

Activation Energy and Curing Behavior of Resol- and Novolac-Type Phenolic Resins by Differential Scanning Calorimetry and Thermogravimetric Analysis

Young-Kyu Lee,¹ Dae-Jun Kim,¹ Hyun-Joong Kim,¹ Teak-Sung Hwang,² Miriam Rafailovich,³ Jonathan Sokolov³

¹Laboratory of Adhesion & Bio-Composites, School of Biological Resources and Materials Engineering, Seoul National University, Suwon 441-744, South Korea

²Department of Chemical Engineering, Chungam National University, Daejeon 305-335, South Korea

³Department of Materials Science & Engineering, State University of New York at Stony Brook, Stony Brook, New York 11794-2275

Received 18 March 2002; accepted 2 December 2002

ABSTRACT: The thermal behavior, thermal degradation kinetics, and pyrolysis of resol and novolac phenolic resins with different curing conditions, as a function of the formaldehyde/phenol (F/P) molar ratio (1.3, 1.9, and 2.5 for the resol resins and 0.5, 0.7, and 0.9 for the novolac resins) were investigated. The activation energy of the thermal reaction was studied with differential scanning calorimetry at five different heating rates (2, 5, 10, 20, and 40°C/min) between 50 and 300°C. The activation energy of the thermal decomposition was investigated with thermogravimetric analysis at five different heating rates (2, 5, 10, 20, and 40°C/min) from 30 to 800°C. The low molar ratio resins exhibited a higher activation energy than the high molar ratio resins in the curing process. This meant that less heat was needed to

cure the high molar ratio resins. Therefore, the higher the molar ratio was, the lower the activation energy was of the reaction. As the thermal decomposition of the resol resins proceeded, the activation energy sharply decreased at first and then remained almost constant. The activation energy of the thermal decomposition for novolac resins with F/P = 0.5 or F/P = 0.7 was almost identical in all regions, whereas that for novolac resins with F/P = 0.9 gradually decreased as the reaction proceeded. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2589–2596, 2003

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

INTRODUCTION

Phenolic resins constituted the first type of thermosetting resin to be synthesized when they were first introduced in 1907. This type of resin has become the subject of further studies because of its excellent fire-resistant properties. Phenolic resins have recently been used in the manufacture of transportation systems. However, the relationship between the synthesis conditions and the structure and mechanical properties of the resins is not yet fully understood. One of the reasons for this is that the polymerization of the resins has a complicated reaction mechanism.¹ One reaction involves the addition of formaldehyde to the *ortho*-phenol and *para*-phenol positions of the formaldehyde.

Two different types of condensation reactions can occur: (1) between the phenol-free position and the methylolphenols producing an ether bridge and (2) between the methylolphenols themselves producing a methylene bridge.^{2,3}

Although phenolic resins were the first commercial synthetic polymeric materials, their synthesis, structure, and curing reactions are still a matter of great interest. Our ability to analyze the structure and network formation of these resins with modern instrumental techniques increases our understanding of these phenomena and allows for better product quality control. The structure and, consequently, the properties of the resins depend on the molar ratios of the reactants, as well as the type and concentration of the catalyst.

The kinetics of the curing reactions strongly depend on the nature and amount of reactive positions available in the phenol resins.⁴ Increasing attention is being paid to investigating the reaction between phenol and formaldehyde, particularly from the viewpoint of the kinetics and the mechanism of the synthesis yielding resol and novolac types of phenol–formaldehyde resins. This situation has arisen because of the continuing

Correspondence to: H.-J. Kim (hjokim@snu.ac.kr).

Contract grant sponsor: Korea Research Foundation; contract grant number: KRF-2000-G00078.

Contract grant sponsor: Brain Korea 21 Projects in 2003, NSF-MRSEC.

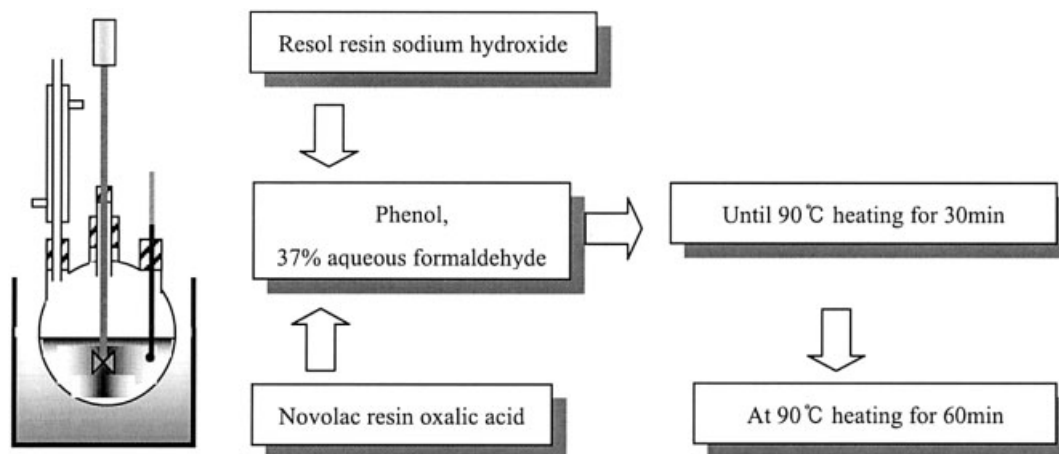


Figure 1 Apparatus used in the preparation of the resol and novolac resins.

demand for plastics produced from phenolic resins and because of the development of new analytical methods that make it possible to study the chemical compositions and structures of these resins.

Previous studies⁵ have detailed the use of an atomic force microscope to investigate Si_3N_4 tip interactions under various curing conditions with three different molar ratios. Also, the surface free energy and acid/base character of resol resins have been investigated with contact-angle analysis. It has been concluded from that study that the hydrophobic effect constitutes a significant part of the adhesion force. Depending on the contact angle, surface free energies express a stronger negative surface charge toward their environment and are considered to be relatively more hydrophobic. Because the uncured resin is more hydrophobic, it appears that increasing the substrate hydrophobicity results in a stronger adhesion force.

In some cases, the thermal stability of phenolic resins has also been evaluated. To assess their utility as thermally stable materials or their use in applications requiring such properties, we must examine their relative thermal stability and degradation.

In this study, we focus on the relative thermal behavior, the kinetics of thermal degradation, and the pyrolysis in relation to the curing conditions as a function of the formaldehyde/phenol (F/P) molar ra-

tio. The activation energy (E_a) values of the thermal reaction were studied with differential scanning calorimetry (DSC), and the E_a values of thermal decomposition were investigated with thermogravimetric analysis (TGA).

EXPERIMENTAL

Synthesis of the resol and novolac resins

The resin syntheses were carried out in a laboratory glass reactor equipped with a stirrer, a thermometer, and a reflux condenser, as shown in Figure 1. The mixture of phenol and 37% aqueous formaldehyde was heated up to a temperature of 45°C, and then the catalyst, a 10% sodium hydroxide solution for resol resins and a 2% oxalic acid solution for novolac resins, was added. After the components were heated to 90°C over a period of 30 min, the temperature was kept at 90°C for 60 min.

The characteristics of the resol and novolac resins are listed in Table I.

DSC

DSC analysis with a PerkinElmer DSC-7 (State University of New York at Stony Brook, Stony Brook, NY)

TABLE I
Characteristics of the Resins

| Code | Resol | | | Novolac | | |
|-------------------------|-------|------|------|---------|------|------|
| | 1 | 2 | 3 | 1 | 2 | 3 |
| F/P molar ratio | 1.3 | 1.9 | 2.5 | 0.5 | 0.7 | 0.9 |
| M_n | 240 | 380 | 400 | 380 | 390 | 390 |
| M_w | 460 | 630 | 670 | 540 | 560 | 580 |
| M_w/M_n | 1.92 | 1.66 | 1.67 | 1.44 | 1.42 | 1.49 |
| Nonvolatile content (%) | 59.2 | 53.5 | 50.4 | 46.6 | 45.4 | 45.9 |
| Viscosity (mPa · s) | 157 | 445 | 1390 | 22.6 | 25.7 | 29.8 |

M_n = number-average molecular weight; M_w = weight-average molecular weight.

equipped with a thermal analysis data station enabled the curing exotherms of the phenol–formaldehyde resins to be determined. This study was performed with a sealed aluminum capsule pan, under a nitrogen atmosphere, at 5 different heating rates (2, 5, 10, 20, and 40°C/min) between 50 and 300°C. For the removal of moisture from the resins, the resins were mounted in a vacuum-dried oven at 40°C for 48 h.

TGA

Phenol–formaldehyde resins were subjected to TGA in a nitrogen atmosphere at five different heating rates (2, 5, 10, 20, and 40°C/min) from 30 to 800°C with a thermogravimetric analyzer (Rheometric Scientific TGA 1000, NICEM, Seoul National University, Seoul, Korea). For the removal of moisture from the resins, they were mounted in a vacuum-dried oven at 40°C for 48 h.

RESULTS AND DISCUSSION

E_a values of chemical curing by DSC analysis

Thermosetting resins play an important role in industry today because of their high flexibility, which allows the properties of the end product to be tailored for a particular use. Because, in industrial formulations, a variety of additives are included in the cure system, resulting in complex cure kinetics, a good understanding of the cure process is the most important prerequisite for optimizing the production of the composites. The methods employed to monitor the progress of the curing process fall into two categories:⁶

1. Methods based on the monitoring of the changes in the concentrations of the reactive groups consumed, or in the process of being consumed, over the course of the reaction. These methods include chemical analysis, as well as IR and UV spectroscopy.
2. Methods based on the effects of network formation on the physicochemical properties of the sample.

Among the available methods, only a few can be employed to follow the whole cure process from beginning to end. One of the most frequently used methods is thermal analysis by DSC, in both the isothermal and nonisothermal modes.^{7,8} Thermal analysis is a powerful technique for studying the kinetics of physicochemical processes.⁹ Moreover, it is a useful technique for making time–temperature predictions and for the optimization of process variables. Another popular technique, which is based on the heat evolution during the course of a reaction, is the adiabatic reactor method. This method requires there to be a

highly reactive polymerizing mixture at the initial temperature.

One of the most widely used techniques for cure kinetic studies of thermoset materials is DSC. In this study, DSC has the advantage of being based on the same assumption as the heat equation, which is the proportionality between the rate of heat generation and the rate of reaction. Different errors may affect the accuracy of the cure kinetic parameter determination based on DSC measurements: the use of an inappropriate kinetic model function, intrinsic defaults of the apparatus, or errors in the interpretation of the DSC thermogram.¹⁰ It is well known that the baseline of a DSC scan experiment for a thermoset is not a straight line, but obtaining its real shape is a complicated process. It can be obtained by heat capacity measurements with temperature-modulated DSC. Nevertheless, this recently developed method is still not commonly used, and most kinetic studies are performed with conventional DSC. Moreover, the type of baseline used is generally a simple straight line drawn from the beginning to the end of the exothermic signal.

As reported in the literature,⁶ n th-order and autocatalytic kinetics are the two reaction mechanisms used to describe curing reactions. They can be expressed as follows. For n th order kinetics,

$$d\alpha/dt = k(1 - \alpha)^n \quad (1)$$

where α , the extent of the curing reaction, is defined as $\alpha = \Delta H_t / \Delta H_{\text{Total}}$. ΔH_t and ΔH_{Total} are the enthalpy of the curing reaction at time t and the enthalpy of the curing reaction at the end of curing, respectively, and they can be determined from DSC thermograms.

The rate constant (k) can be expressed as

$$k = Ae^{-E_a/RT} \quad (2)$$

where A is the frequency factor. Then,

$$\ln k = \ln [(d\alpha/dt) / (1 - \alpha)^n] = \ln A - E_a/RT \quad (3)$$

When the order of this reaction is properly assumed, a plot of $\ln k$ versus $1/T$ allows us to predict A and E_a .

Kissinger¹¹ proposed that

$$E_a\beta(RT_p^2) = Ae^{-E_a/RT_p} \quad (4)$$

where β is the heating rate, which is expressed as $\beta = dT/dt$. By taking the logarithm of eq. (4), we obtain the Kissinger equation:

$$-\ln(\beta T_p^2) = -\ln(AR/E_a) + (1/T_p)(E_a/R) \quad (5)$$

A and E_a were obtained by the plotting of $-\ln(\beta T_p^2)$ versus $1/T_p$, where T_p is the peak temperature. The curing kinetics from DSC at different heating rates,

TABLE II
Kinetic Parameters of Resol Resins: Obtained
by Kissinger's Analysis

| Resol resin | β ($^{\circ}\text{C}/\text{min}$) | T_p ($^{\circ}\text{C}$) | E_a (kJ/mol) |
|-------------|---|------------------------------|-------------------|
| F/P = 1.3 | 2 | 110.0 | 17.65 |
| | 5 | 131.0 | |
| | 10 | 145.2 | |
| | 20 | 153.1 | |
| | 40 | 160.6 | |
| F/P = 1.9 | 2 | 103.8 | 17.91 |
| | 5 | 106.7 | |
| | 10 | 107.8 | |
| | 20 | 119.4 | |
| | 40 | 129.5 | |
| F/P = 2.5 | 2 | 91.7 | 15.23 |
| | 5 | 106.7 | |
| | 10 | 124.9 | |
| | 20 | 132.7 | |
| | 40 | 143.9 | |

required to obtain the fundamental kinetic constants of the activation energy (E_a), were obtained from the plotting of $-\ln(\beta/T_p^2)$ against $1/T_p$ (Tables II and III). The obtained E_a values of the resol and novolac resins decreased as the F/P molar ratio increased.

The DSC curing curves for a resol resin with F/P = 2.5 as a function of the heating rate are shown in Figure 2. There was an endothermic peak in the curing process. This could be attributed to the condensation of the methylol group with phenol, forming methylene bridges, and to the condensation of two methylol groups, forming dibenzyl ether bridges to the methylene bridges, thereby eliminating formaldehyde. In a previous report,¹² the DSC thermograms of phenol-formaldehyde resol resins showed a peak between 98 and 129 $^{\circ}\text{C}$, which corresponded to the addition of formaldehyde to the phenolic rings to form hydroxy-

TABLE III
Kinetic Parameters of Novolac Resins Obtained
by Kissinger's Analysis

| Novolac resin | β ($^{\circ}\text{C}/\text{min}$) | T_p ($^{\circ}\text{C}$) | E_a (kJ/mol) |
|---------------|---|------------------------------|-------------------|
| F/P = 0.5 | 2 | 105.0 | 22.93 |
| | 5 | 106.7 | |
| | 10 | 117.4 | |
| | 20 | 130.9 | |
| | 40 | 136.6 | |
| F/P = 0.7 | 2 | 116.5 | 21.34 |
| | 5 | 112.8 | |
| | 10 | 114.2 | |
| | 20 | 138.6 | |
| | 40 | 136.8 | |
| F/P = 0.9 | 2 | 104.9 | 16.02 |
| | 5 | 110.7 | |
| | 10 | 120.0 | |
| | 20 | 139.9 | |
| | 40 | 154.4 | |

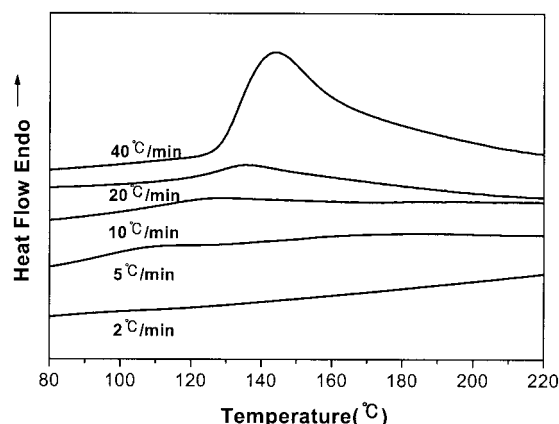


Figure 2 DSC curves of a resol resin (F/P = 2.5) with the heating rate.

methyl phenols, and a peak in the range of 139–151 $^{\circ}\text{C}$ corresponding to the crosslinking reactions. With an increasing heating rate, a shift of the condensation reaction to a higher temperature was observed.

With the same method, the DSC curves of the resol and novolac resins were obtained as a function of the molar ratio and the heating rate. As shown in Figure 3, T_p of the novolac resins increased as the heating rate increased. In addition, as the heating rate increased, the temperature of the peak also increased.

In a comparison of novolac resins with resol resins, Chow et al.¹³ reported interesting DSC results showing an endothermic peak for a novolac reaction. Their results provided an explanation for the nature of the inconsistencies between the exothermic and endothermic reactions observed for different types of resins.

The plots of $-\ln(\beta/T_p^2)$ against $1/T_p$ for resol and novolac resins are shown in Figures 4 and 5, respectively. The curing kinetics with DSC at different heating rates, used to obtain the fundamental kinetic constants of the activation energy (E_a), were obtained from the plotting of $-\ln(\beta/T_p^2)$ against $1/T_p$. The

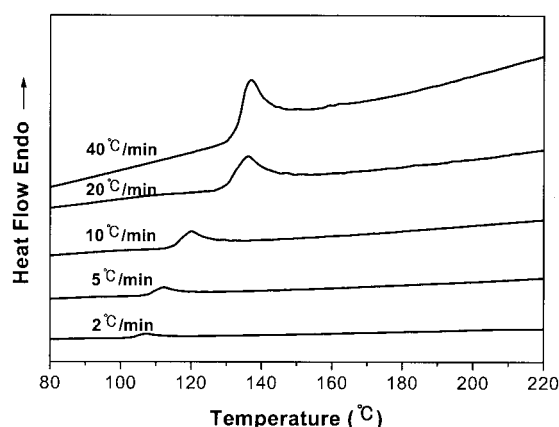


Figure 3 DSC curves of a novolac resin (F/P = 0.5) with the heating rate.

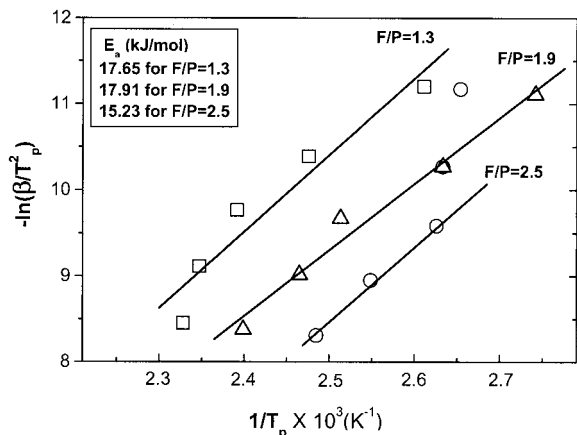


Figure 4 Plot of $-\ln(\beta/T_p^2)$ versus T_p^{-1} for the resol resins.

obtained values of E_a for the resol and novolac resins decreased as the F/P molar ratio increased. The E_a values of the resol and novolac resins as a function of the F/P molar ratio are shown in Figure 6. E_a decreased with increasing molecular weight. In other words, a lower value of E_a was needed for higher molar ratio resins, which cured faster than lower molar ratio resins.

The increasing F/P value enhanced the concentration of the methylol groups. This resulted in increasing amounts of methylene and ether bridges and in rigid resin structures, which made the condensation of the dibenzyl ether bridges more difficult.¹⁴

On the basis of previous results,¹⁰ the amount of free ortho and para positions decreased, and the number of ortho methylol groups, *p-p'* methylene bridges, and hemiformal structures increased as a function of an increasing F/P molar ratio. The further weakening of the phenolic O—H bond was likely to lead to a stronger negative charge delocalized on the ortho and para portions of the aromatic ring. The phenol–formaldehyde self-condensation reaction, a bimolecular re-

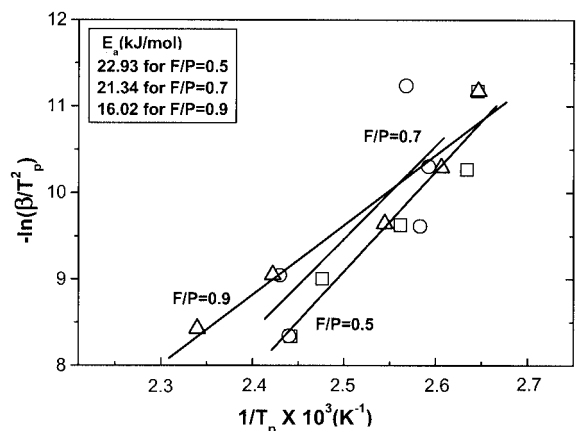


Figure 5 Plot of $-\ln(\beta/T_p^2)$ versus T_p^{-1} for the novolac resins.

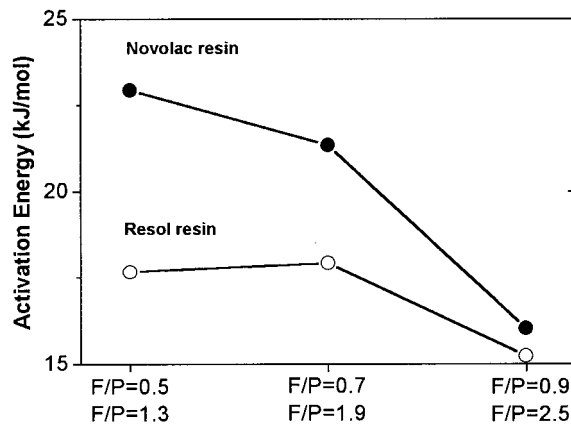


Figure 6 E_a values of the resol and novolac resins from the Kissinger expression.

action, was then more rapid as a result of the substrate-induced activation of the only two types of reactive sites of phenolic oligomers. In the case of *ortho*- and *para*-hydroxybenzyl alcohols, the maximum energies of interaction were 19.7 and 13.3 kcal/mol, respectively.

Roczniak et al.¹⁵ identified the band at approximately 1450 cm^{-1} , which was assigned to methylene bridges in *p-p'*, whereas the band at 1460 cm^{-1} was assigned to the methylene bridge in *o-o'*, and the band at 1480 cm^{-1} was assigned to the *o-p'* position. These bands were higher for the completely cured resin than for the prepolymer of the uncured resin. This was an indication that the crosslinking reaction occurred to a greater extent in the curing step than during the synthesis of the resin. The application of this analysis to the resin allowed us to determine that the quantity of *p-p'* bridges was higher than that of *o-p'* bridges.¹⁶

To evaluate the effect of the F/P molar ratio on E_a , we obtained curves for a series of model compounds with different F/P molar ratios. Before the DSC measurements, it could be concluded that a substantial

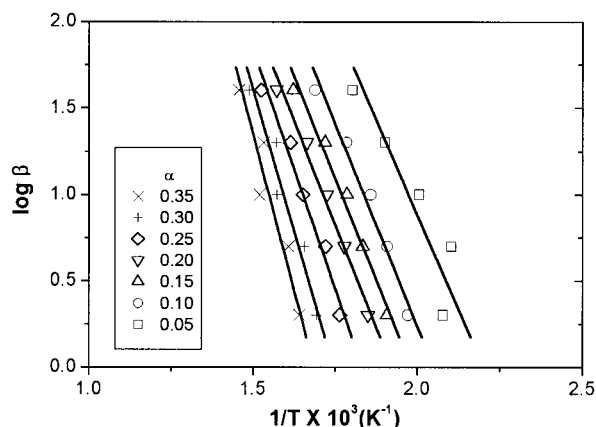


Figure 7 Isoconversional curves for a novolac resin (F/P = 0.5) from the Flynn–Wall expression.

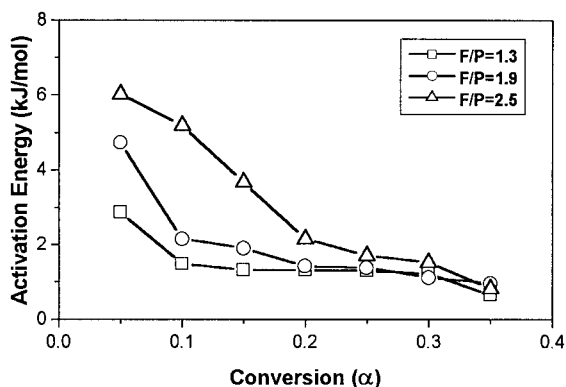


Figure 8 E_a values of thermal decomposition for the resol resins from the Flynn–Wall expression.

part of the condensation reaction took place during the heating stage. The advancement of the curing process to this stage could be assumed to be due to the high proportion of formaldehyde in the resin. For this reason, a cured resin with a higher proportion of formaldehyde gave lower values for the heat of reaction than a resin with lower F/P ratios.

E_a values of thermal decomposition by TGA

To evaluate the E_a values of thermal decomposition, we used the Flynn–Wall expression:¹⁷

$$E_a = \frac{-R}{0.457} \frac{a(\log \beta)}{d(T^{-1})} \quad (6)$$

where R is the gas constant and T is the absolute temperature. To obtain E_a , we plotted a linear relationship between $\log \beta$ and $1/T$ at selected fractions of the thermal decomposition in Figures 7 and 8, and we then evaluated E_a from the slopes. The selected fraction varied from 0.05 to 0.50, and the resulting values of E_a for each fraction were compared.

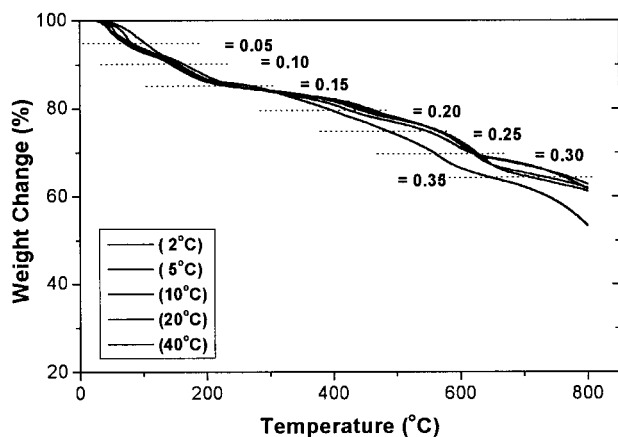


Figure 9 Thermograms of a resol resin (F/P = 1.3) with the heating rate.

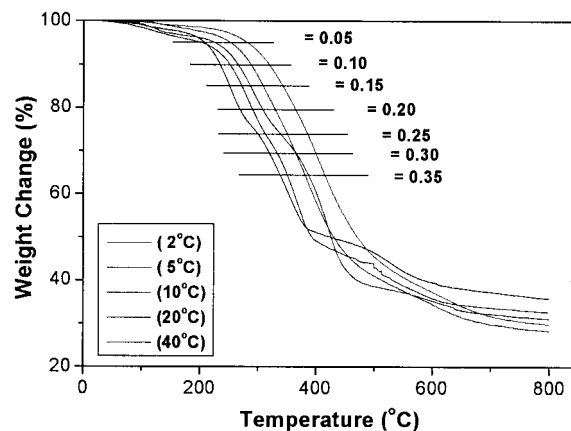


Figure 10 Thermograms of a novolac resin (F/P = 0.5) with the heating rate.

The TGA curves for the resol and novolac resins at five different heating rates are shown in Figures 9 and 10. According to Conley,¹⁸ the degradation process, accelerated by the presence of phenolic groups adjacent to the methylene bridge, is dependent on the dihydroxy phenyl methane units present in the resin. The degradation process, accelerated by the presence of phenolic groups adjacent to the methylene bridges, is dependent on the dihydroxy phenyl methane units present in the resin.

Trick and Saliba¹⁹ studied the thermal degradation of phenol–formaldehyde resins. They explained the formation of phenol and cresols due to the scission of a terminal benzene ring depending on the position of scission, as shown in Figure 11. Previous studies^{2,3} pointed out the possibility of xylenol or trimethylphenol being formed during the pyrolysis of the highly condensed phenol–formaldehyde resin.

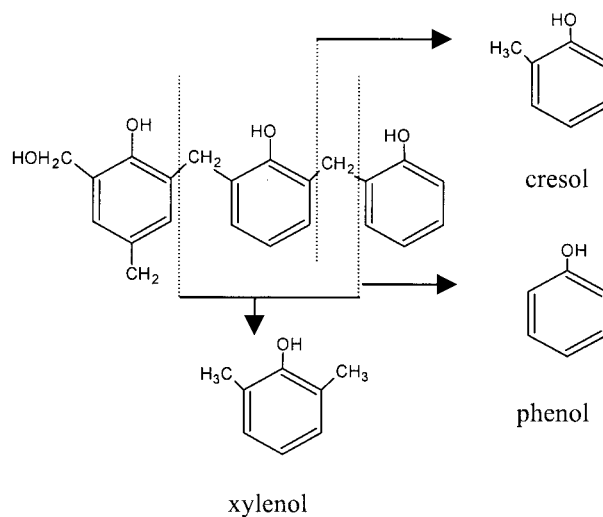


Figure 11 Formation of phenols in the major weight-loss region.

TABLE IV
Relationship Between $\log \beta$ and T^{-1} for Resol Resin (F/P = 1.3)

| $\log \beta$ | $1/T \times 10^3 \text{ (K}^{-1}\text{)}$ | | | | | | |
|--------------|---|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | $\alpha = 0.05$ | $\alpha = 0.10$ | $\alpha = 0.15$ | $\alpha = 0.20$ | $\alpha = 0.25$ | $\alpha = 0.30$ | $\alpha = 0.35$ |
| 0.301 | 2.925 | 2.399 | 1.956 | 1.508 | 1.321 | 1.203 | 1.106 |
| 0.699 | 2.918 | 2.397 | 1.949 | 1.448 | 1.223 | 1.125 | 0.975 |
| 1.000 | 2.846 | 2.351 | 1.935 | 1.413 | 1.194 | 1.119 | 0.969 |
| 1.301 | 2.818 | 2.329 | 1.946 | 1.392 | 1.121 | 1.012 | 0.987 |
| 1.602 | 2.763 | 2.279 | 1.909 | 1.372 | 1.195 | 1.112 | 1.036 |

According to Lin,²⁰ the strength of the C—H bond of the aliphatic bridge decreases with increasing temperature, and this indicates the cleavage of the methylene bridges. As the temperature increases, the ratio of the concentration of the diphenyl ether links to that of the phenol structures increases. The diphenyl ether link structures constitute the intermediate structures that are generated for phenolic resins during the process of thermal degradation.

As the heating rate increased, the decomposition temperature (T_d) increased. T_d was obtained from the point at which the weight loss increased. The fact that T_d is affected by the heating rate of pyrolysis has already been reported by other researchers.²¹ The initial degradation temperature of the resol and novolac resins decreased as the heating rate increased, as previously reported in the literature.

As shown in Figure 9, the temperature at $\alpha = 0.5$ (5% thermal degradation region) for the five heating rates was measured where the lines crossed the TGA curves. To obtain the E_a values for the thermal decomposition, we converted these data into $\log \beta$ and $1/T$, as listed in Table IV.

With the same method, the temperatures at different α values were obtained. The relationships between $\log \beta$ and $1/T$ are listed in Table IV, based on Figure 12. The E_a value for each α value was calculated from the slope of each straight line, as listed in Table V.

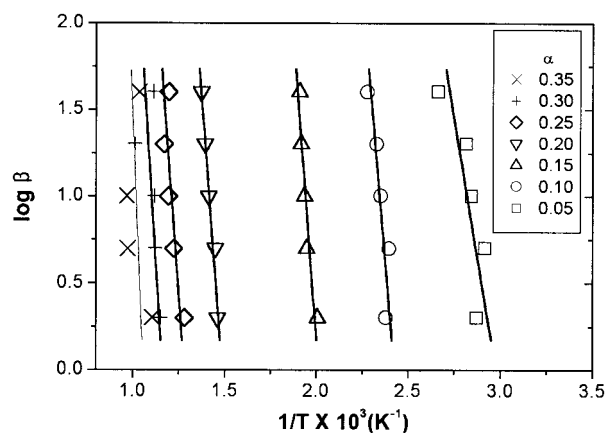


Figure 12 Isoconversional curves for a resol resin (F/P = 1.3) from the Flynn-Wall expression.

The E_a values of the thermal decomposition curves for resol and novolac resins at the degradation conversion (α) were obtained and are shown in Figures 8 and 13.

As the thermal decomposition of resol resins proceeded, E_a sharply decreased at first and then remained almost constant.

The E_a values of thermal decomposition for novolac resins with F/P = 0.5 and F/P = 0.7 were almost identical in all the regions, whereas the E_a value of thermal decomposition for the novolac resin with F/P = 0.9 gradually diminished, as shown in Figure 13.

It can be seen from these results that the E_a values of thermal decomposition for the resol at the initial stage were quite high compared with the corresponding values at the final stage. These observations were rationalized as follows. The magnitude of the E_a values is expected to reflect the extent of crosslinking of the resins. However, it should be noted that E_a for the decomposition of the phenolic resins was reported by Rama Rao et al.²¹ to be about 9 kJ/mol, whereas for glass-phenolic composites, a value of 270 kJ/mol was reported by Henderson et al.²² and a value of 42–77 kJ/mol was reported by Ninan.²³ This indicates clearly that the extent of curing has a significant influence on the calculated E_a values.

CONCLUSIONS

The E_a values of chemical curing (thermal reaction) were studied by DSC, and the E_a values of thermal decomposition were investigated by TGA as a func-

TABLE V
 E_a Values of the Thermal Decomposition for a Resol Resin (F/P = 1.3) from the Flynn-Wall Expression

| α | Linear expression of Figure 10 | E_a (kJ/mol) |
|----------|--------------------------------|----------------|
| 0.05 | $Y = -0.1578X + 2.979$ | 2.87 |
| 0.10 | $Y = -0.0815X + 2.427$ | 1.48 |
| 0.15 | $Y = -0.0723X + 2.014$ | 1.31 |
| 0.20 | $Y = -0.0724X + 1.488$ | 1.31 |
| 0.25 | $Y = -0.0717X + 1.283$ | 1.30 |
| 0.30 | $Y = -0.0604X + 1.163$ | 1.22 |
| 0.35 | $Y = -0.0395X + 1.057$ | 0.65 |

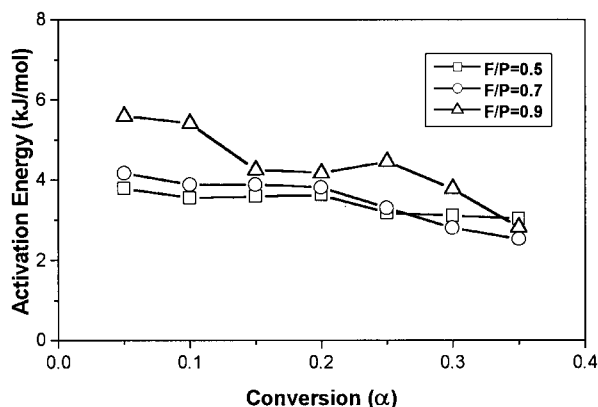


Figure 13 E_a values of thermal decomposition for the novolac resins from the Flynn–Wall expression.

tion of the F/P molar ratio. The low molar ratio resins had higher E_a values than the high molar ratio resins. This meant that less heat was needed to cure high molar ratio resins than low molar ratio resins. In general, lower E_a values indicated that the reaction proceeded faster at a given temperature. Therefore, the higher the molar ratio was, the lower E_a was for the reaction. This might be due to the presence of more reactive sites remaining in the lower molar ratio resins than in the higher molar ratio resins. E_a decreased with increasing molecular weight. In other words, a lower E_a value was needed for higher molar ratio resins, which cured faster than lower molar ratio resins.

Phenol–formaldehyde resin decomposition was found to occur in two stages, with the initial stage involving predominantly the cleavage of formal ($-\text{CH}_2-\text{O}-\text{CH}_2-$) linkages and the second stage

involving chemical reactions. The extent of curing depends on the nature of the resin.

References

- Knop, A.; Pilato, L. *Chemistry and Application of Phenolic Resins*; Springer-Verlag: Berlin, 1979; p 28.
- Grenier-Loustalot, M. F.; Larroque, S.; Grenier, P.; Bedel, D. *Polymer* 1996, 37, 955.
- Jones, R. T. *J Polym Sci Part A: Polym Chem* 1985, 21, 1801.
- Markovic, S.; Dunjic, B.; Zlatanic, A.; Djonlagic, J. *J Appl Polym Sci* 2001, 81, 1902.
- Lee, Y.-K.; Kim, H.-J.; Rafailovich, M.; Sokolov, J. *Int J Adhes Adhes* 2002, 22, 375.
- Yousefi Lafleur, P. G. *Polym Compos* 1997, 18, 157.
- Fang, D. P.; Frontini, P. M.; Riccardi, C. C.; Williams, R. J. *J Polym Eng Sci* 1995, 35, 1359.
- Liu, S. B.; Yang, J. F.; Yu, T. L. *Polym Eng Sci* 1995, 35, 1884.
- Khanna, Y. P.; Taylor, T. J. *Polym Eng Sci* 1987, 27, 764.
- Dupuy, J.; Leroy, E.; Maazouz, A. *J Appl Polym Sci* 2000, 78, 2262.
- Kissinger, H. E. *Anal Chem* 1957, 29, 1702.
- Waage, S. K.; Gardner, D. J.; Elder, T. J. *J Appl Polym Sci* 1991, 42, 273.
- Chow, S.; Steiner, P. R.; Troughton, G. E. *Wood Sci* 1975, 8, 343.
- Holopanen, T.; Alvila, L.; Raino, J.; Pakkanen, T. T. *J Appl Polym Sci* 1997, 66, 1183.
- Roczniak, K.; Biernacka, T.; Skarzynski, M. *J Appl Polym Sci* 1983, 28, 39.
- Lee, Y.-K.; Kim, H.-J. *Adhes Interface* 2001, 2(3), 16.
- Flynn, J. H. *Polym Eng Sci* 1980, 20, 675.
- Conley, R. T. *Thermal Stability of Polymers*; Marcel Decker: New York, 1970; Chapter 11.
- Trick, K.; Saliba, T. *Carbon* 1995, 33, 1509.
- Lin, J.-M.; Ma, C.-C. M. *Polym Degrad Stab* 2000, 69, 229.
- Rama Rao, M.; Alwan, S.; Scariach, K. J.; Sastri, K. S. *J Therm Anal* 1997, 49, 261.
- Henderson, J. B.; Tant, M. R.; Moore, G. R.; Wiebelt, J. A. *Thermochim Acta* 1981, 44, 253.
- Ninan, K. N. J. *Space Craft Rockets* 1986, 23, 347.