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Thermal degradation of polyethylene oxide blended with novolac type phenolic resin

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The miscibility and thermal degradation of poly(ethylene oxide) (PEO) toughened novolac type phenolic resin were investigated. Differential scanning calorimetry (DSC) results confirmed that phenolic resin/PEO blend was blended completely. Infrared spectra show that hydrogen bonding existed in the blends. Thermal degradation of poly(ethylene oxide) blended with novolac type phenolic resin has been 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/PEO blends takes place in multiple steps. Chemical structure and components of blends affected thermal degradation, which coincided with the data from thermal degradation of novolac type phenolic resin/PEO blends by thermogravimetric analysis (TGA). *© 2001 Kluwer Academic Publishers*

1. Introduction

Polymer blends have received much attention for the past decades. The preparation of a polymer blend generally requires a processing technique in which the polymers are subjected to high temperature. It is important to understand 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 Arrhenius 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 nitrogen atmosphere, sample mass, sample shape, flow rate, heating rate, etc., but also on the mathematical treatment used to evaluate the data. The dynamic thermogravimetric analysis curve and its derivative 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 on the toughness of phenolic resin is an important task for further application. Phenolic resin contains a high density 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 phenolic resin and modifier. One method of modifying phenolic resin is to blend it with poly(ethylene oxide), as described in our previous papers [10]. Recently, several researchers have studied the miscibility, mobility and thermodynamical properties in the novolac type phenolic resin blend. It is interesting to investigate the thermal stability of PEO blends with novolac type phenolic resin: their thermal decomposition has been investigated by thermogravimetric analysis to obtain the different parameters involved in this blend system.

2. Experimental

2.1. Materials

Poly(ethylene oxide) (PEO) was purchased from Aldrich Chemical Company Inc., U.S.A. The molecular weight of poly(ethylene oxide) is 20,000; repeated unit is -$(CH_2CH_2O)_n$-. Novolac type phenolic resin was synthesized in this laboratory.

2.2. Sample preparation

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

2.3. Differential scanning calorimeter (DSC)

Glass transition temperatures (T_g) of the polymer blends were measured by differential scanning calorimeter

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(Du Pont, DSC Model 2900). The heating rate was 20 °C/min. within a temperature range of 0–280 °C. The measurements were made with 3∼4 mg of sample on a DSC plate after the specimens were quickly cooled to room temperature following the first scan. This procedure was adopted to ensure entire mixing of the polymer blends and to remove the residual solvent and water in the specimen completely. T_g values were determined at the midpoint of the transition point of the heat capacity (C_p) changed, and the reproducibility of T_g values was estimated to be within ±2 °C.

2.4. Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) was performed with a Dupont 951 instrument coupled to a 1050 Thermal Analyzer. Polymer samples (10 ± 3 mg) were stacked on the top of each other in an open platinum sample pan and the experiment was conducted in nitrogen gas with various heating rates (i.e. 5, 10, 20, 40°C/min). Although throughout this study, the machine selected heating rates were reported and used in the calculations, the actual heating rates were determined from the appropriate plots.

Prior to multiple heating rate kinetic 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 PEO. On the multiple heating rate kinetic experiments, the sample was placed into the TGA pan until the sample reached thermal degradation in nitrogen atmosphere.

2.5. Fourier transfrom infrared spectroscopy (FTIR)

Infrared spectra were measured 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 hours to remove residual solvent and to ensure the polymer blend was mixed completely. A minimum scan of 16 scans was signal averaged with a resolution of 2 cm^{-1}.

3. Results and discussion

3.1. Glass transition temperature of phenolic/poly(ethylene oxide) blend

Fig. 1 shows the DSC curves of phenolic resin blended with various contents of poly(ethylene oxide)(PEO). The glass transition temperatures were 75 ± 2, -67 ± 2°C for pure phenolic resin and PEO, respectively. After quenching from the molten state, the rescanning results of samples show a single T_g throughout the whole blend range at various compositions of phenolic blends. This phenomenon suggests that the phenolic resin/PEO blend system is miscible. An obvious molten peak appears when the PEO content is higher than 60 wt% that indicating a crystalline phase was formed, this result is consistent with the result of IR spectra in Fig. 3. The melting point is gradually shifted to higher temperature with increasing PEO content due to the increasing of the equilibrium melting temperature of the resulting blend, implying the phenolic/PEO blend is miscible in the molten state.

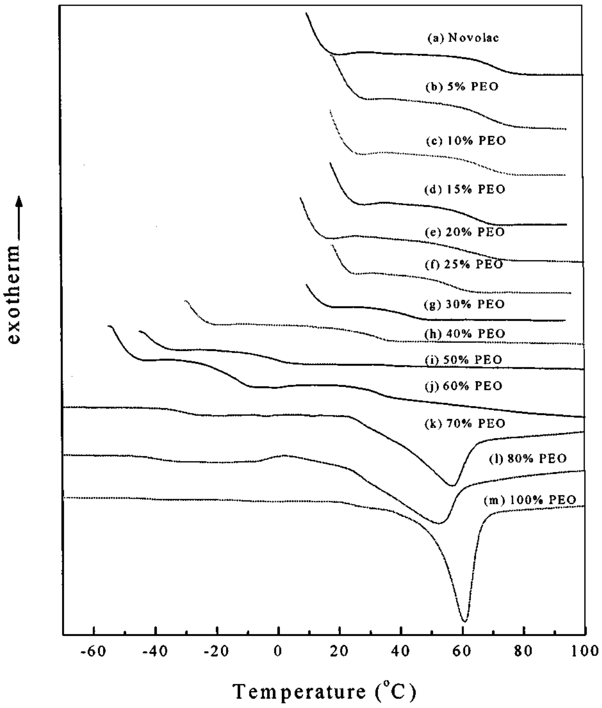

Figure 1 DSC thermogram curves of PEO/novolac type phenolic rein blends with various compositions (wt%): (a) 0/100, (b) 5/95, (c) 10/90, (d) 15/85, (e) 20/80, (f) 25/75, (g) 30/70, (h) 40/60, (i) 50/50, (j) 60/40, (k) 70/30, (l) 80/20, (m) 100/0.

In the phenolic resin-deficient region, the hydrogen bonding of the blend may decrease with PEO content and the hydrogen bonding no longer plays a key role in affecting the molecular motion of phenolic resin/PEO blend. An endothermic peak in the DSC curve can be seen when the PEO content exceeds 60 wt% PEO in this system. The hydrogen bonding is gradually replaced by random dispersion forces in the phenolic resin deficient region. The crystalline phase of PEO is exhibited in the DSC curve for the phenolic resin deficient region because phenolic resin cannot provide enough hydroxyl groups to destroy the crystalline lattice of the PEO.

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 [11–14]. The theoretical treatments of the glass transition temperature had been stimulated by several important findings with respect to the structural features polymer and polymer blend [14]. Fig. 2 shows the DSC results of various phenolic resin/PEO blends obtained from second scans, the samples were rapidly quenched from molten phase. A reproducible quantitative thermal method (i.e. T_g and T_m data) was employed to investigate the change of entropy in phenolic resin/PEO blends.

The variation of T_g and T_g deviation with composition of phenolic/PEO blend are summarized in Fig. 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 PEO is -67 ± 2°C. The appearance of the series of polymer blends shows a single T_g, which is a generally accepted criterion of miscibility. It is apparent that the T_g versus composition curve does not obey either the

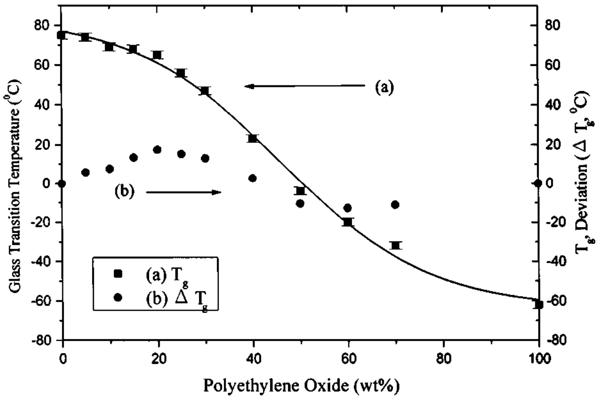

Figure 2 T_g and T_g deviation versus composition of Phenolic/PEO blends. (a) T_g (b) T_g deviation.

Fox [13] nor the Gordon-Taylor [14] relationships. The deviation of T_g, ΔT_g, is defined as [13, 14].

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

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

3.2. IR spectra of phenolic/PDMSA

IR measurements provide further information regarding the interaction existing among the polymer blends, in the stretch absorption spectrum of the hydroxyl group of various phenolic blends. This can be used to infer the balance between self association of the phenolic and the inter-association of the polymer, which was obtained from the T_g versus composition curve. Fig. 3 shows the FTIR spectra of various phenolic resin/PEO blends in the absorption region of 3800–3100 cm^{-1} at room temperature. The presence of the IR transmittance component supports the idea of hydrogen bonds presented in the polymer blends. All of 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.

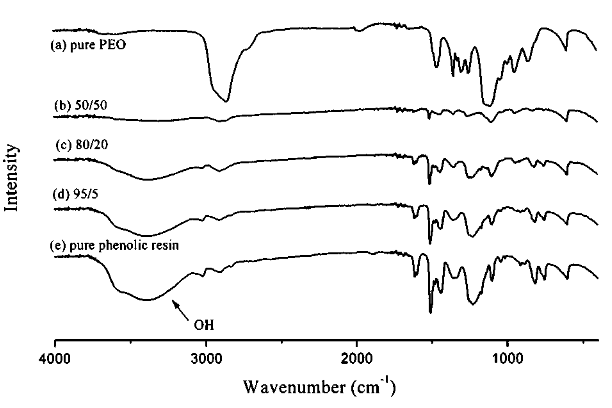

Figure 3 Infrared spectra in 4000–400 cm^{-1} of various phenolic resin/PEO blends (w/w). (a) pure PEO, (b) 50/50, (c) 80/20, (d) 95/5, (e) pure phenolic resin.

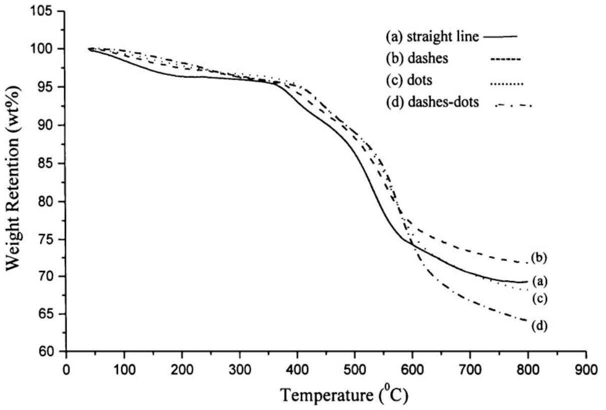

Figure 4 The thermogravimetric curves of novolac type phenolic resin versus temperature. (a) 5°C/min (straight line); (b) 10°C/min (dashes); (c) 20°C/min (dots); (d) 40°C/min (dashes-dots).

3.3. Thermogravimeteric analysis

The thermogravimetric analysis curves of phenolic resin, PEO, phenolic resin/PEO (85/15,w/w) obtained by thermal degradation study are shown in the Figs 4 to 6. Fig. 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 [15]: the first step is from 300 to 500°C, crosslinking density is increased as reported by Kimberly *et al.* [15]; the second step is from 400 to 800°C, the vibration of molecule increases with temperature, at this step the crosslink network will be broken; the third step is from 560 to 800°C, the C-H group in phenol is broken and hydrogen gas is formed. Fig. 5 shows that the thermal degradation mechanism of PEO is only one step, whereas phenolic resin/PEO blend shows a three step thermal degradation mechanism, as can be seen in Figs 4 to 6. The char yield of phenolic resin is higher than that of PEO.

The temperature interval of every degradation step (the difference in temperatures at the beginning and at the end) is evidence from the derivative TGA curves

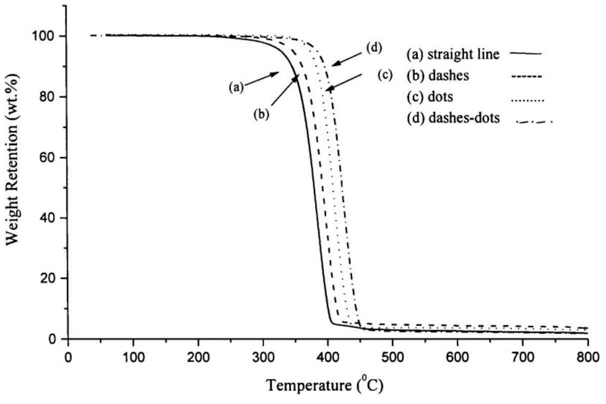

Figure 5 The thermogravimetric curves of PEO against temperature. (a) 5°C/min (straight line); (b) 10°C/min (dashes); (c) 20°C/min (dots); (d) 40°C/min (dashes-dots).

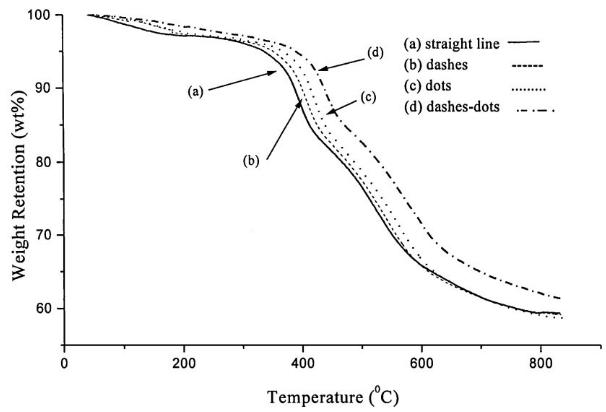

Figure 6 The thermogravimetric curves of phenolic resin/PEO (85/15, w/w) against temperature. (a) 5°C/min (straight line); (b) 10°C/min (dashes); (c) 20°C/min (dots); (d) 40°C/min (dashes-dots).

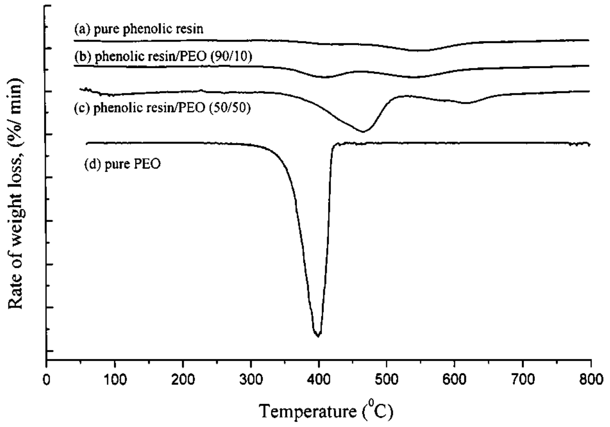

Figure 7 DTG curves for phenolic/PEO blends of different compositions at heating rate 10°C/min (a) Pure phenolic resin; (b) phenolic resin/PEO (10/90, w/w) (c) phenolic resin/PEO (50/50, w/w) (d) pure PEO.

(Fig. 7). The maximum of weight loss flow rate and temperature at multiple heating rate of phenolic resin/PEO blends are summarized in Table I. Meanwhile, the random chain scission of phenolic resin and PEO can be characterized by maximizing the weight loss rate at a fractional weight loss of 1.78 g/min (PEO), 0.48 g/min (phenolic resin). In the complex process of thermal degradation of phenolic resin/PEO blends, the first step is the most rapid one (Fig. 7). The results are in good agreement with those from the thermal degradation process of phenolic resin/PEO blends.

Experimental data from thermogravimetric analysis (TGA) show that the PEO has a low char yield, while, phenolic resin has a high char yield after thermal degradation. The chemical structure of PEO is a linear aliphatic component and the chemical structure of phenolic resin is a network consisting of aliphatic and aromatic components. The phenolic resin/PEO blend is a semi-interpenetrating structure. The benzyl ring is stable and the resonance structure has good thermal stability. The free radical content caused by broken benzyl rings at high temperature is more than that caused by a broken crosslink network at low temperature. Comparison of results of the experimental data, shows that the thermal degradation of phenolic resin and PEO are not the same, which is not only affected by chemical structure, but also by the composition of the blend.

TABLE I The maximum of weight flow rate and temperature at multiple heating rate of phenolic resin/PEO blends

Phenolic resin/ PEO (wt%)	β (°C/min)	The maximum of weight 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	0.1215	463.95
95/5	40	0.203	508.55
	20	0.1635	485.6
	10	0.1465	476
	5	0.1525	462.15
90/10	40	0.1685	505.7
	20	0.172	484.4
	10	0.165	474.75
	5	0.177	456.95
85/10	40	0.1545	404.8
	20	0.1765	484.35
	10	0.1765	473.6
	5	0.151	456.05
0/100	40	2.731	425.5
	20	2.343	411.1
	10	2.2	390.0
	5	2.171	384.6

4. Conclusions

A single T_g throughout the whole blend range at various compositions of phenolic blends suggests that the phenolic resin/PEO blend system is miscible. In the phenolic resin deficient region, the hydrogen bonding of the blend may decrease with PEO content and the hydrogen bonding no longer plays a key role in affecting the molecular motion of the phenolic resin/PEO blend. An endothermic peak in the DSC curve can be seen when PEO content exceeds 60 wt% PEO in this system. The hydrogen bonding is gradually replaced by random dispersion forces in the phenolic resin deficient region.

The thermal degradation of phenolic resin/PEO blends was investigated in the range from room temperature to 800°C, a multiple step process was found. The weight loss in the degradation process depends on the composition and the chemical structure of polymer. The most rapid part of the degradation process is the first step. The random chain scission of phenolic resin and PEO can be characterized by maximizing the weight loss rate at a fractional weight loss of 1.78 g/min (PEO), 0.48 g/min (phenolic resin).

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