Curing Reaction of Molybdenum–Phenolic Resins

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ABSTRACT: The curing behavior and curing reaction kinetics of novel molybdenum–phenolic resins were studied with differential scanning calorimetry and thermogravimetry methods, the thermal degradation properties of the cured products were studied with thermogravimetry, and the mechanism of the curing reaction was investigated with Fourier transform infrared. When the mixing ratio of the molybdenum–phenolic resin (with 12% molybdenum) to the curing agent was 100/10 (w/w), the curing temperature and activation energy were at a minimum, the thermal degrada- tion stability of the cured product was optimal, and the temperature corresponding to the maximum extent of cur- ing was 200°C. The curing mechanism was similar to that of conventional phenolic systems. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1410–1415, 2003

Key words: resins; curing of polymers; thermal properties; differential scanning calorimetry (DSC); thermogravimetric analysis (TGA)

INTRODUCTION

Phenolic resin composites are ablative-resistant polymer materials. For the improvement of their ablative properties, studies have been made of phenolic resins containing metallic elements, including molybdenum–phenolics (Mo–phenolics).[1,2] Some reports have indicated that the ablative properties of Mo–phenolic resin composites at high temperatures are superior and are especially outstanding under conditions of high heat flux.[3]

Some systematic studies of the curing and thermal properties of phenolic resins have been discussed in the literature,[4] but few studies of phenolic resins containing metallic elements have been reported.[5–7]

In this study, the reactions of Mo–phenolic resins with hexamethylene tetramine as a curing agent and their kinetics were studied. The thermal degradation properties of the cured resins were investigated, and the curing mechanism was explored. A theoretical foundation is set for improving the processing technology of composites, and an effective evaluation of their properties is made.

EXPERIMENTAL

Materials

Mo–phenolic resins labeled 1, 2, and 3, with molybdenum contents of 8, 12, and 18% and number-average molecular weights of 791, 624, and 829 g/mol, respec-

tively, were supplied by Jinan Institute 53. The curing agent, hexamethylene tetramine, was obtained from Jinan Corp. of Chemical Reagent.

Methods

Differential scanning calorimetry (DSC)

A PerkinElmer DSC-2C instrument was used, and the samples were sealed in an aluminum volatile sample pan (with a small hole in the cover). The sample weight was about 5 mg, and the flow of N_2 was 20 mL/min.

Nonisothermal curing. The temperature range was 323–523 K. The kinetics of the curing reaction were studied by the variation of the peak exotherm temperature (T_p) at various heating rates (ϕ). The relationship between the activation energy (E), ϕ, and T_p is based on the Ozawa equation:[2]

$$E \approx \frac{-R}{0.4567} \cdot \frac{\Delta \log \phi}{\Delta(1/T_p)} \approx \frac{-R}{1.052} \cdot \frac{\Delta \ln \phi}{\Delta(1/T_p)}$$

Isothermal curing. Isothermal software was employed. Samples were rapidly heated from 323 K to the required isothermal curing temperature (130–150°C) at 160 K/min, with a delay time of 1 min and a dwell time of 10 min. Because of the temperature balance between the rapid heating and isothermal process, the now cured samples could be rerun under identical conditions after the isothermal curing experiment was completed. Subtracting this blank run from the curing run should achieve a partial correction of the interference phenomena.
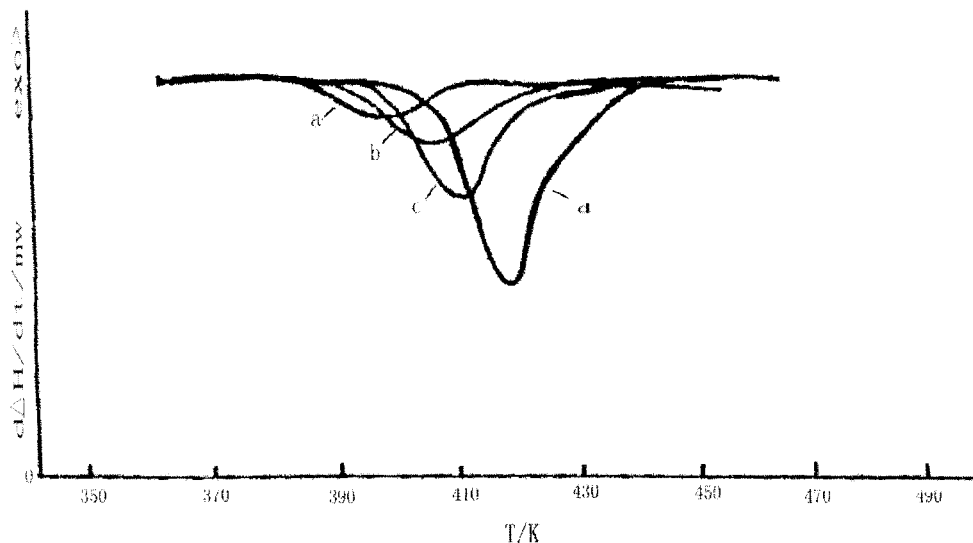
Figure 1 DSC curves for the number 2 resin/curing agent (100/12) at different values of ϕ: (a) 2.5, (b) 5, (c) 10, and (d) 20°C/min.

The Arrhenius equation was employed in the kinetic study of the curing reaction:

$$v = d\alpha/dt = Kf(\alpha) = Ae^{-E/RT}f(\alpha)$$

$$\ln v = \ln[Af(\alpha)] - E/RT$$

For the curing reaction, $f(\alpha)$ was constant when the degree of conversion (α) was fixed. Therefore, by the plotting of $\ln v$ against the inverse of the temperature ($1/T$), the apparent activation energy (E) was obtained.

In the calculations, α at different curing times for each temperature was first obtained from the DSC

TABLE I
Values of T_{onset}, T_p, ΔH and E for Samples of the Number 2 Resin/Curing Agent with Different Weight Ratios at Different Values of ϕ

Number 2 resin/curing agent (weight ratio)	ϕ (°C min^{-1})	T_{onset} (K)	T_p (K)	ΔH (Jg^{-1})	$E -$ (kJ mol^{-1})
100/6	2.5	389	399	−58.2	127
	5	394	405	−77.9	
	10	400	413	−72.9	
	20	409	421	−78.3	
100/8	2.5	391	399	−73.7	126
	5	397	407	−74.9	
	10	402	414	−74.9	
	20	409	421	−77.0	
100/10	2.5	389	398	−58.2	108
	5	395	407	77.5	
	10	401	413	−71.2	
	20	409	423	−76.2	
100/12	2.5	389	397	−70.8	126
	5	395	405	−74.1	
	10	401	412	−69.5	
	20	409	420	−74.1	
100/14	2.5	390	401	−67.0	134
	5	395	406	−69.9	
	10	402	414	−69.9	
	20	409	421	−74.9	
100/16	2.5	391	401	−56.9	134
	5	396	407	−71.2	
	10	402	413	−73.7	
	20	409	422	−72.9	

TABLE II
T_{onset}, T_p, ΔH **and** E **for Samples of the Number 1 and 3 Resin/Curing Agent Formulations (100/12) at Different Values of** ϕ

Mo–phenolic/curing agent		ϕ (°C min^{-1})	T_{onset} (K)	T_p (K)	ΔH (J g^{-1})	E (kJ mol^{-1})
1	100/12	2.5	401	409	−44.4	
		5	405	414	−73.7	140
		10	412	422	−69.1	
		20	418	429	−71.2	
3	100/12	2.5	400	415	−43.1	
		5	407	419	−71.2	182
		10	411	425	−71.2	
		20	416	431	−68.2	

curve ($\alpha = A_{\text{partial}}/A_{\text{total}}$). When α was 0.5, the value of $(d\alpha/dt)_{0.5}$, that is, $v_{0.5}$, was obtained.

Thermogravimetry (TG)

Isothermal curing. A PerkinElmer TGS-2 instrument was used. The measurements were carried out under a nitrogen atmosphere (45 mL/min), with a sample weight of about 5 mg. The sample was heated to the required isothermal curing temperature (120–240°C) at 160°C/min, the weight was recorded immediately, and the isothermal curing process was initiated. The sample weight losses (%) after 10 min of curing at different temperatures were recorded. They were used as a measure of the extent of curing. The initial slope of the TG curve was taken to be a direct measurement of the reaction rate.

Nonisothermal degradation. The instrument, the atmosphere, and the rest were the same as before. ϕ was 10°C/min. The weight loss of the cured resin from 200 to 700°C was determined.

Fourier transform infrared (FTIR)

A Nicolet 60SXB FTIR spectrometer was used, and the spectra were recorded with samples as KBr disks.

RESULTS AND DISCUSSION

Nonisothermal curing reaction of mo–phenolic resins and its kinetics

Figure 1 shows the DSC curves for a sample of the number 2 resin/curing agent (100/12 w/w) at four different values of ϕ. Those of the remaining samples are omitted.

The values of T_{onset}, T_p, ΔH, and E for six samples with different composition are given in Table I. As the proportion of the curing agent increases from 100/6 to 100/16, T_{onset} is almost constant, and T_p varies only slightly. E changes more significantly and has a minimum for the 100/10 sample.

According to the literature on phenolic resins,[2] 10–15% is an appropriate amount for a curing agent. These results are generally in agreement with ours.
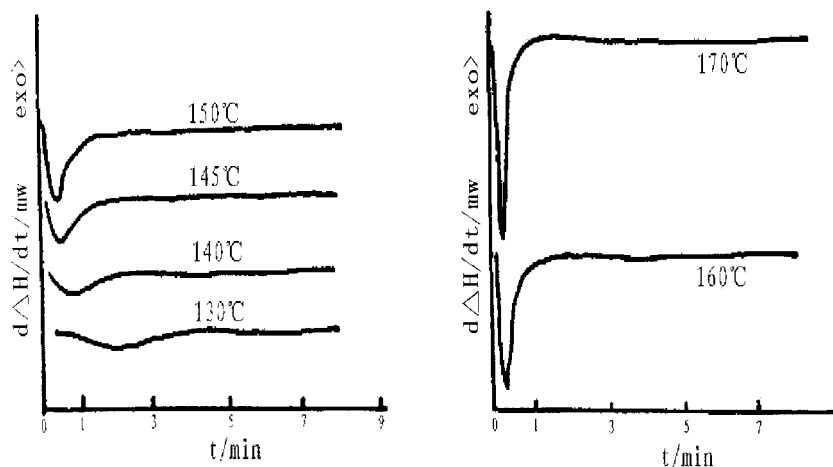

Figure 2 DSC isothermal curing curves for the number 2 Mo–phenolic resin/curing agent (100/10) at different temperatures.

TABLE III
Values for $(d\alpha/dt)_{0.5}$ and E derived from DSC curves

T (°C)	$(d\alpha/dt)_{0.5}$ (min^{-1})	E (kJ mol^{-1})
130	0.279	
140	0.564	
145	1.014	101.2
150	1.578	
160	2.840	
170	3.800	

The values of T_{onset}, T_p, ΔH, and E for samples of the number 1 and 3 resin/curing agent formulations (100/12) at different values of ϕ are shown in Table II. Comparing the results of Table II with those of Table I, we can conclude that when the resin/curing agent ratio is 100/12, the sequences of the curing temperature and E are as follows: number 3 ≥ number 1 > number 2. That is, among the three samples with resin/curing agent ratios of 100/12, both the curing temperatures and E values are lowest for the number 2 resin. This is a result of the effects of both the molybdenum content and the molecular weight of the resin on the curing reaction.

Isothermal curing reaction of mo–phenolic resins and its kinetics

Isothermal curing seems to be more important in terms of actual practical applications. The DSC isothermal curing curves for sample of the number 2 Mo–phenolic resin/curing agent (100/10 w/w) at 130, 140, 145, 150, 160, and 170°C are shown in Figure 2. The values for $(d\alpha/dt)_{0.5}$ and E at different temperatures are shown in Table III. The results indicate that $(d\alpha/dt)_{0.5}$ increases with increasing curing temperature, and the value of E is similar to that for the nonisothermal curing reaction.

Figure 3 shows the TG isothermal curing curves at 120, 140, 160, 180, 200, 220, and 240°C for the number 2 resin/curing agent (100/10 w/w). The weight (%), weight loss (%) over 10 min, and initial slope of the TG curve are all shown in Table IV. The results show that the amount and rate of weight loss are small when the sample is cured at 120°C. However, above 130°C, the reaction rate increases rapidly over 1 min and then declines sharply. As the curing temperature increases from 120 to 200°C, the sample weight over 10 min decreases gradually, and the weight loss increases gradually. At 220°C, however, the change in the weight loss is opposite; that is, the extent of curing is smaller than that at 200°C. Therefore, it can been seen that 200°C is the optimum choice for maximizing the extent of curing of Mo–phenolic resins.

According to the literature,[2] the maximum extent of isothermal curing by TG for common phenolic resins is observed at 240°C. The decrease in the extent of curing above 240°C may be attributed to oxidative crosslinking. Our results have the same regularity that has been reported in the literature. It can be concluded that TG is a viable approach for studying the curing reactions through the monitoring of the apparent weight loss.

Thermal degradation properties of cured mo–phenolic resins

Figure 4 shows the TG curves measured under nitrogen for a cured sample of the number 2 resin/curing agent with different ratios by weight. At 700°C, the weight losses of the samples are as follows: (a) 23.95, (b) 21.86, (c) 21.69, and (d) 22.69%. It can be concluded that for the 100/10 and 100/12 samples, the extent of thermal degradation is lowest and the yield of carbon is highest. Thermal degradation resistance declines slightly with an excess amount of the curing agent and more significantly for low amounts of the curing
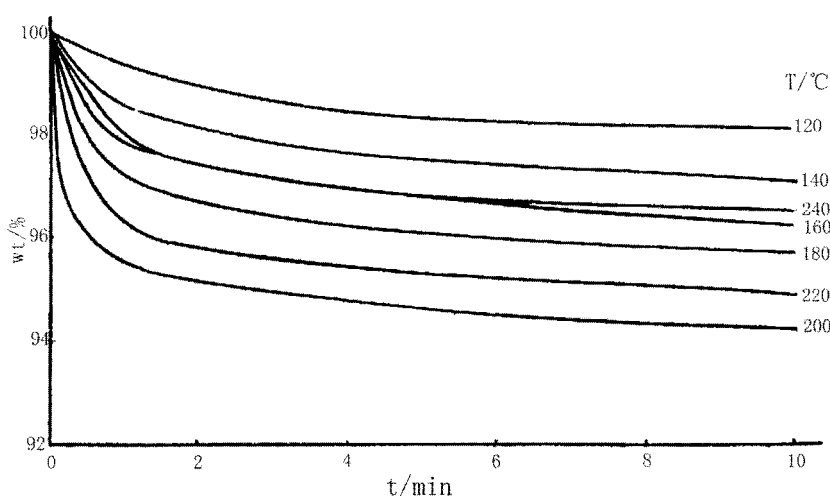

Figure 3 TG isothermal curving curves for the number 2 Mo–phenolic resin/curing agent (100/10) at different temperatures.

TABLE IV
Weight (%) and Weight Loss (%) over 10 min and Initial Slopes of TG Curve for the Sample

T (°C)	10 min weight (%)	10 min weight (%)	Initial slope of the TG curve
120	98.02	1.95	0.253
140	97.32	2.48	0.667
160	96.76	3.02	0.827
180	95.80	3.84	1.104
200	94.39	4.35	3.200
220	95.33	3.10	2.050
240	97.29	2.18	1.143

agent.[2] By comparing the experimental results for other samples (numbers 1 and 3; figures are omitted), we find that cured products of number 2 give the best thermal degradation resistance and yield of carbon.

It is known that gaseous decomposition products and carbon with condensed rings may be produced after ablation. The essential difference between TG analysis and ablative testing is ϕ. With the TG method, it is 1–30°C/min, whereas in the ablation process, it is 5000–50,000°C/min. The intense rate of the increase may lead to extremely high decomposition temperatures. Therefore, the yield of carbon by TG can be used as an evaluation of ablative properties.[8,9]

In terms of the curing temperature, the value of E, the reaction rate of the samples, and the thermal degradation resistance and yield of carbon of the cured resultants, number 2 is the most desirable choice.

Investigation of the curing mechanism

FTIR spectra for a sample of the number 2 Mo–phenolic resin/curing agent (100/10) before and after isothermal curing for 1, 5, and 10 min at 130°C are shown in Figure 5. The results indicate that during the curing,
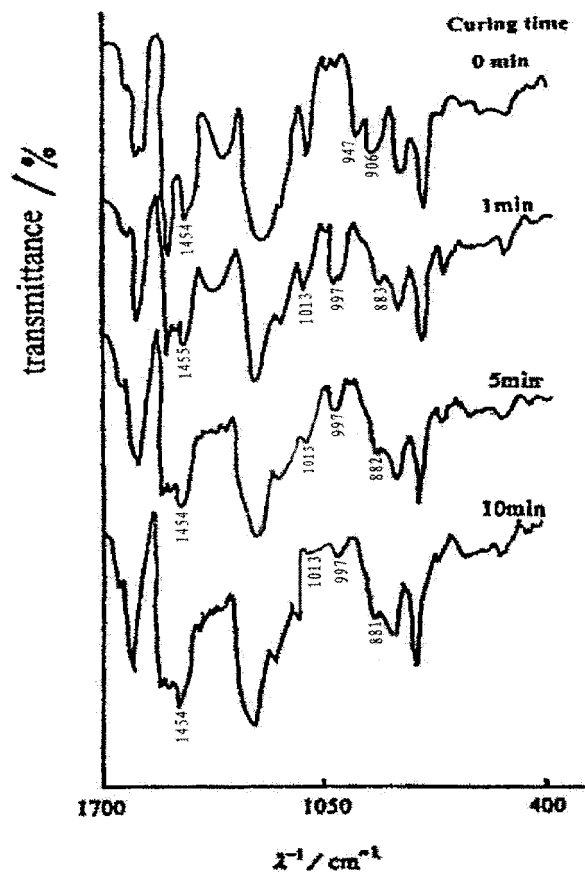
Figure 5 FTIR spectra for the number 2 Mo–phenolic resin/curing agent (100/10) before and after isothermal curing at 130°C.

absorption peaks that can be assigned to —CH$_2$OH appear at 1013 cm^{-1}, and their intensity decreases gradually as curing is continued. Simultaneously, the intensity of peaks assigned to —CH$_2$ at 1454 cm^{-1} increases gradually, and this suggests that curing involves methylenated crosslinking condensation. The
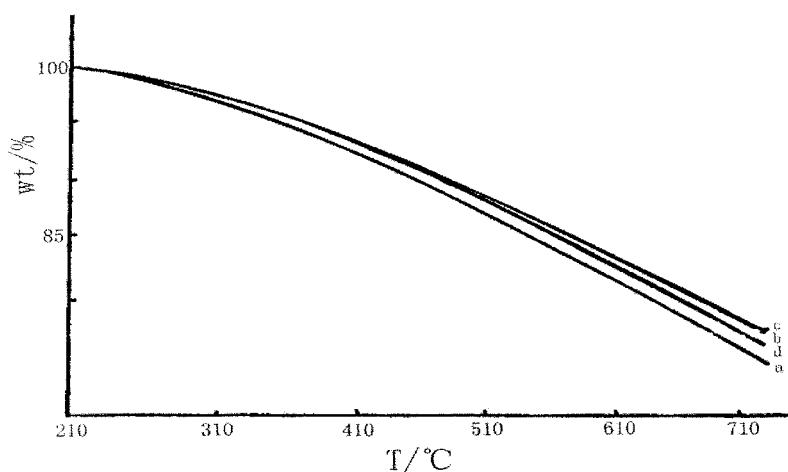
Figure 4 TG curves for the cured number 2 resin/curing agent with different ratios of the resin to the curing agent: (a) 100/6, (b) 100/10, (c) 100/12, and (d) 100/16.

absorption peaks assigned to Mo=O and Mo—O at 947 and 906 cm^{-1} undergo a shift, and further study is needed to explain this observation.

CONCLUSIONS

1. The lowest curing temperature, the minimum value of E, the largest reaction rate, the best thermal degradation resistance, and the highest yield of carbon at 700°C were observed by DSC and TG for the number 2 Mo–phenolic resins with 12% molybdenum, with a resin/curing agent ratio of 100/10 (w/w).

2. The isothermal weight loss over 10 min during the curing of the aforementioned sample by TG increases gradually from 120 to 200°C but decreases above 220°C. The temperature giving the maximum extent of curing is about 200°C.

3. The curing mechanism can be explained by methylenated crosslinking condensation of hydroxy–methylene groups.

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