

Thermomechanical Properties and Morphology of Polyethylene Oxide and Phenolic Resole Blends

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ABSTRACT: Blends of poly(ethylene oxide) (PEO) and resole type phenolic resin were prepared by a solution cast method using water as a solvent. The cured blends were made by heat curing without using any catalyst. The blends were characterized by dynamic mechanical analysis (DMA), which indicated that PEO forms compatible blend with the resole. The glass transition values, read from the DMA traces, showed a positive shift as compared to the theoretical values calculated by the Fox equation. This suggests a strong H-bonding interaction between the phenolic resole and PEO as established by Fourier transformed infrared spectroscopy. Flexural test indicated an enhanced flexibility of the blends when compared to the neat phenolic resin. The fracture surface analysis by using a scanning electron microscope (SEM) revealed an increase in plastic deformation with increasing PEO concentration in the blend. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Phenolic resin or phenol formaldehyde (PF) resin is considered as the first polymer material produced commercially from a low molecular weight compound.^{1,2} Phenolic resins are available in two varieties: (i) novolac which is thermoplastic type and can be used as it is or can be cured with hexamethylene tetramine to get a crosslinked structure, and (ii) resole, which is a multi-functional reactive compound that can be cured thermally without any catalyst or with an acidic catalyst.

Poly(ethylene oxide) (PEO) is a crystalline thermoplastic polymer with the general structure $H(-O-CH_2-CH_2)_n-OH$, where n is the number of repeat units. PEO finds a wide range of applications such as tougheners/flexibilizers for thermosets,^{3,4} solid polymer electrolyte,^{5,6} and crystallizable component in shape memory polymer systems.^{7,8} The polyether chain of PEO provides a flexibilizing effect when blended or chemically attached to a rigid polymer chain.^{9,10}

PEO/phenolic and PEO-polycaprolactone block copolymer/phenolic blends have been investigated.^{11,12} Recently, Ratna et al.^{13,14} studied PEO/novolac blends and proposed for their potential applications in shape memory polymer systems having adjustable switching temperature. They have reported that

incorporation of novolac in PEO tend to enhance the mechanical strength up to 10 wt % of novolac. The use of such blend will offer not only the possibility to reduce the switching temperature but also to adjust the switching temperature as a function of blend composition. In the aforementioned studies, particular attention has been given to the blends in which PEO is the main component. This is because a sufficient amount of PEO (crystalline part) is necessary to carry out the switching function. The aim of the present work is to study the effect of incorporation of PEO on the properties of phenolic resins keeping phenolic resin as a major component. Interestingly, there is little investigation on the blends of PEO and resole. This is probably due to the difficulty to avoid macro-phase separation when a thermoset resin cures in presence of a second polymer. This has prompted us to study the blends of resole and PEO. The thermal properties and morphology of the related blends along with spectroscopic characterization will be presented in this article.

EXPERIMENTAL

Materials

The PEO with weight average molecular weight of 20,000 g/mol was purchased from Aldrich. Resole was supplied by Dynea

(Berlin, Germany) as aqueous solution with a solid content of 70 wt %.

Preparation of Blends

A required amount of aqueous solution of resole was put in a reaction flask fitted with a stirrer and condenser. PEO was added into it and stirred at 70°C until a homogeneous solution is formed. The amount of PEO was varied to adjust the blend compositions (15, 30, and 45 wt % of PEO). The solution containing the required amount of resole and PEO was cast in an aluminum mold. The water was removed by keeping the mold at 80°C in an air-forced ventilation oven for 8 h. The samples were further cured at 100°C for over night.

Characterization of Blends

Spectroscopic Analysis. Fourier transform infrared (FTIR) spectra of thin films (0.2 mm), prepared by compression molding were taken by a Nicolet 510 FTIR spectrometer, Germany, from 2500 to 4000 cm^{-1} with a nominal resolution of 2 cm^{-1} . For each spectrum 64 runs were collected and averaged.

Dynamic Mechanical Analysis. Dynamic mechanical analysis (DMA) of the blend samples were carried out using a DMA Q800 instrument (TA Instruments, New Castle, DE). The specimens were cut from the compression-molded sheets with dimensions of $\sim 20 \times 8 \times 1 \text{ mm}^3$ (length \times width \times thickness). The PEO and resole/PEO (55/45 w/w) test specimens were cooled to -120°C with liquid nitrogen, allowed to stabilize and then heated at a rate of 3°C min^{-1} to room temperature. Other samples were analyzed from 30 to 180°C . All the samples were tested in tensile mode and the frequency of oscillation was fixed at 1 Hz. The storage and loss moduli and the mechanical loss factor ($\tan \delta$ representing the ratio of dynamic loss modulus to storage modulus) were measured during the test and plotted against temperature.

Flexural Test. The flexural properties were measured with rectangular samples according to ASTM D-790, using a Zwick 1445 (Ulm, Germany) universal testing machine at crosshead speed of 2 mm min^{-1} . The sample size was $120 \times 25 \times 2.5 \text{ mm}^3$ (length \times width \times thickness). The fracture strength (F.S.) was determined from the following formula:

$$F.S. = \frac{3 L_p \cdot x \cdot 9.8}{2 \cdot w \cdot t^2} \quad (1)$$

where L is the peak load, x is span, w is the width, and t is the thickness of the sample. The results represent the average of three parallel tests. The flexural deformation was determined by a linear variable differential transducer system.

Scanning Electron Microscopy

The morphology of resole/PEO blends was also investigated using a high resolution Zeiss Supra 40 VP SEM (Carl Zeiss SMT, Oberkochen, Germany). Compression-molded samples were quenched in liquid nitrogen and cryogenically fractured. The fracture surfaces were sputter coated with carbon prior to the scanning electron microscope (SEM) observation to avoid charging.

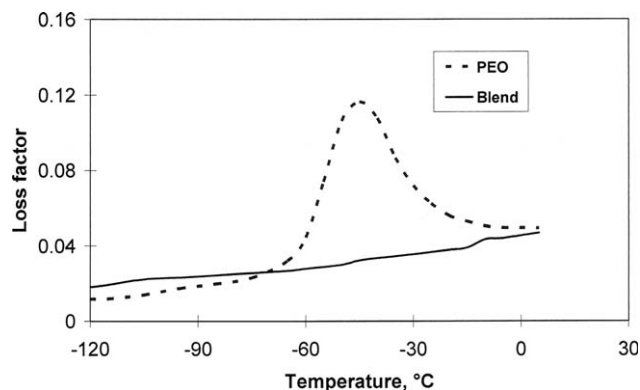


Figure 1. Low temperature transition of PEO and resole/PEO blend (45 wt %).

RESULTS AND DISCUSSION

To examine the compatibility of resole/PEO blends, pure PEO and resole/PEO blend (55/45) were characterized by DMA from -120°C to 0°C . The loss factor versus temperature plots are shown in Figure 1. As temperature was increased, it was observed that the $\tan \delta$ for the pure PEO sample went through a maximum in the transition region (temperature at about -45°C) and then decreased in the rubbery region. The damping is low below the glass transition temperature (T_g) as the chain segments in that region are frozen. Below T_g , the deformations are thus primarily elastic and the molecular slips resulting in viscous flow is low. Also above T_g , in the rubbery region, the damping is low because the molecular segments are free to move, and consequently there is little resistance to oscillation loading. In the transition region, on the other hand, the damping is high because of the initiation of micro-Brownian motion of the molecular chain segments and their stress relaxation. However, all the segments will not be able to take part in such relaxation together. A frozen-in segment can store much more energy for a given deformation than a free to move rubbery segment. Thus, every time a stressed frozen-in segment becomes free to move, its excess energy is dissipated. Micro-Brownian motion is concerned with the cooperative diffusional motion of the main chain segments. The maximum damping occurs in a region where most of the chain segments take part in this co-operative motion under oscillating stress. The blend sample does not show any peak in this region. The absence of glass transition peak (relaxation peak) corresponding to PEO in the blend indicates that PEO is miscible with resole.

Since, no peak was observed for resole/PEO blend with highest concentration of PEO (45 wt %), the DMA studies of all the blends were carried out from 25 to 180°C in order to study the effect of incorporation of PEO on the viscoelastic properties of resole/PEO blends. The $\tan \delta$ versus temperature and dynamic modulus (E') versus temperature plots of cured resole and the blends are shown in Figures 2 and 3, respectively. The DMA results are summarized in Table I. The blends display a single T_g , which lie in between the T_g of resole (158°C) and the T_g of PEO (-45°C). The theoretical

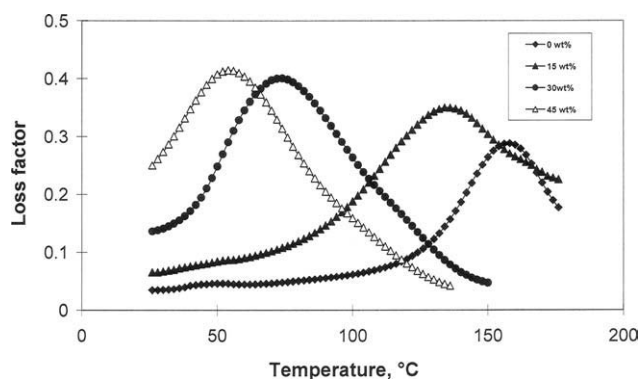


Figure 2. Loss factor versus temperature plots of resole/PEO blends with varying concentration of PEO.

T_g value for the blend was calculated by using Fox equation as given below¹⁵:

$$\frac{1}{T_g} = \frac{(1 - C)}{T_{g1}} + \frac{C}{T_{g2}} \quad (2)$$

where T_g is the glass transition temperature of the blend, T_{g1} = glass transition temperature of the phenolic resin, T_{g2} = glass transition temperature of PEO and C is the weight fraction of PEO. The T_g value of the blend shows a positive deviation with respect to the value calculated by the Fox equation (Table I). Positive deviation with respect to the theoretical value is generally explained by considering special interaction between the components. In this case it can be attributed to the inter-association H-bonding discussed below. This interaction helps to prevent phase segregation after curing. Generally, in a system comprising a thermoplastic and a thermoset material, phase separation (either micro or macro) takes place due to the decrease in combinatorial entropy of mixing, which makes free energy of mixing positive before gelation. However, in the present case due to strong H-bonding interactions, enthalpy of mixing is always negative. Hence, even after a significant decrease in combinatorial entropy of mixing, the free energy of mixing remains negative. As a result phase separation does not take place.

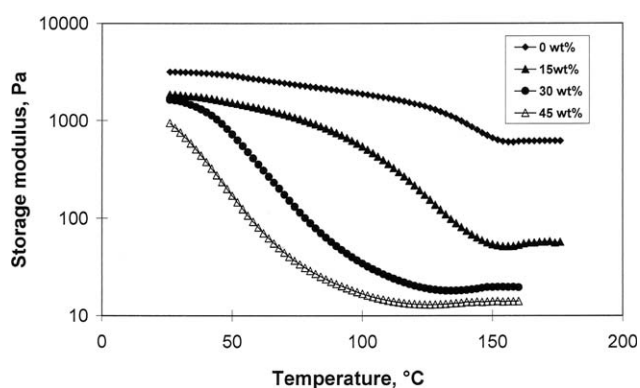


Figure 3. Storage modulus versus temperature plots of resole/PEO blends with varying concentration of PEO.

Table I. Dynamic Mechanical Analysis of PF Resole/PEO Blends

Blend composition resole/PEO (wt %)	Dynamic storage modulus (MPa)	T_g (°C)	$\tan \delta_{max}$
0	3134	158	0.28
15	1824	136 (107)	0.35
30	1572	74 (68)	0.40
45	751	55 (35)	0.41

The DMA T_g values shown are the measured values for the virgin resole and resole/PEO blends with varying concentration of PEO. The values shown in the bracket are calculated values for the blends using Fox equation.

The FTIR spectra of resole and resole/PEO (55/45 w/w) blend are presented in Figure 4. Resole shows a broad band consisting of two peaks at 3350 and 3500 cm^{-1} , which are assigned to the self-associated hydroxyl groups and nonassociated free hydroxyl groups, respectively.¹⁶ In the blend, the band corresponding to the nonassociated —OH groups remains unchanged; however, the same corresponding to self-associated —OH group shifted to 3300 cm^{-1} . This clearly indicates that there are polar interactions between the —OH groups of PEO with ether chain of PEO via H-bonding.^{17,18} Further support for this interaction in the blends has been provided by mechanical tests as discussed next.

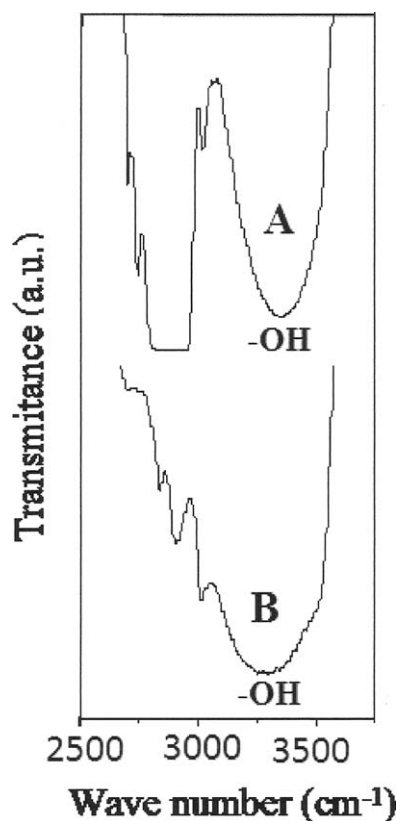


Figure 4. FTIR spectra of (A) resole, (B) resole/PEO blend (45 wt %).

Table II. Flexural Properties of PF Resole/PEO Blends

Blend composition resole/PEO (w/w)	Flexural strength (MPa)	Flexural modulus (MPa)	Flexural strain (%)
100/0	97 ± 4	4097 ± 25	1.9 ± 0.2
85/15	72.1 ± 3.5	3122 ± 30	2.4 ± 0.1
70/30	38.3 ± 3.5	1238 ± 20	3.9 ± 0.3
55/45	11.3 ± 1.5	185 ± 10	10.4 ± 0.5

Table II compares the flexural properties of resole and resole/PEO blends. The results show a typical flexibilization behavior, i.e., the flexural strength decreased and the flexural strain increased with increasing PEO concentration. A macrophotograph of flexural strained specimen of a resole/PEO blend (55/45 wt %) sample is shown in Figure 5. This figure clearly demonstrates a much higher flexibility of the blend compared to pure resole, which is otherwise brittle. Similar results were reported¹⁹ for the blend of unsaturated polyester resin and PEO. The enhancement in flexibility can be attributed to the increase in plastic deformation during break as confirmed by SEM analysis shown below.

The SEM pictures from the fracture surfaces of resole and the blends are shown in Figure 6. SEM photographs of the blends indicate single phase morphology, which supports the DMA results, i.e., appearance of a single T_g . It can be clearly seen that the fracture surface of the pure resole is smooth and shows the typical river-like pattern. This indicates brittle failure with lack of plastic deformation for pure resole network. On the other hand the fracture surfaces of the blends are rough indicating pronounced plastic deformation.²⁰ This plastic deformation is responsible for significant improvement in flexibility of resole/PEO blends when compared to the pure crosslinked resole network as evident from the flexural properties which was discussed earlier.

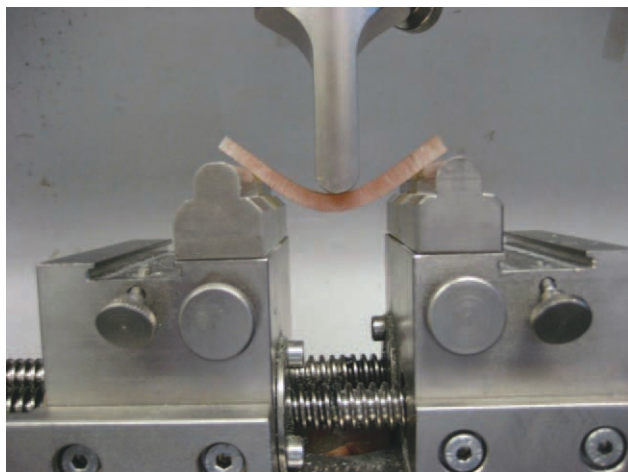


Figure 5. A picture of PEO/resole blend (45 wt %) during flexural test showing high flexural deformation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

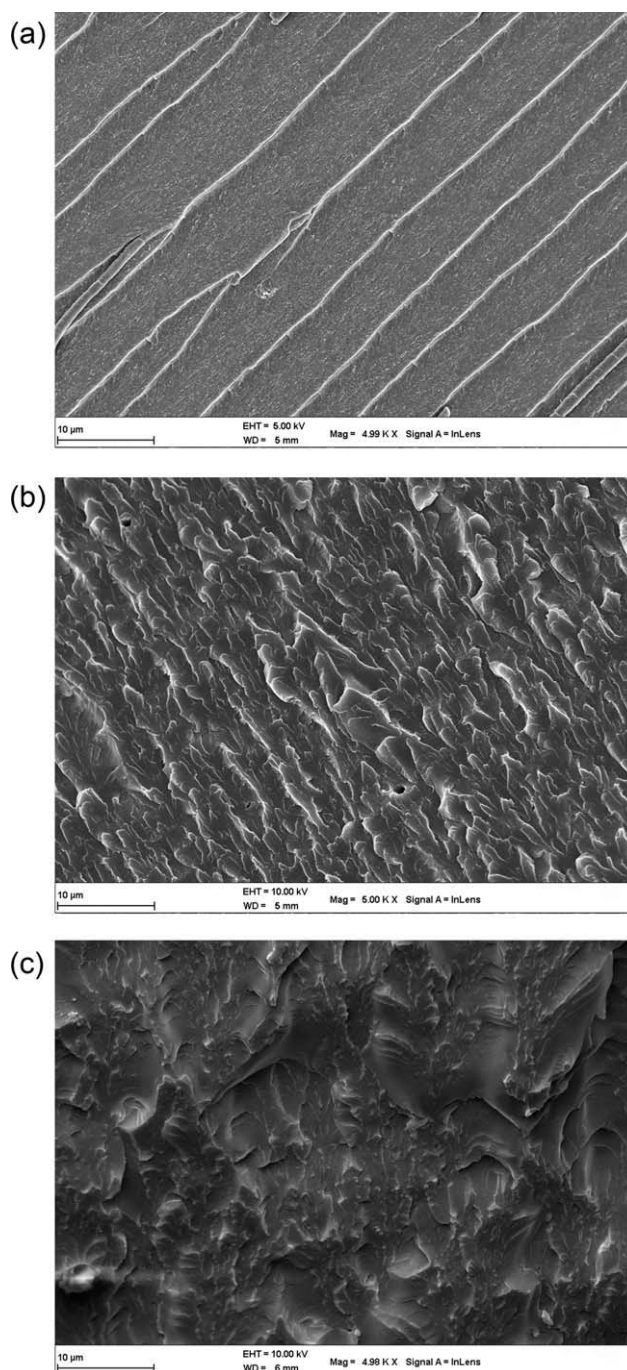


Figure 6. (a) SEM microphotographs of the fracture surfaces of cured resole sample. (b) SEM microphotographs of the fracture surfaces of cured resole/PEO (15 wt %) blend. (c) SEM microphotographs of the fracture surfaces of cured resole/PEO (45 wt %) blend.

CONCLUSION

PEO/PF resole blends were prepared by solution cast technique and their dynamic mechanical, flexural properties, and morphology were investigated. The PEO/resole blends are compatible confirmed by single T_g (DMA) and single-phase morphology (SEM analysis). The flexural strain and toughness of resole can be enhanced significantly by incorporation of PEO

into it. The blends can find use as toughened matrix resin for fiber reinforced composites and for shape memory applications.

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