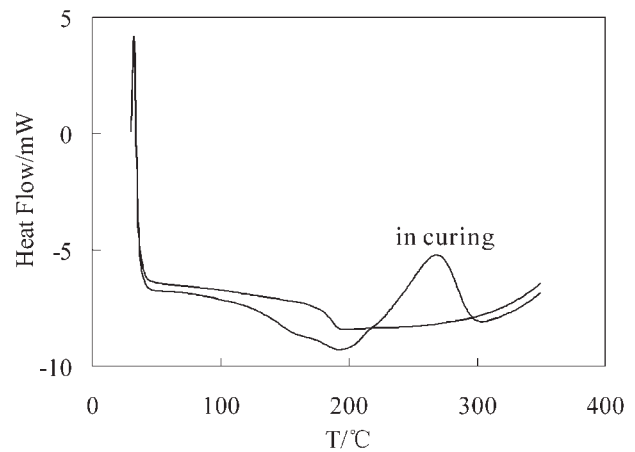**Figure 2** Exploration of DSC feature temperature versus β.

Figure 3 DSC curves of allyl PPO during and after curing.

and is independent of β, Kissinger[5] proposed that E_a could be determined by calculating a variation of T_p with β as follows:

$$\frac{d \ln(\beta/T_p^2)}{d(1/T_p)} = -\frac{E}{R} \tag{1}$$

With the assumption that chemical conversion is constant at T_p and independent of β, the Ozawa equation[6]

$$\frac{d \ln \beta}{d(1/T_p)} = -1.052 \frac{E}{R} \tag{2}$$

was the basis for the following relationship between E_a, β, and T_p. The E_a of the curing reaction was calculated using the slopes of $\ln(\beta/T_P^2)$ and $\ln \beta$ versus $1/T_P$. The $\ln(\beta/T_P^2)$, $\ln \beta$, and $(1/T_P)$ values are shown in Table II. The E_a was 121 kJ/mol according to the Kissinger equation and 123 kJ/mol according to the Ozawa equation, and the average activation energy was 122 kJ/mol.

Figure 3 shows the DSC scans of allyl PPO during and after its cure reaction at the same heating rate, 25 K/min. The postreaction scan shows that the exothermic peak had disappeared and the T_g was about 180°C.

Thermal stability and thermal decomposition kinetics of cured allyl PPO

The TG curves of the cured allyl PPO are shown in Figure 4. Table III shows the temperatures of a set of mass loss values as a function of heating rate.

It can be seen from Figure 4 that at a temperature below 300°C, the sample was very stable, and almost no mass loss was detected. At a temperature above 300°C, the rate of mass loss increased rapidly. This means the bond of the PPO main chain broke at this temperature, and the crosslinking was not sufficient to make a difference.

All values of $T_{1\%}$ (the temperature when mass loss equals 1%) shown in Table III were above 300°C, which means no mass loss in soldering; for example, the cured allyl PPO resin would exhibit good heat resistance during a soldering process.

Kinetics information for cured allyl PPO during degradation was determined using a comparative method[7]: (1) activation energy was determined by the KAS and Ozawa equations; and (2) the Coats–Redfern integral equation and the Achar differential equation were used together to confirm the most probable mechanism, $f(\alpha)$, of the reaction and to calculate the preexponential factor, A. E_a, $f(\alpha)$, and A are also called kinetic triplets.

TABLE II
Data on β, T_P, $(1/T_P) \times 10^{-3}$, $\ln(\beta/T_P^2)$, and $\ln \beta$

β (°C/min)	T_P (K)	$(1/T_P) \times 10^{-3}$	$-\ln(\beta/T_P^2)$	$\ln \beta$
2.5	499.6	2.002	11.511	0.916
5.0	512.1	1.953	10.868	1.609
15.0	530.8	1.886	9.839	2.708
20.0	535.6	1.867	9.571	2.996

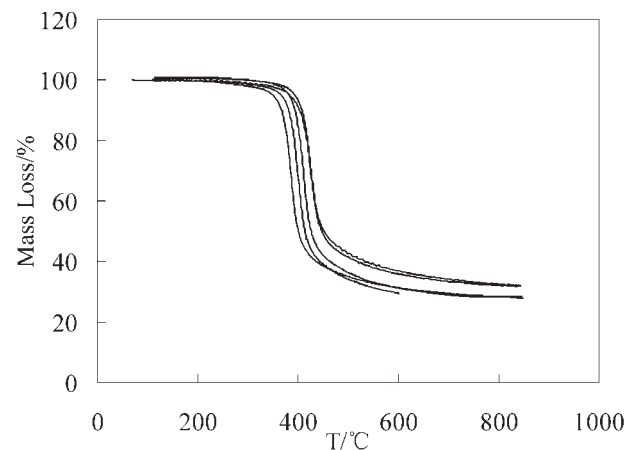**Figure 4** TG curves of cured allyl PPO.

TABLE III
Set Mass Loss Temperature Variation on Heating Rate

β (K/min)	Temperature (°C)		
	$T_{1\%}$	$T_{5\%}$	$T_{10\%}$
5	321.5	350.0	362.6
10	336.7	366.6	377.7
15	347.8	376.3	387.7
20	350.3	382.0	397.0
25	358.0	388.3	400.8

Activation energy was determined by the Ozawa equation[6]

$$\ln \beta = \ln \left[\frac{0.0048 A E_a}{g(\alpha) R} \right] - 1.052 \frac{E_a}{RT} \tag{3}$$

and the KAS equation[5,8]

$$\ln \frac{\beta}{T^2} = \ln \left[\frac{A E_a}{g(\alpha) R} \right] - \frac{E_a}{RT} \tag{4}$$

where α is the reaction fraction of decomposition, $f(\alpha)$ is the differential expression of kinetic function, $g(\alpha)$ is the integral expression of kinetic function, E_a is the activation energy, A is the preexponential factor, R is the gas constant, and β is the heating rate.

The two methods of plotting a linear regressive curve at the same fractional conversion, α, different heating rates β are isoconversional methods. The plots of $\ln \beta$ versus $1/T$ in eq. (3) and $\ln(\beta)/T^2$ versus $1/T$ in eq. (4) have been proven to give activation energy.

The most probable mechanism function was estimated with the Coats–Redfern integral equation[9] and the Achar differential equation.[10] The typical 31 kinetic functions of thermal decomposition[11] were applied in these two equations.

The Coat-Redfern integral equation is

$$\ln \frac{g(\alpha)}{T^2} = \ln \left(\frac{AR}{\beta E_a} \right) - \frac{E_a}{RT} \tag{5}$$

where the plot of $\ln[g(\alpha)/T^2]$ versus $1/T$ is a straight line; E_a is the activation energy, which can be obtained from the slope, $-E_a/R$; and A is the preexponential factor, which can be obtained from the intercept, $\ln(AR/\beta E_a)$.

The Achar differential equation is

$$\ln \left[\frac{1}{f(\alpha)} \frac{d\alpha}{dT} \right] = \ln \left(\frac{A}{\beta} \right) - \frac{E_a}{RT} \tag{6}$$

where E_a, $\ln A$, and the linear correlation coefficient, r, are calculated from the linear least-squares plot of $\ln\{[1/f(\alpha)][d\alpha/dT]\}$ versus $1/T$, in which the slope is $-E_a/R$ and the intercept is $\ln(A/\beta)$.

The basic parameter, α, and the corresponding temperature, T from the TG curves were inserted into eqs. (3) and (4). Then the decomposition activation energies of the cured allyl PPO were obtained.

The E_a obtained with the KAS method was 125 kJ/mol with an α of 0.15–0.65 and 117 kJ/mol with an α of 0.10–0.90.

The basic data, α, T and $d\alpha/dT$, and the 31 functions, $f(\alpha)$ and $g(\alpha)$, were inserted into eqs. (5) and (6). The kinetic parameters E_a and A and the linear correlation coefficient, r, were calculated by the linear least-squares method. From the data obtained, the function for which E_a values were in close range and the r was better is the most probable mechanism function. Thus, function 21—namely, the 1.5-order reaction, $f(\alpha) = 2(1 - \alpha)^{3/2}$ or $g(\alpha) = (1 - \alpha)^{-1/2} - 1$—was the most probable mechanism function of the decomposition of cured allyl PPO. Nonisothermal kinetic parameters from the Coats–Redfern integral and Achar differential equations at different heating rates are listed in Table IV.

Physical properties of thermocompressed plates

The results of a group of physical experiments on these five thermocompressed plates of different samples are listed in Table V.

It can be seen that role of the allyl function groups was sufficient to increase the solvent resistance of both the neat and composite allyl PPO samples. The neat allyl PPO plate could not stand to trichloroethylene extraction, and mass loss increased to 30%. This was reasonable for the very low degree of cross-

TABLE IV
Kinetic Parameters of T-PPO from Differential and Integral Methods at Different Heating Rates

β (°/min)	Function number	Coats–Redfern method			Achar method		
		E_a (kJ/mol)	$\ln A$ (A : s^{-1})	R	E_a (kJ/mol)	$\ln A$ (A : s^{-1})	r
5	21	251	39.65	0.982	198	29.90	0.896
10	21	200	29.76	0.944	107	13.46	0.695
15	21	220	33.33	0.957	132	17.96	0.754
20	21	172	24.17	0.941	92.3	10.73	0.661
25	21	198	28.93	0.947	109	13.95	0.699

TABLE V
Physical Properties of Thermocompressed Samples

	Neat PPO	PPO composite	Neat allyl PPO	Allyl PPO composite	Glass fiber reinforced allyl PPO composite
Trichloroethylene treatment	Fall to pieces	Fall to pieces	Small etch holes on the surface	Remain glossy	Remain glossy
Mass loss in extraction			30 wt %	2 wt %	3 wt %
Water absorption				0.06 wt %	0.13 wt %
Dielectric constant, ε (1 MHz)				2.57	3.46
Dielectric dissipation factor, tan δ (1 MHz)				0.0008	0.008

linking in the samples in the present study, as discussed earlier.

The composite allyl PPO plate exhibited, as did the its glass-fiber-reinforced sample, solvent resistance and dielectric parameters that are very desirable in a PCB substrate used in high-frequency devices. The composition used could most probably find practical applications.

CONCLUSIONS

1. DSC spectra can give detailed information on allyl PPO in a curing reaction. In our experiments we determined the specific temperatures T_{gel}, T_{cure}, and T_{treat}, which were 173.6°C, 225.4°C, and 237.7°C, respectively. The average activation energy was calculated as 122 kJ/mol by the Kissinger and Ozawa equations. From the reaction heat $(-\Delta H)$, we estimated that the length of a molecular segment containing a crosslinked point was about 20 PPO molecular units in the present work.
2. The kinetics parameters and the most probable mechanism function of degradation could be studied from the TG curves of the cured allyl PPO resin. In the present work, the activation energy for degradation was 125 kJ/mol when α ranged from 0.15 to 0.65 and 117 kJ/mol when α ranged from 0.10 to 0.90; the most probable mechanism function of cured allyl PPO resin during degradation was optimized as $f(\alpha) = 2(1 - \alpha)^{3/2}$ or $g(\alpha) = (1 - \alpha)^{-1/2} - 1$ through the Coat–Redfern and

Achar equations by the linear least-squares method. The TG curves also gave the temperature at which mass loss equaled 1% ($T_{1\%}$). All $T_{1\%}$ values at various heating rates were higher than 300°C. This meant the cured allyl PPO exhibited good heat resistance and would not cause mass loss during soldering when used as a PCB substrate.
3. From the physical test results of different thermocompressed plates, it was deduced that the allyl groups had obviously enhanced the solvent resistance of PPO. Especially when cooperating with an additive crosslinkable resin made up of BDM and DP, the material displayed a good integrated balance of multiple desirable properties.

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