Kinetic Parameters of Thermal Degradation of Polyethylene Glycol-Toughened Novolac-Type Phenolic Resin

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ABSTRACT: The miscibility and thermal degradation of poly(ethylene glycol) (PEG)-toughened novolac-type phenolic resin were investigated. Differential scanning calorimetry (DSC) results confirmed that the phenolic resin/PEG blend was blended completely. Infrared spectra show that hydrogen bonding existed in the blends. Thermal degradation of PEG blended with novolac-type phenolic resin was studied utilizing a dynamic thermogravimetric technique in a flowing nitrogen atmosphere at several heating rates (i.e., 5, 10, 20, 40°C/min). Thermal degradation of phenolic resin/PEG blends takes place in multiple steps. The thermal behavior and the thermal stability affected the thermal degradation, which coincided with the data from the thermal degradation of novolac-type phenolic resin/PEG blends by thermogravimetric analysis (TGA). © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 188–196, 2001

Key words: novolac-type phenolic resin; poly(ethylene glycol); kinetic parameters

INTRODUCTION

Polymer blends have received much attention in the past decades. The preparation of polymer blends generally requires a processing technique in which the polymers are subjected to high temperature. It is important to know the effect of each polymer on the thermal stability of the other. Many aspects of polymer blends containing polyethers have been studied extensively; however, their thermal stability is still ambiguous.

The derivation of kinetic data for polymer decomposition using multiple thermogravimetric analysis has received increasing attention in the past decade.[1] However, many criticisms concern its use in the determination of rate constants, activation energies, reaction orders, and the Ar-

rhenius exponential *A* factors.[2–8] This situation has arisen because the actual values obtained in the majority of studies are dependent not only on factors such as the nitrogen atmosphere, sample mass, sample shape, flow rate, and heating rate, but also on the mathematical treatment used to evaluate the data. The dynamic thermogravimetric analysis curves and their derivatives have been analyzed using a variety of analytical methods in the literature to obtain information on the kinetic parameters.[9]

Phenolic resins have been widely used as paint, adhesive, and matrix materials due to their excellent flame resistance, dimensional stability, and chemical resistance. Improvement of the toughness of phenolic resin is an important task for further application. Phenolic resin contains a hydroxyl group, which will interact with other polymers containing a hydrogen-bonded functional group. The miscibility of phenolic blends depends on both the strength of self-association of the phenolic resin and the interassociation between the phenolic resin and the modifier. One

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method of modifying phenolic resin is to blend it with poly(ethylene glycol) (PEG), as described in our previous article.[10] Recently, several researchers studied the miscibility, mobility, and thermodynamical properties in a novolac-type phenolic resin blend. It is interesting to investigate the thermal stability of PEG blends with novolac-type phenolic resin. The thermal decomposition of blends were studied by thermogravimetric analysis to obtain kinetic parameters for this process.

Ozawa's method was utilized to analyze the residual weight curves. Ozawa's method represents a relatively simple method to determine the activation energies of thermal degradation directly from weight loss data versus temperature at several heating rates.[11,12]

EXPERIMENTAL

Materials

PEG was purchased from the Aldrich Chemical Co. (Milwaukee, WI). The molecular weight of PEG is 20,000; the repeat unit of PEG is HO—$(CH_2CH_2O)n$—H. Novolac-type phenolic resin was synthesized in this laboratory.[10]

Sample Preparation

The phenolic/PEG blend was prepared by the solution-casting method. Both phenolic resin and PEG were mixed in THF [1% (w/v)] at room temperature according to the designed compositions at 55°C. The mixed solution was stirred for 6–8 h and then allowed to evaporate slowly at room temperature for about 24 h. The blends were then dried at 50°C for 2 days and annealed at 140°C for 2 h, under a vacuum.

Differential Scanning Calorimeter (DSC)

The glass transition temperature (T_g) of the polymer blend was measured by a differential scanning calorimeter (DuPont, DSC Model 2900). The heating rate was 20°C/min within a temperature range of 0–280°C. The DSC measurements were conducted with 3–4 mg of the sample on a DSC plate after the specimens were quickly cooled to room temperature following the first scan. This procedure was adopted to ensure complete mixing of the polymer blends and to remove residual solvent and water in the specimen completely. The T_g value was determined at the midpoint of the heat capacity (Cp) transition change, and the

reproducibility of T_g values was estimated to be within ±2°C.

Thermogravimetric Analysis (TGA)

TGA was performed with a DuPont 951 instrument coupled to a 1050 thermal analyzer. The polymer sample (10 ± 3 mg) was stacked in an open platinum sample pan and the experiment was conducted under a nitrogen gas atmosphere with various heating rates (i.e., 5, 10, 20, 40°C/min). Although machine-selected heating rates are reported and used in the calculations, the actual heating rates were determined from the appropriate plots.

Prior to multiple-heating-rate kinetics experiments, samples (ca. 10 ± 3 mg) were heated using a TGA at the range of 20–800°C to obtain the residual weight curves of phenolic resin and PEG. For the multiple-heating-rate kinetic experiments, the sample was placed into the TGA pan and heated until the sample reached thermal degradation in a nitrogen atmosphere.

Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra were recorded with a Nicolet 5 DXC spectrometer. Thin films were prepared by the solution-casting method. All the samples were annealed at 140°C for 2 h to remove the residual solvent and to ensure that the polymer blend was mixed completely. A minimum of 16 scans was signal-averaged with a resolution of 2 cm^{-1}.

RESULTS AND DISCUSSION

Glass Transition Temperature of Phenolic/PEG Blend

Figure 1 shows the DSC curves of phenolic resin blended with various contents of PEG. The glass transition temperatures were 75 ± 2°C and −62 ± 2°C (ref. 10) for pure phenolic resin and PEG, respectively. After quenching from the melting state, the rescanning results of samples show a single T_g throughout the whole blend range at various compositions of the phenolic blends. This phenomenon suggests that the phenolic resin/PEG blend system is miscible. An obvious melting peak appears when the PEG content is higher than 60 wt %, indicating that crystallinity was formed; this result is consistent with the result of IR spectra in Figure 3. The melting point is gradually shifted to higher temperature with increas-
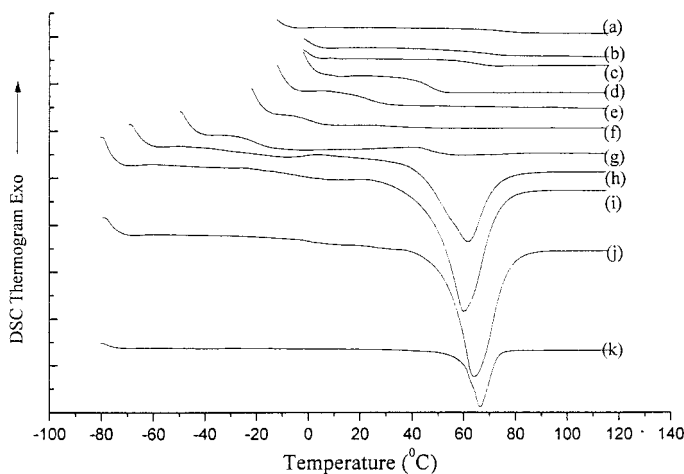
Figure 1 DSC thermogram curves of PEG/novolac-type phenolic resin blends with various compositions (wt %): (a) 5/95; (b) 10/90; (c) 20/80; (d) 30/70; (e) 40/60; (f) 50/50; (g) 60/40; (h) 30/70; (i) 20/80; (j) 10/90; (k) 100/0.

ing PEG content due to the increasing of the equilibrium melting temperature of the resulting blend, implying that the phenolic/PEG blend is miscible in the molten state.

In the phenolic-resin-poor region, hydrogen bonding of the blend may decrease with the PEG content and hydrogen bonding no longer plays a key role in affecting the molecular motion of the phenolic resin/PEG blend. An endothermic peak in the DSC curve can be seen when the PEG content is in excess of 60 wt % PEG in this system. Hydrogen bonding is gradually replaced by random dispersion forces in the phenolic-resin-poor region; the crystalline phase of PEG is exhibited in the DSC curve for this region because phenolic

resin cannot provide enough hydroxyl groups to destroy the crystalline lattice of the PEG.

In general, the glass transition temperature can be used to determine the miscibility and the strength of molecular interaction within polymer blends; furthermore, it reflects the change of entropy upon blending.[13–16] The theoretical treatment of the glass transition temperature was stimulated by several important findings with respect to the structural features of polymers and polymer blends.[16] Figure 2 shows the DSC curves of various phenolic resin/PEG blends obtained from a second scan; the samples were rapidly quenched from the molten phase. A reproducible quantitative thermal method (i.e., T_g and T_m
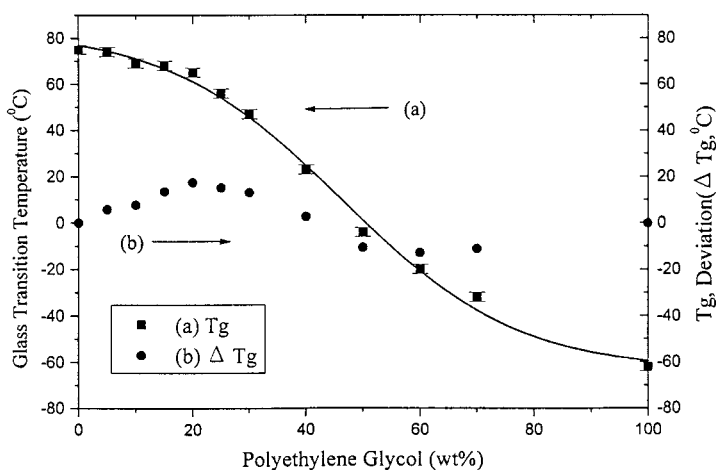

Figure 2 T_g and T_g deviation versus composition of phenolic/PEG blends: (a) T_g; (b) T_g deviation.
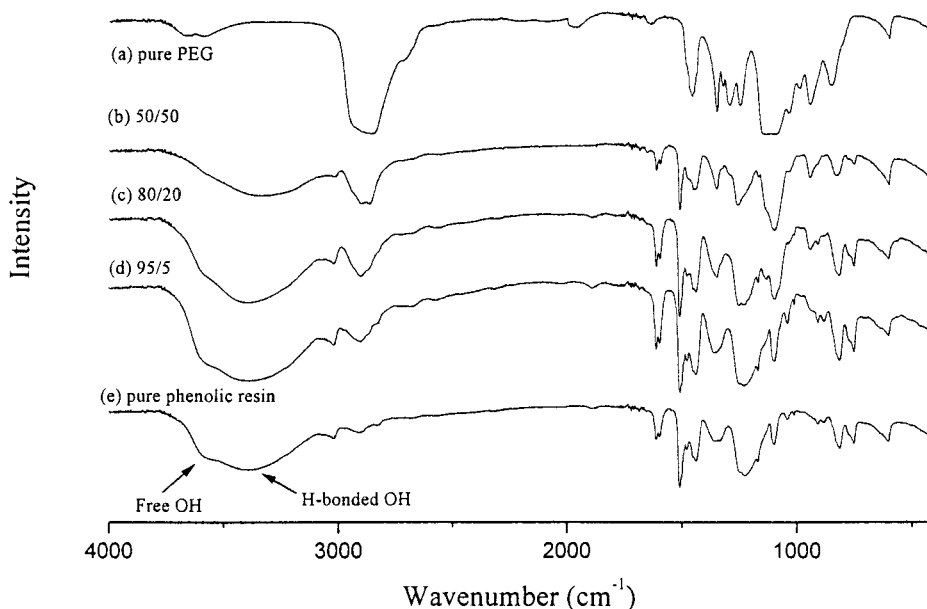
Figure 3 Infrared spectra in $4000-400$ cm^{-1} of various phenolic resin/PEG blends (w/w): (a) pure PEG; (b) 50/50; (c) 80/20; (d) 95/5; (e) pure phenolic resin.

data) was employed to investigate the change of entropy in the phenolic resin/PEG blends.

The variations of T_g and T_g deviation with the composition of the phenolic/PEG blend are summarized in Figure 2 for comparison. The T_g value of pure phenolic resin is 75 ± 2°C and exhibits a higher T_g value due to a higher intramolecular hydrogen-bonding density; the T_g value of PEG is -62 ± 2°C. The appearance of the series blends shows a single T_g, which is a generally accepted criterion of miscibility of a polymer blend. It is apparent that the T_g versus the composition curve does not obey either the Fox[15] or the Gordon–Taylor[16] relationships. The deviation of T_g, ΔT_g, is defined as[15,16]

$$\Delta T_g = T_g - \frac{1}{\dfrac{\omega_a}{T_{ga}} + \dfrac{\omega_b}{T_{gb}}} \qquad (1)$$

where ω_i is the weight fraction of component i, and T_{gi}, the glass transition temperature of the pure component, i. Following the conclusion of Painter et al.,[14] T_g deviation is a result of the change of entropy that corresponds to the change of the number of hydrogen-bonding interactions within the phenolic/PEG blend.

IR Spectra of Phenolic/PEG

IR spectroscopy provides further information regarding the interaction existing in the polymer blends, especially the peak absorption of the hydroxyl group contained in the blends. This can be used to verify the inference of the balance between the self-association of the phenolic resin and the interassociation of the polymer, which was obtained from the T_g composition curve. Figure 3 shows the FTIR spectra of various phenolic resin/PEG blends in the absorption region of $4000-400$ cm^{-1} at room temperature. The presence of the IR transmittance component confirmed, in Figure 3, that hydrogen bonds exist in the polymer blends. All the hydroxyl bands could be further resolved into "free" hydroxyl peaks ranging from 3450 to 3550 cm^{-1} and the associated "hydrogen-bonded hydroxyl" peak ranging from 3300 to 3450 cm^{-1}, which is attributed to a wide distribution of hydrogen-bonded hydroxyl-strength frequencies. In the phenolic resin/PEG blends, it was found that hydrogen bonding in the ether groups of PEG reacted with hydroxyl groups of the phenolic resin. The hydrogen-bonded hydroxyl peak includes intramolecular hydrogen bonding and intermolecular hydrogen bonding. Figure 3 also shows that the hydrogen-bonded hydroxyl increases with the PEG content. The free hydroxyl peak is higher than the hydrogen-bonded hydroxyl peak in the phenolic resin-rich region.

TGA

The TGA curves of the phenolic resin, PEG, and the phenolic resin/PEG (85/15, w/w) obtained by
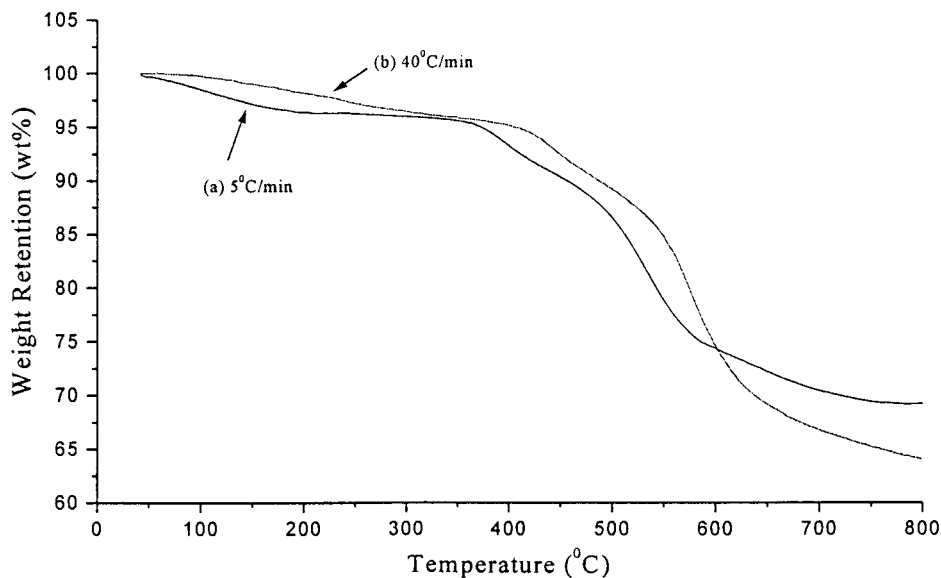
Figure 4 Thermogravimetric curves of novolac-type phenolic resin versus temperature: (a) 5°C/min; (b) 40°C/min.

thermal degradation studies are shown in Figures 4–6. Figure 4 shows that the heating rate is slow enough to investigate the thermal degradation mechanism of novolac-type phenolic resin clearly. The thermal degradation mechanism of phenolic resin includes three steps[17]: The first step is from 300 to 500°C—crosslinking density is increased as reported by Trick and Saliba.[17] The second step is from 400 to 800°C—vibration of the molecule increases with temperature, and, at this step, the crosslinking network will be broken. The third step is from 560 to 800°C—the C—H group

in phenol is broken and formed hydrogen gas. Figure 6 shows that the thermal degradation mechanism of PEG is only one step. The phenolic resin/PEG blend shows a three-step thermal degradation mechanism. In Figure 7, the char yield of the phenolic resin is higher than that of PEG. One can apply the Perkin–Elmer Standard Program to obtain the characteristics of the TGA curves as shown in Figures 4–6. The kinetic parameters are listed in Table I. Meanwhile, the random chain scission of phenolic resin and PEG can be characterized by maximizing the weight
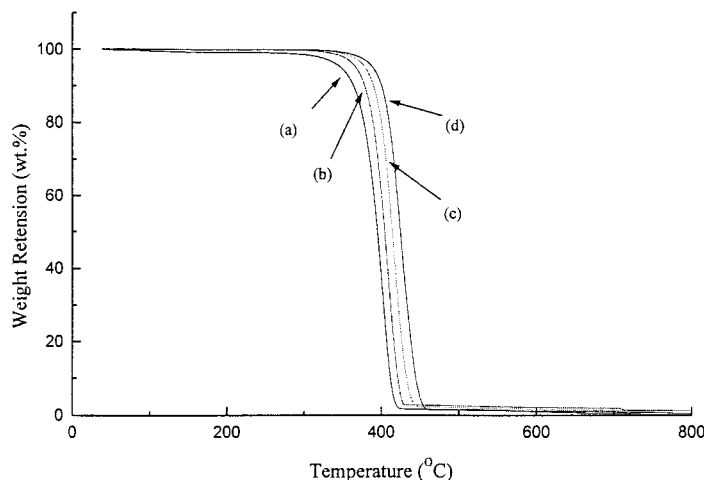

Figure 5 Thermogravimetric curves of PEG versus temperature: (a) 5°C/min; (b) 10°C/min; (c) 20°C/min; (d) 40°C/min.
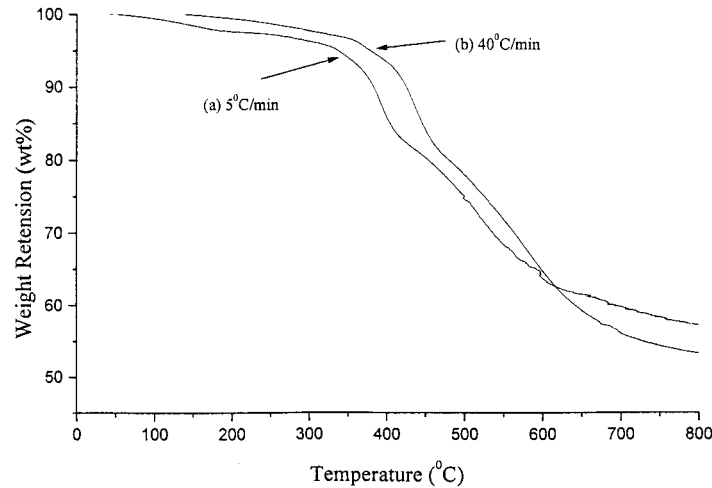
Figure 6 Thermogravimetric curves of phenolic resin/PEG(85/15, w/w) versus temperature: (a) 5°C/min; (b) 40°C/min.

loss rate at a fractional weight loss of PEG blended with phenolic resin.

Ozawa's method is essentially similar to the Flynn and Wall method[18] that represents a relatively simple method for determining activation energies of thermal degradation directly from weight loss versus temperature at several heating rates. This technique assumes that A, $(1 - \alpha)^n$, and E are independent of T, and A and E are independent of α, where α is the conversion of thermal degradation by the weight loss; A, a collision factor; and E, the activation energy.

The degradation kinetic is expressed by

$$dC/dt = Kf(C) \qquad (2)$$

$$f(C) = C_0(1 - \alpha)^n \qquad (3)$$

and

$$K = A \exp(-E/RT) \qquad (4)$$

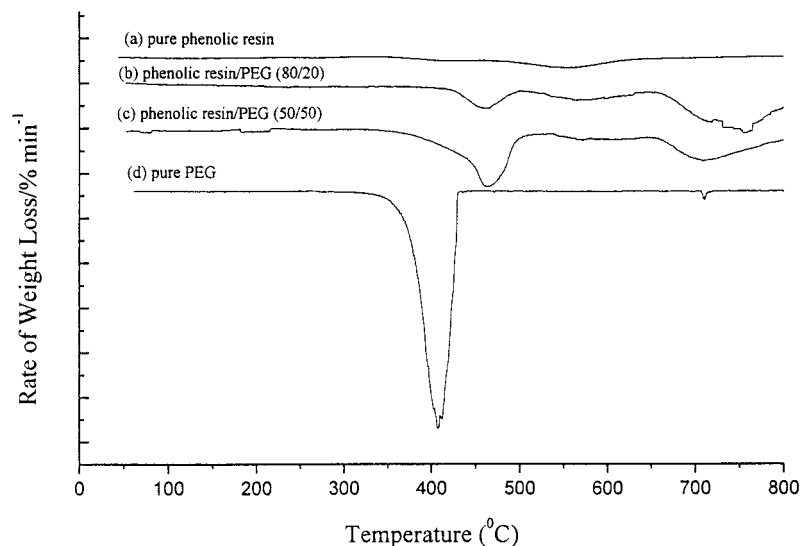Assumptions for the linear heating rate are

Figure 7 DTG curves for phenolic/PEG blends of various compositions at heating rate of 10°C/min: (a) pure phenolic resin; (b) phenolic resin/PEG (80/20, w/w); (c) phenolic resin/PEG (50/50, w/w); (d) pure PEG.

Table I   Kinetic Parameters of PEG Blended with Novolac-Type Phenolic Resin at Different Conversion Levels

Conversion (%)	Phenolic Resin/PEG	Activation Energy E (kJ/mol)	Log(pre-exp. factor) Log A (L/min)
22–34%	100/0	169.8	11.38
	85/15	184.5	12.75
	50/50	215.7	15.94
55–70%	100/0	282.7	17.57
	85/15	280.8	18.01
	50/50	273.95	19.04
22–70%	0/100	265.2	20.5

$$T = \beta t + T_0 \quad (5)$$

$$dT/dt = \beta \quad (6)$$

where β is the heating rate. The rate of thermal degradation can be expressed as follows:

$$dC/dt = dT/dt \times dC/dT = \beta dC/dT \quad (7)$$

Substituting eq. (4) and eq. (7) into eq. (3),

$$\beta dC/dT = f(C)[A \exp(-E/RT)] \quad (8)$$

This differential equation can be solved easily since the C and T variables are separable from the assumed kinetic model. The solution can be rearranged into the following equation:

$$\beta = AE/RF(Cc)P(Xc) \quad (9)$$

where Xc is E/RT_c and where T_c is the temperature at the conversion level C_c:

$$F(C_c) = \int_0^{C_c} \frac{dC}{C} \quad (10)$$

$$P(x) = \int_0^{+\infty} \frac{\exp(-y)}{y^2} \, dy \quad (11)$$

Using Dolye's approximation[19] for the integral which allows for $E/RT > 20$, then $\log[P(X)]$ may be expressed as eq. (12).

Doyle[19] noted that $\log[P(X)]$ is nearly a linear function of x:

$$\text{Log}[P(X)] \approx -0.457X + 2.315 \quad (12)$$

Substituting eq. (9) to eq. (12), the result is

$$\log(\beta) \approx \log[AE/RF(C_c)] + 2.315$$
$$- 0.457E/RT_c \quad (13)$$

Thus, if a series of experiments are run at different heating rates, the apparent activation energy, E, can therefore be obtained from a plot of log β against $1/T_c$ for a fixed degree of conversion. The slope of such a line is given by $-0.457E/R$. In addition, a value of log A can be found from the intercept on the log β axis.

The observations of previous reports clearly indicate the problems and pitfalls in the selection and utilization of an analytical method to solve complex multistage thermal degradations.[12,19] Straight lines are drawn by the least-square method. From these lines, the activation energies are determined from Ozawa's method and are listed in Table I. Ozawa's method was adopted to solve complex multistage thermal degradations such as occur in the decomposition of phenolic resin and PEG.

Table I summarizes the kinetics parameters of thermal degradation at different conversions in PEG and phenolic resin. Log(pre-exp. factor) is Log A, and A is a collision factor. One can find that the activation energy of thermal degradation and Log(pre-exp. factor) of phenolic resin and PEG are not constant. The multiple-heating-rate method was utilized to calculate all kinetic parameters for the blend systems. For a phenolic resin system at low conversion (i.e., 22, 26, 30, 34%), the activation energy and Log(pre-exp. factor) are 169.8 kJ/mol and 11.38 L/min. However, at high conversion (i.e., 55, 60, 65, 70%), the activation energy and Log(pre-exp. factor) are 282.7 kJ/mol and 17.57 L/min. From Table I, we find that the activation energy and Log(pre-exp. factor) increased with increase of the conversion (α). When the conversion is over 55%, the benzyl ring started to degrade. The benzyl ring is a stable, resonant structure, which has good thermal stability; consequently, the activation energy is increased with increasing conversion (α). The content of free radicals caused by broken benzyl rings at high temperature is more than that caused by a broken crosslink network at low temperature. Therefore, the Log(pre-exp. factor) is increased with increasing conversion (α). The molecular structure of PEG has the same repeat unit; hence,

the activation energy is similar. Comparison results of the experimental data are summarized in Table I; one can see that the thermal degradation of phenolic resin, PEG, and the blends are affected by the chemical structure and the composition of the blend.

Experimental data from TGA and the Ozawa's method show that PEG has a low char yield, while phenolic resin has a high char yield after thermal degradation. The activation energies obtained from TGA can explain the thermal stability of this polymer. From Ozawa's technique,[12] apparent activation energies of thermal degradation were calculated: that of PEG is 266.4 $\pm$ 4.3 kJ/mol and that of phenolic resin is 282.7 $\pm$ 15.7 kJ/mol for one decomposition stage and 269.5 $\pm$ 2.6 (PEG) and 169.8 $\pm$ 10.0 (phenolic resin) for the prestage at low conversion. The activation energy of thermal degradation of PEG is almost constant since the chemical structure of PEG is a linear aliphatic component. The activation energy of thermal degradation of phenolic resin is not constant, since the chemical structure of pure phenolic resin is a network containing aliphatic and aromatic components. The activation energy of thermal degradation is proportional to the collision factor. The activation energy of thermal degradation of PEG is higher than that of phenolic resin in the prestage (low conversion). However, the activation energy of the thermal degradation of phenolic resin is higher than that of PEG at the main decomposition stage (high conversion).

The temperature interval of every degradation step (the difference in temperatures at the beginning and at the end) can be obtained from the derivative TGA curves (Fig. 7). The maximum of the weight-loss flow rate and temperature at multiple heating rates of phenolic resin/PEG blends are summarized in Table II. In the complex process of thermal degradation of phenolic resin/PEG blends, the first step is the most rapid one (Fig. 7). The results are in good agreement with those from Ozawa's method and from the thermal degradation process of phenolic resin/PEG blends.

CONCLUSIONS

The thermal degradation of phenolic resin/PEG blends was investigated in the range from room temperature to 800°C and a multiple degradation step was found. The weight loss of mass in the degradation processes depends on the compositions and the chemical structure of polymer. The

Table II Maximum of Weight-Loss Flow Rate and Temperature at Multiple Heating Rates of Phenolic Resin/PEG Blends

Phenolic Resin/PEG	β (°C/min)	Maximum of Loss Flow Rate (%/min)	T_{max} (°C)
100/0	40	0.157	507.2
	20	0.13	504.8
	10	0.107	489.2
	5	0.121	463.95
95/5	40	0.211	503.94
	20	0.1565	493.22
	10	0.1645	476.79
	5	0.155	454.52
90/10	40	0.1865	500.68
	20	0.172	493.22
	10	0.169	476.79
	5	0.177	454.52
85/10	40	0.165	497.42
	20	0.175	493.25
	10	0.165	476.75
	5	0.151	454.57
0/100	40	2.824	442.03
	20	2.45	427.63
	10	2.311	406.53
	5	2.28	401.13

most rapid part of the degradation process is the first step.

The random chain scission of phenolic resin and PEG can be characterized by maximizing the weight loss rate at a fractional weight loss of 2.82%/min (PEG) and 0.157%/min (phenolic resin). From Ozawa's technique, the apparent activation energies can be obtained, which are 266.4 $\pm$ 4.3 kJ/mol for PEG and 282.7 $\pm$ 15.7 for phenolic resin for one decomposition stage and 269.5 $\pm$ 2.6 (PEG) and 169.8 $\pm$ 10.0 (phenolic resin) for the prestage at low conversion. These kinetic parameters depend on the composition of the blend.

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