



Miscibility and Biodegradability Studies of Polystyrene/Linseed Oil Epoxy Blend Derived from a Sustainable Resource

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Received 28 January 2007; accepted 19 August 2007

ABSTRACT

This study highlights the utilization of linseed oil epoxy (LOE) (a product from a sustainable resource), to obtain blends of LOE with polystyrene (PS) forming tough and flexible free-standing films. The blends were prepared by mechanical mixing of the requisite amounts of the two components in the weight ratios of LOE/PS are 85/15, 65/35, 55/45, 45/55, 35/65, and 15/85 through a solution method by mixing in tetrahydrofuran. Free-standing films of the blend were cast. The miscibility of the two components in a solution phase was investigated by reduced as well as relative viscosities and density measurements while the miscibility in a solid phase was examined by scanning electron microscopy (SEM). At all the concentrations, calculated values of reduced viscosity were found to be higher than the observed values of the reduced viscosity for the blends with 15-85 wt% of PS. Viscosity measurements reveal that miscibility occurs between the composition range of LOE/PS 85/15 to 45/55. At composition LOE/PS 35/65, phase inversion takes place which indicates the onset of immiscibility of the two components in the solution phase. The immiscibility of the two compositions at this composition (LOE/PS 35/65) is also shown by the SEM micrographs which exhibits two distinct phases. The mechanical properties of LOE/PS blend films were found to match with LDPE at composition LOE/PS 65/35. The potential applications for such sustainable resource based blend include packaging films and production biodegradable plastic sheets which can be formed into products such as bio-bags.

Key Words:

biodegradable;
blends;
polystyrene;
renewable resource;
blending.

INTRODUCTION

Vegetable oils of non-edible seeds constitute a major resource for several polymeric resins namely alkyd, polyesters, polyurethanes, epoxies and others [1-4]. In addition to their other applications, vegetable oil based products like epoxies and esters are also used as plasticizer and additives to com-

mercial polymers to improve upon their toughness, tensile strength and biodegradability [3]. Linseed oil is a yellowish drying oil derived from the dried ripe seeds of the flax plant (*Linum usitatissimum*, *Linaceae*). It is used in animal feeds; sealants; brake linings; linoleum; foundry products;

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polishes, varnishes and oil paints; animal care products; wood preservation; and synthetic resins. Among other applications, medium-chain-length polymers derived from linseed oil have a relatively small molar mass and contain a high concentration of unsaturated side-chains. As such, these polymers are amorphous and take on the consistency of a viscous liquid at room temperature. In order to increase the application potential of this material, the side-chain olefinic groups are converted to epoxy. Epoxidation helps in increasing the polarity of the oil molecules and helps increase the chance of interaction with commercial polymers in a blend.

The formulation of polymer blends has been an active area of research for the past three decades owing to the enhancement in the physical and mechanical properties of the blends achieved via synergism [5-7]. The physical as well as chemical properties of the blend depend on the degree of miscibility of the blend components. Although even immiscible or partially miscible blends have found commercial applications, the complete miscibility of the components in the blend is desirable because mixing on molecular scale results into superior physical as well as mechanical properties with change in composition [8-10]. Polystyrene is a well-known non-biodegradable commercially polymer, which makes hard rigid and transparent films and sheets. However, its major drawback is its brittleness and non-biodegradability [11].

Several attempts have been made to improve upon its fracture resistance by blending it with elastomers like natural rubber [12], polyurethane (PU) [13], ethylene polypropylene rubber [14], polybutadiene (PB) [15], polyethylene [16], high-density polyethylene [17], poly(acrylic acid) [18], polypropylene [19], ethylene vinyl acetate [20], polycarbonate [21], and poly (amide) [22]. The morphology, miscibility and mechanical properties of these blends are well documented. In these blends however, the problem of immiscibility and phase separation is overwhelmingly encountered that ultimately hampers the synergism in the physicochemical properties of the blend [16]. Alternatively, the improvement in the toughness, flexibility and tensile strength of a polymer of high molar mass can also be achieved by blending it with a substance of low molar mass. Low molar mass products

from vegetable resource like lactose [23] and starch cinnamate [8-9] have also been used to modify the properties of poly(acrylic acid), poly(methyl-methacrylate) and other polymers.

Linseed oil epoxy (LOE) fails to form free-standing films under ambient conditions. Therefore, we have investigated the miscibility of LOE and polystyrene (PS) blends by reduced viscosity, relative viscosity, heat of mixing and density measurements while the morphology of the blends was analyzed by scanning electron microscopy (SEM). The blend of LOE with PS was found to yield free-standing films and sheets even with 80% of LOE in the blend. The synergism attained in the properties of the two components is expected to hold potential for obtaining commercially viable as well as easily processible sustainable resource based blends.

EXPERIMENTAL

Materials

Linseed oil epoxy (LOE) and polystyrene (PS) were purchased from M/s Atul Chemicals Pvt. Ltd. Delhi (India). The oil was dewaxed by keeping it in a refrigerator at 15°C and filtering before use. LOE was prepared after a reported method, which yielded LOE of epoxy equivalent 260 [36]. PS was purified by solvent/non-solvent method. Molar mass of PS was determined by viscosity and was found to be 140,000.

Preparation of LOE/PS Blends

The blends of LOE with PS were prepared by mixing the epoxy and the polymer in LOE/PS weight ratios: 85/15, 65/35, 55/45, 45/55, 35/65, and 15/85 by taking the requisite amounts of the two components to obtain 100 mL of 4 wt% and 6 wt% solutions of the blend in tetrahydrofuran (THF), (Merck, A.R. Grade). All solutions were thoroughly mixed by agitation on a magnetic stirrer for 2 h. Selected samples were kept for over a week. The appearance of turbidity or precipitation was not noticed in any case.

Preparation of LOE/PS Films

Solutions (6 wt%) of selected composition of the blend in THF were cast on transparency sheet and

were allowed to dry under ambient conditions. In 10 days time the free-standing films were obtained. The films were further dried in vacuum oven kept at 60°C for 10 h.

Characterization

Viscosity of the blend solutions was measured at temperatures 20°C, 30°C, and 40°C (accuracy = $\pm 0.05^\circ\text{C}$) in a thermostatic bath using an Ubbelohde suspended level viscometer. Time of fall was repeatedly taken and the value of three concordant readings was taken to be the exact falling time. The densities of the solutions were measured at the above temperatures by a pycnometer with a capacity of 10 mL. The standard deviation obtained was 0.0045. The morphology of a cross-section of the cryogenically fractured blend films were examined by the scanning electron microscope (SEM, Jeol, JSM-840 SEM) at different magnifications. SEM Micrographs were taken after coating the fractured surface with a thin layer (10-20 nm) of gold. Tensile strength studies were performed on Instron digital tensile tester interfaced with a PC. Five samples were tested for each composition. The maximum stress and elongation percentage at that point were taken to be the average of the five tests for each composition. The data showed standard deviation of 1.2 MPa.

RESULTS AND DISCUSSION

Viscosity Measurement

The miscibility studies of LOE and PS in solution phase (THF as solvent) were determined by viscometric, ultrasonic velocity and density measurements. Mamza et al. [25] adopted viscometric methods for the determination of miscibility of PS and polyvinyl alcohol in toluene; THF and MEK. They found that the choice of the solvent did not affect the miscibility. Likewise Kulshreshta et al. [26] also concluded that the miscibility of the two polymers in solution were unaffected by the choice of the solvent used. The variation of relative viscosity against composition of the blends of 4 wt% and 6 wt% at 30°C is shown in Figure 1. The plots are non-linear with sharp inflections at 65 wt% PS in the blend. The nature of variation of the relative viscosity at these compositions indicates

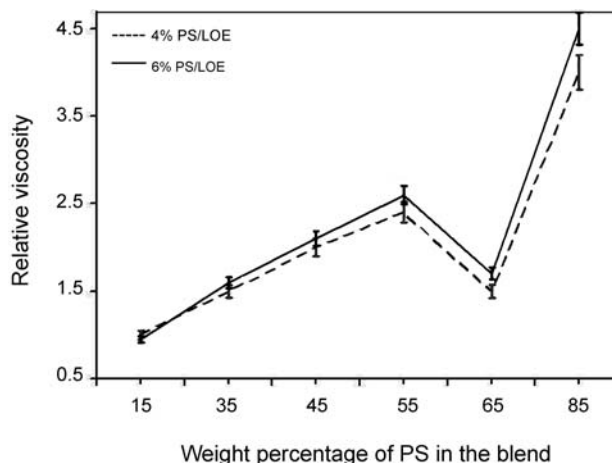


Figure 1. Effect of varying compositions on the relative viscosity of LOE/PS blends.

phase inversion. The overall non-linearity of the plot with phase inversions indicates immiscibility of LOE with PS in solution especially at composition LOE/PS 35/65. Mamza et al. [25] and Kulshreshta et al. [26] have observed that the plot of the relative viscosity of the blend solutions against composition is linear when the components are completely miscible. When the plots are non-linear or S shaped, the components are incompatible with reversal of phase at intermediate composition. The miscibility of LOE with PS was also be examined by comparing the observed and calculated reduced viscosities of blend solutions of different compositions at a given concentration or varying concentrations of the blend solutions of the same composition. Singh et al. [27-29] have reported that the reduced viscosity of blend compositions follows the simple additive rule of mixture when the polymers are miscible. Figure 2 shows the plots of calculated and observed reduced viscosity against varying compositions of blends of concentrations 4 wt% and 6 wt%, respectively. At all concentrations, the calculated values of reduced viscosity were found to be higher than the observed values of the reduced viscosity for the blends with 15-85 wt% of PS. Phase inversion occurred at 65 wt% PS indicating immiscibility of the components at and beyond this composition. Singh et al. [28-29] observed similar deviation of the observed values of reduced viscosity in case of poly(acrylic acid) and poly(vinyl pyrrolidone/polyvinylalcohol). The lower values of the reduced viscosity than the

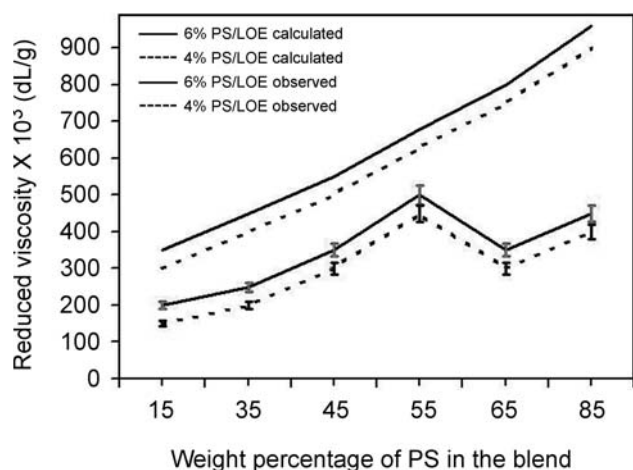


Figure 2. Variation of reduced viscosity with composition of the blend.

calculated values indicate some polar interaction between PS and LOE. The increase in the values of the reduced viscosity with the increase in the amount of PS in the blends shows that the size of LOE/PS composite molecule increases accordingly.

Density Measurements

Figure 3 shows the plots of calculated and observed densities of LOE/PS blends against composition in 6 wt% solutions at 30°C. The densities of the blends of different compositions were calculated on the basis of additivity of volumes and compared with the corresponding observed densities. For immiscible blends, the observed densities have been reported to agree with the calculated densities [12,13,23] or to be lower than the latter while those of miscible blends have been found to be greater by 5% than the calculated densities [32]. In all the cases, the calculated densities were higher than the observed densities. The observed density shows that LOE/PS is more or less miscible up to composition 65 wt% PS in the blend.

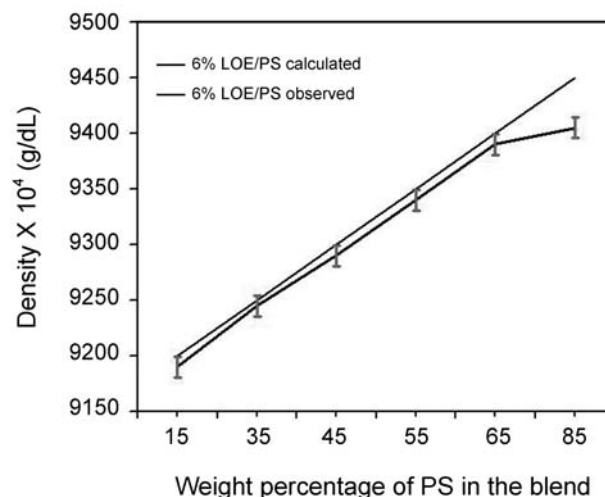


Figure 3. Variation of density with composition of the blend solution.

Film Study

The film with 65 wt% LOE in the blend was opaque and fairly hard. The blend composition with 85 wt% PS and 15 wt% LOE was opaque and highly tough. It appears that toughness of the films increased as the ratio of PS in the blend increased. In a separate experiment, 5 films of each composition LOE/PS:65/35 and 85/15 ratios were cast (10×1 cm) for tensile strength studies on Instron digital tensile tester (interfaced with a PC). The average of the maximum tensile strength and elongation percentage were recorded. The combined standard deviation for the two films and the maximum stress were found to be 1.2 MPa and 5.47%. The average maximum stress in the first case was observed to be 13 MPa and in the second case 11 MPa. The elongation-at-break percentage for the first composition was obtained at 580% and for the second composition was obtained at 266%. The standard deviation for maximum tensile strength in the samples LOE/PS 65/35 was found to be 1.2 MPa and the same

Table 1. Mechanical properties of LOE/PS blends.

Composition	Maximum tensile strength (MPa)	Standard deviation	Elongation-at-break (%)	Standard deviation
PS pure*[24]	36-52	-	1.2-2.5	-
LOE/PS 65/35	13	1.2	580	5.5
LOE/PS 85/15	11	1.3	266	5.7

for elongation percentage was 5.5%. The standard deviation in case of LOE/PS 85/15 was found to be 1.3 MPA with elongation percentage of 5.7% (Table 1). The film thickness for these studies was 80 micron. Compared with the curve of pure polystyrene, which shows maximum stress of 36-52 MPa at 1.2-2.5% elongation [24]. LOE increases the plasticity and flexibility of polystyrene enormously. The blend shows the tensile strength behaviour similar to low density polyethylene which shows a maximum stress of 8.31-31 MPa and 100-600% elongation-at-break [24]. The blend therefore is promising a sustainable resource based product LOE in the rigid commercial polymer polystyrene to obtain flexible films of medium strength by various substitutions.

Heat of Mixing, ΔH_{mix}

The two polymers in a blend are thermodynamically miscible if ΔG_{mix} is negative. Since entropy of mixing of polymers has insignificant value, ΔG_{mix} , depends upon ΔH_{mix} . ΔH_{mix} Values are therefore indicative of miscibility of blend components. ΔH_{mix} can be calculated using Schneier's equation [33]:

$$\Delta H_{mix} = \left\{ x_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 \left[\frac{x_2}{(1-x_2) M_2 \rho_2 + (1-x_1) M_1 \rho_1} \right]^2 \right\}^{1/2}$$

where ΔH_{mix} is the heat of mixing, subscripts 1 and 2 represent the component polymers and x , M , ρ , and δ , respectively are the weight fraction, molar mass of one repeat unit, density and solubility parameter of the component polymers. Value of solubility parameter for PS, 9.06, has been taken from [34], while that of LOE has been calculated using cohesive energy values of different structural units as given by Krause [35] and was found to be 8.17. The densities of PS and LOE were found to be 0.9811 and 1.057 g/cm³, respectively. The molar mass of LOE was taken to be that of one epoxidized fatty acid chain, equal to 925 g. This normalizes the molar mass of LOE with that of a repeating unit of PS. Using these values where ΔH_{mix} is the heat of mixing, subscripts 1 and 2 represent the component polymers and x , M , ρ , and δ , respectively are the weight fraction, molar mass of one repeat unit, density and solubility parameter of the component polymers. ΔH_{mix} was calculated with PS and LOE alternately as component 1 for different compositions

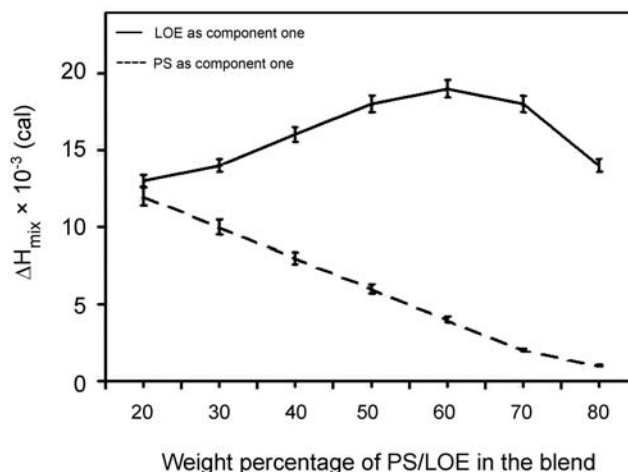
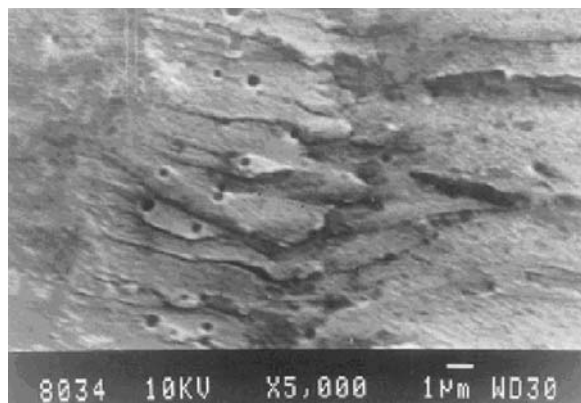


Figure 4. Variation of heat of mixing with composition of the blend.

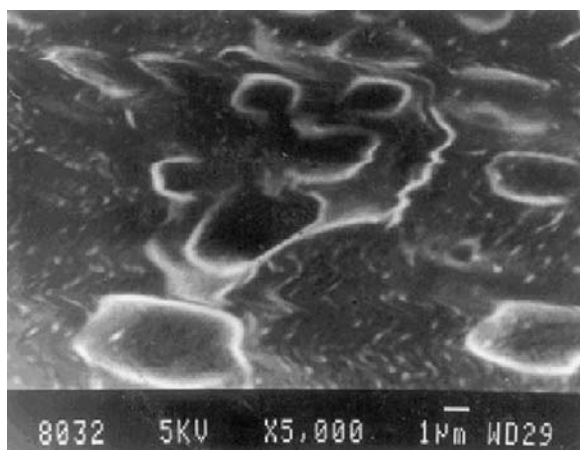
of the blend and it is plotted against increasing wt% of PS/LOE as component 1 of the blend in Figure 4. It is observed by Schneier [33] that the components are miscible if ΔH_{mix} is lower than 10×10^{-3} cal uniformly for all compositions. Figure 4 shows that ΔH_{mix} values for different compositions of the blend are lower than 10×10^{-3} cal except for composition with 20 wt% of PS with the former as component 1 while LOE being taken as component 1, ΔH_{mix} values are found to be fairly higher than 10×10^{-3} cal. This discrepancy in the calculated values of ΔH_{mix} by changing the order of the components indicates the immiscibility of LOE with PS. However, the result does not match with the obtained reduced viscosity measurements. It appears that because of low molar mass of LOE, the entropy factor will contribute to lower ΔG_{mix} . This factor if taken into consideration, will therefore increase the miscibility window beyond the composition LOE/PS 80/20. The latter one shows $\Delta H_{mix} 10 \times 10^{-3}$ cal calculated by taking PS and LOE as components 1 and 2, alternately.

Morphological Studies

SEM Micrograph, Figure 5a, of the fractured surface of the film of blend LOE/PS 85/15 at magnification 5000 \times , Figure 5a shows a single uniform phase having layered surface. However, SEM micrograph of the film of the blend LOE/PS 35/65, Figure 5b, shows a two phase system one appearing bright (epoxy phase) and the other appearing black (polystyrene phase) in



(a)



(b)

Figure 5. SEM Micrographs of LOE/PS: (a) 85/15 (5000X), and (b) 65/35 (5000X).

the micrograph. Large macrodomains of LOE appear to be dispersed in the dark phase of PS. Likewise LOE phase engulfs PS phase. This shows the heterogeneity of the phases and immiscibility of LOE with PS at this composition. It has already been observed from viscosity studies that phase inversion takes place at this composition, which is further confirmed from the morphological studies. The above results show that LOE/PS system is immiscible at and beyond composition LOE/PS:35/65 indicative of phase inversion.

CONCLUSION

Blends of LOE with PS were found to be miscible in solution phase in the composition range of LOE/PS 85/15 to 45/55 as confirmed by viscosity and density measurements. At composition LOE/PS, 35/65 phase inversion takes place which indicates the onset of

immiscibility. The morphological investigation revealed a two phase system in case of LOE/PS 35/65 while a uniform single phase morphology was observed in case of LOE/PS 85/15. The toughness of the films was found to increase with the increasing content of PS in the blend. The mechanical properties of LOE/PS blend films were found to match with LDPE at composition LOE/PS 65/35. The above study shows that linseed oil epoxy (a product from sustainable resource), can be substituted up to 65% or even higher with polystyrene to obtain tough and flexible films.

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