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Investigation of Miscibility of Linseed Oil Epoxy with Poly(vinyl alcohol)

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Blending of two polymers in solution is a simple and cost effective technique to improve upon the physical and mechanical properties of the component polymers. Maximum synergism in the properties of the two polymers occurs when they are thermodynamically miscible. Poly(vinyl alcohol) (PVA) yields tough, flexible and water sensitive films. Linseed oil epoxy(LOE), a product from sustainable resource, used as a plasticizer and corrosion resistant coating, does not produce free standing film. A blend of PVA with LOE may yield films of good toughness and flexibility, and low water absorption if the two components are miscible with each other. Blends of PVA with LOE were prepared in weight ratios 80/20, 60/40, 40/60 and 20/80 through solution method by mixing in dimethyl sulphoxide. In the first instance, the miscibility the two components were investigated using the techniques of viscosity and ultrasonic measurements. The study revealed that the two components showed miscibility up to below 60 wt% PVA in the blend as at the composition LOE: PVA 40/60, phase inversion occurs. Above this composition, immiscibility is indicated; differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) delineates the above behavior in the solid phase.

Keywords: linseed oil epoxy; poly(vinyl alcohol); blend; miscibility; morphology; phase inversion

1 Introduction

Blending of two different polymers in solution is a conventional and cost effective technique for improvement of their physical and mechanical properties (1, 2). Blends in which the component polymers are miscible on the molecular scale are called compatible and most desirable because of the maximum synergy in their properties and direct dependence of the later on the composition. The blends in which the component of the two polymers are immiscible form a heterogeneous phase, which in most cases, do not yield desirable improvement in physical and mechanical properties. However, examples are available where a heterogeneous/incompatible blend yields improvement in some mechanical properties (3). In view of the industrial significance, blending of commercial polymers has been rigorously investigated for the last three decades (4–6).

For improving the properties of a polymer of high molecular mass, blending is normally done with another polymer of a high molar mass. However, the improvement in toughness tensile strength and flexibility of a polymer of a high molar mass can also be achieved by blending with a substance of low molecular mass. Dibutyl sebacate, tricresyl phosphate and dioctylphthalate have been used for improving the mechanical properties poly (vinyl chloride) and other commercial polymers as plasticizers (7). Low molecular mass materials from vegetable resources like lactose (8), starch acetate (9), starch cinnamate (10) have been used to modify the properties of poly(vinyl chloride) poly(methyl methacrylate) and other polymers. These plasticizers and additives of low molar mass are also required to be miscible for being effective in improving the properties of commercial polymers and also for preventing the oozing of the former.

Lately, bioartificial polymers, which are obtained by blending natural polymer with a commercial polymer, have attracted the attention of scientists. Poly(vinyl alcohol), among other polymers, which makes tough and water sensitive film has been variously used to make blends with lignin (11), chitosan (12), polysaccharides (13), and collagen (14) to obtain a blend of desired physical and mechanical properties. Most studies are focused on the investigation of miscibility of the components in the blend and the transport mechanical properties of the latter.

Vegetable oils constitute a major resource of several polymers, viz., alkyd, polyesters, polyurethane, epoxies and others (15, 16). Poly(vinyl alcohol) can be used to modify the properties of polymers from vegetable oil resource. Vegetable oil epoxies, which have been used to obtain corrosion resistant coatings (17) and as plasticizers (18, 19), do not

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make free standing films, these epoxies are also water insoluble. It would be profitable to study the compatibility of poly(vinyl alcohol) with a vegetable oil epoxy with attendant enhancement in the miscibility of the two components and the synergism in physical/mechanical characteristics of the resulting bioartificial polymer. In the first instance, we report the investigations of the miscibility of PVA with linseed oil epoxy in solution by viscosity and ultrasonic measurement and in solid phase by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM).

2 Experimental

2.1 Materials

The linseed oil was procured from M/s Atul Chemicals Pvt. Ltd. (Delhi). The oil was dewaxed by keeping it in a refrigerator at 15°C and filtered before use. Polyvinyl alcohol (CDH (P) Ltd. New Delhi), mol. wt. approx. 14,000, was used without further purification. Linseed oil epoxy (LOE) was prepared after a reported method (20), which yielded epoxidized oil of epoxy of an equivalent weight of 260.

2.2 Blending

Blends of LOE with PVA were prepared by mixing the LOE and the PVA in weight ratios LOE: PVA, 80/20, 60/40, 40/60,20/80, by taking the requisite amounts of the two components to obtain 100 ml of 2 wt% and 4 wt% solutions of the blend in dimethyl sulphoxide [DMSO], (Merck, A.R.). All solutions were thoroughly mixed by agitation on a magnetic stirrer for 2 h. Selected samples were kept for over a week to observe the appearance of turbidity or precipitation, which was not noticed in any case.

2.3 Film Preparation

6 Wt% solutions of a selected composition of the blend in DMSO were cast on a transparency sheet and were allowed to dry under ambient conditions. In 10 days, free standing films were obtained. The films were further dried in vacuum oven kept at 60°C for 24 h.

2.4 Experimental Investigations of the Blends

LOE-PVA blends were studied experimentally by viscosity measurements, ultrasonic velocity measurements, differential scanning calorimeter (DSC), and scanning electron microscopy (SEM). DSC thermograms were recorded on differential scanning calorimeter (Dupont 910, TA Instruments), in N_2 atmosphere at a heating rate of $10^\circ C\ min^{-1}$. Viscosity of the blend solutions was measured at temperatures 20, 30 and 40°C (accuracy $= \pm 0.05^\circ C$) in a thermostatic bath using an Ubbelhode suspended level viscometer. The ultrasonic velocity of the blend solutions were measured by an ultrasonic interferometer Model MX- 20 (Mittal Enterprises, New Delhi, India). The temperature in the sample cell was maintained at 20°C, 30°C and 40°C by circulating water from a thermostatic bath through the outer jacket of the sample cell with a thermal stability of $\pm 0.1^\circ C$. The densities of the solutions were measured at the above temperatures by a pycnometer. The morphology of a cross section of the cryogenically fractured blend films was examined by a scanning electron microscope (SEM), JEOL, JSM-840 scanning electron microscope) at different magnifications. SEM micrographs were taken after coating the fractured surface with a thin layer (10–20 nm) of gold. Moisture absorption properties of the pure polymer blends were studied using a standard technique. Weighed portions of the perfectly dried samples were exposed to a desiccator containing a saturated $NaNO_3$ solution (maintaining 65% relative humidity inside) until a constant weight was reached. From the weight gain, the moisture absorption (wt%) was calculated.

3 Results and Discussion

3.1 Viscosity Measurements

The variations of relative viscosity with the change in the blend composition at temperature 20°C, 30°C and 40°C have been plotted for an overall 2 wt% and 4 wt% of the blend in the solution (Figure 1). It shows a progressive increase in the relative viscosity with the increasing proportion of PVA in the blends. Two linear portions in all the curves were observed with inflection at 60% PVA in the blend, which shows phase inversion. It has been observed by Y. N. Sharma et al. (21, 22) and Mamza et al. (2) that the plot of the relative viscosity of the blend solutions against their composition is linear at all concentrations and temperature when the components are miscible with each other. However, if these plots are not linear at any of the concentrations and temperatures, the components are incompatible or semi-compatible and phase separation or phase

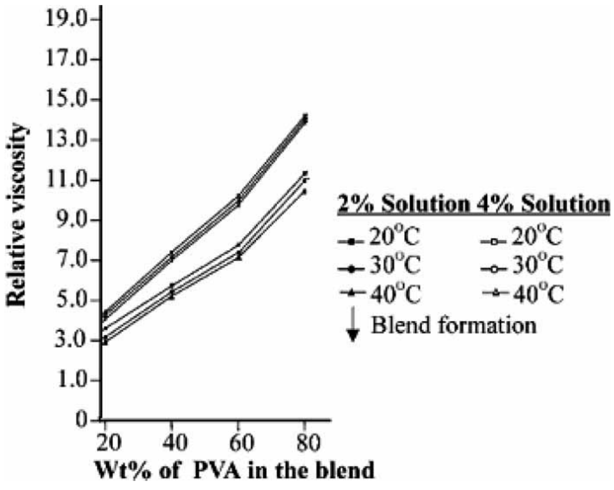


Fig. 1. Effect of varying composition of LOE: PVA blend on the relative viscosity of 2% and 4% solution.

inversion in the blend occurs. Since the increase in relative viscosity is similar at 20°C, 30°C, and 40°C, it can be inferred that association of the components is stable even at relatively higher temperatures. It has also been observed that the blend of all compositions in 2 wt% and 4 wt% solution were transparent and on keeping even for several weeks, no turbidity appeared. Also, the viscosity variation with composition is linear before phase inversion composition. This shows that the blend is miscible and homogeneous before phase inversion.

On comparing the observed and calculated reduced viscosities of the blend solutions of different compositions at concentrations of 2 wt% and 4 wt%, (Figure 2 (a, a′ and b, b′)), respectively, we see that the observed reduced viscosity curve crosses over the calculated viscosity curve at and beyond 60 wt% PVA in 4 wt% and 2 wt% blend solutions. This feature again shows the phase inversion is this blend system with 60 wt% PVA, almost linear nature of the observed reduced viscosity is noticed before the phase inversion composition which indicates miscibility of the components. Paladhi and Singh (23, 24) have observed that the reduced viscosity of blend compositions follows the simple additive rule of mixture when the polymers are miscible. Singh et al. (24) have observed a nonlinear variation of the observed values of the reduced viscosity in the case of poly(ethylene oxide) and poly(vinylalcohol) in water, and also in the case of poly(acrylic acid) and poly(vinyl pyrrolidone/polyvinyl alcohol) and concluded the immiscibility of these pairs. Slightly lower values of the observed reduced viscosities than the calculated values for the same composition show interaction between LOE and PVA and consequently tight binding of the two components as well as enhanced compactness of the blend structure. The blend of composition 20 wt% PVA and 80 wt% LOE shows the lowest reduced viscosity or the most tightly bound structure while the blend of composition 80 wt% PVA and 20 wt% LOE shows highest value of the reduced viscosity that indicates an expanded structure of the blend in solution. However, this observation is inconsistent with the one derived from adiabatic compressibility measurement, which we will see in a later section.

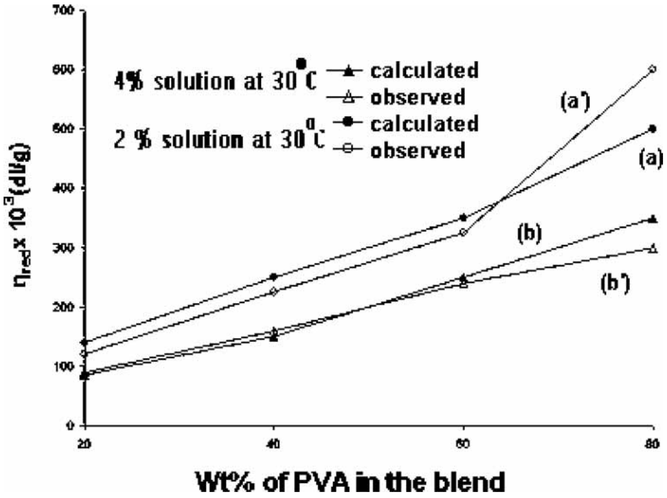


Fig. 2. Variation of reduced viscosity with composition of the blend.

3.2 *Ultrasonic Velocity Measurements*

The ultrasonic velocity (Figure 3) changes linearly in two portions each with different slopes as the proportion of PVA in the blend increases. An inflection is observed in all the curves at composition 60 wt% PVA in the blend. The similar nature of nonlinearity is observed in 2 wt% and 4 wt% solutions at 20°C, 30°C, and 40°C. The sharp inflection at 60 wt% PVA in the blend is attributed to phase inversion. It is well established that for a compatible and miscible blend, the ultrasonic velocity varies linearly with compositions at all concentrations and temperature (23, 25, 26). The similar variations in the ultrasonic velocity in 2 wt% and 4 wt% solutions at 20°C, 30°C and 40°C indicates that the interaction between the two components is stable against the increase in temperature and may be occurring through weak electrostatic weak forces and hydrogen bonding.

3.3 *Adiabatic Compressibility*

Using ultrasound velocity, adiabatic compressibility of the system can be calculated by the following Equation (27):

$$\beta = 1/v^2 \rho$$

Where β is adiabatic compressibility of the medium, v is the velocity of the sound waves and ρ is the density of the medium. Adiabatic compressibility is inversely proportional to the cohesive energy of the polymer molecules (28). Figure 4 shows two linear portions in the adiabatic compressibility curves of 2 wt% and 4 wt% solutions of the blends of different composition at 20°C, 30°C, 40°C. The sharp inflexion in these curves can be seen as a result from phase inversion as the slope of the two linear portions increased very sharply. It is observed that in the first part of the curves,

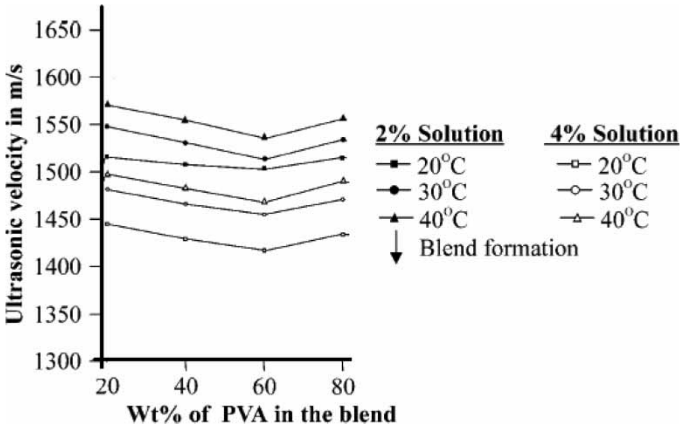


Fig. 3. Effect of varying composition of LOE: PVA blend on the ultrasonic velocity of 2% and 4% solution.

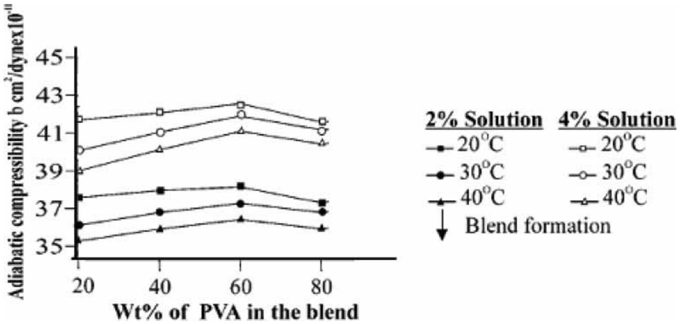


Fig. 4. Effect of varying composition of LOE: PVA blend on the adiabatic compressibility of 2% and 4% solution.

adiabatic compressibility increases which shows expansion in the blend structure as the amount of PVA in the blend increases. However, in the portion after inflexion, the adiabatic compressibility decreases which indicates increasing compactness of the blend structure. This feature varies from the one observed previously in the case of reduced viscosity. After phase inversion, it is the PVA phase in which the LOE is dispersed. Although the sizes of the blend particles are compact, as is shown by the lowering of adiabatic compressibility values, PVA having a large number of exposed hydroxy groups will have higher electrostatic functional interaction with DMSO and hence, higher reduced viscosity values.

3.4 Density Measurements

The density of the blends of different compositions calculated on the basis of additivity of volumes and compared with corresponding observed densities provides evidence of miscibility or immiscibility of the blend components. For immiscible blends, the observed densities have been reported to agree with the calculated densities or to be lower than the latter (9, 15). Those of miscible blends have been found to be larger up to 5% than the calculated densities (29). Figure 5 shows the plots of calculated and observed densities of LOE: PVA blends against composition in 2 wt% and 4 wt% solutions at 30°C (a, a′ and b, b′, respectively), and the observed density plots appear to be nonlinear and slightly above the calculated density lines. The higher values of the density above the calculated values show the some interaction between the two components. However, the decrease in the density beyond 60 wt% PVA is observed in the blend composition as compared to the previous observation of phase inversion which was found to be beyond this composition.

3.5 Film Study

The films of blend of LOE with PVA of different compositions were all found to be transparent, flexible and highly stiff. Even the film of blend with 20 wt% PVA was decidedly stiff, flexible, and transparent. In fact, manually, the stiffness and flexibility film of blend with 20, 40 and 60 wt% PVA was not found to be noticeably different. Unlike the films of the dehydrated castor oil epoxy with polymethacrylic acid (30), these films did not show any stickiness, which highlights the stability of the blend composition in solid phase like the liquid phase. Since the films of the blend with as low as 20 wt% PVA shows high stiffness, flexibility and (low water absorption), they hold promise for commercial application.

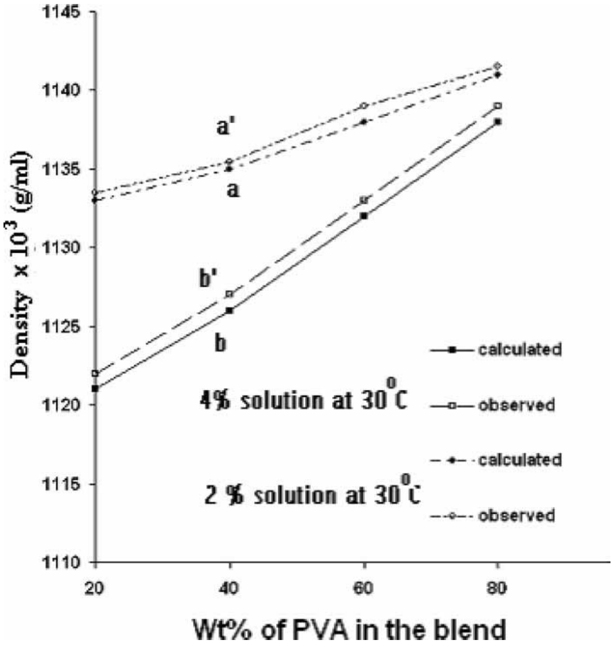


Fig. 5. Variation of density with composition of the blend.

3.6 Thermal Analysis

The DSC thermogram of pure PVA shows a Tg at 69°C (Figure 6a). The DSC cure of composition LOE: PVA,

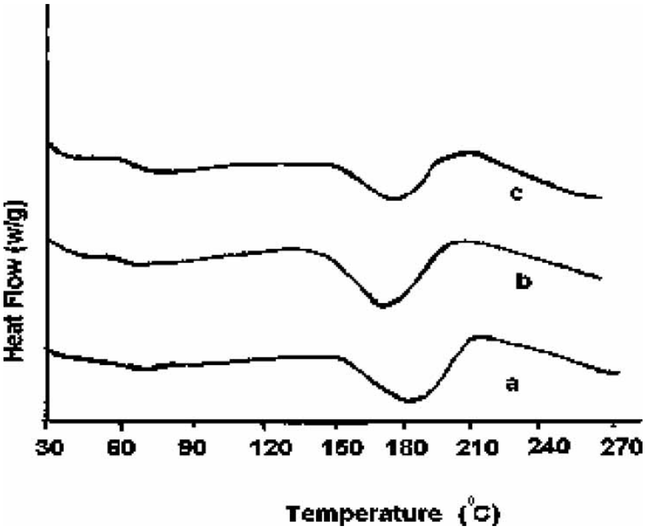
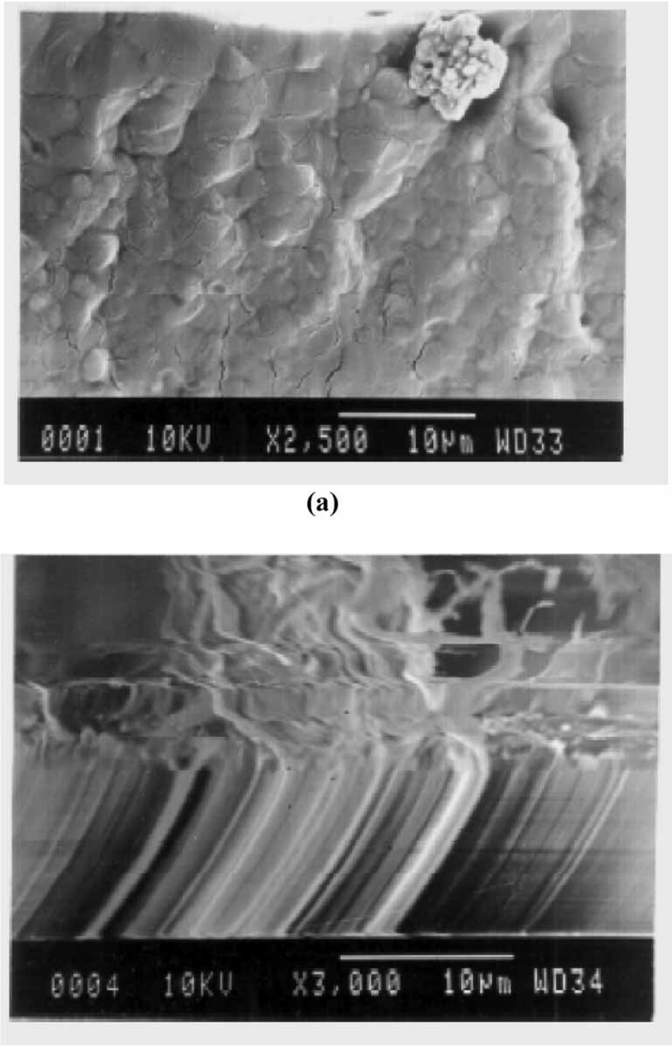


Fig. 6. (a) DSC thermogram of pure PVA, (b) LOE: PVA 60:40, (c) LOE: PVA 40:60.

60:40, shows a Tg at 60°C which may be assigned to the Tg of the blend. Tg of pure PVA, which is 69°C, is not observed in this thermogram. The thermogram therefore, shows miscibility of PVA with LOE for this composition. For, the blend composition of 60 wt% PVA, one Tg at 68.5°C is obtained which coincides with the Tg of pure PVA. In this blend composition, PVA is not miscible with LOE, and it coincides with the blend composition of phase inversion. The DSC studies also establish mixing of the two components before the composition of phase inversion.

3.7 Morphological Studies

The SEM micrograph of the blend of compositions of LOE: PVA, 60:40, 40:60 have been recorded (Figure 7, (a and b)). The SEM micrograph of the blend of LOE: PVA, 60:40 shows single phase small planer units, very snugly formed with each other and appearing as extended thick sheets with protrusions. The microstructure indicates a stiff and flexible structure. It appears that before the composition of phase inversion, the components are miscible with each other as has been observed in previous sections. The blend, LOE: PVA, 40:60 at which phase inversion is obtained clearly shows two phases; one cucumber-shaped outer phase engulfing an inner similar shaped thin phase each joining each other snugly providing a sheet-like structure. The phase inversion observed by viscosity and ultrasound velocity measurement is also corroborated by SEM micrograph.



(a)

(b)

Fig. 7. (a) SEM micrograph of LOE: PVA 60:40, (b) LOE: PVA 40:60.

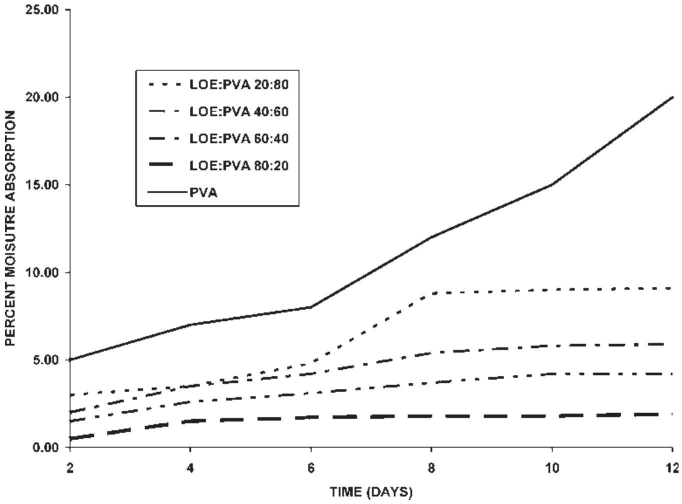


Fig. 8. Moisture absorption capacity of PVA and LOE: PVA blends.

3.8 Moisture Absorption Capacity

The moisture absorption capacity of blends Figure 8 was found to be significantly lower than that of pure PVA. Prisitne PVA showed a moisture absorption capacity of 20 wt%, while LOE: PVA blend containing 80% PVA and 20% LOE exhibited a maximum absorption of around 9 wt%. The blend containing 80% LOE and 20% PVA showed minimum moisture absorption of barely 2 wt%. Hence, with the increase in the LOE content in the blend, the moisture absorption was found to decrease drastically. It is interesting to note that even a lower loading of LOE in the blend (as low as 20%) was found to reduce the moisture uptake by 12 wt%. It can therefore be concluded that blending of LOE with PVA dramatically reduces the moisture absorption capacity of the blends which is an important aspect for the commercial utility of these blends.

4 Conclusions

Blends of LOE with PVA shows phase inversion with 60 wt% PVA in the blend. All the blends having PVA less than 60 wt%. Show miscibility, which is observed by viscosity and ultrasonic velocity measurements, and is also corroborated by SEM and DSC studies. All the blends, including the one with as low PVA as 20 wt%; are highly transparent and flexible. The blend LOE: PVA, 80:20 exhibits minimum moisture absorption of only 2 wt% and shows promise for commercial application.

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