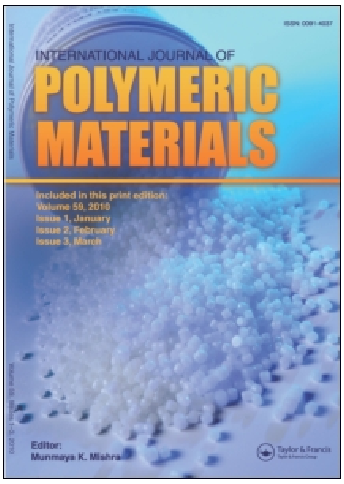

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Miscibility Studies of Polyesteramides of Linseed Oil and Dehydrated Castor Oil with Poly(vinyl alcohol)

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Blends of two polymers have been widely investigated to enhance or modify some of their physical or mechanical characteristics for specific applications. The investigation of miscibility of a pair of polymers is a necessary step in the investigation of the properties of the blends. Poly(vinyl alcohol)(PVA) is a commercial polymer that yields tough films of high tensile strength. They are, however, water soluble, restricting their applications. Vegetable oil constitutes a major resource for several polymeric products, such As alkyds, polyurethanes, polyepoxies, and polyesteramides. Polyesteramides, synthesized from different seed oils, have been used as an anticorrosive material but they fail to form free standing films. They can, therefore, be used for blending with PVA to lower its water sensitivity as well as to obtain free-standing films of a sustainable resource based polymer. In this study, linseed oil polyesteramide (LOPEA) and dehydrated castor oil polyesteramide (DCPEA), the source oils having different unsaturation in their fatty acids chains, were blended with PVA through mixing in solution in the weight ratios LOPEA/DCPEA:PVA: 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80. In the first phase the miscibility of the two components was investigated in solution by viscosity and ultrasonic measurements and in the solid form through differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). Moisture absorption by the films of different compositions of the blends was studied. The viscosity and ultrasonic studies show that both DCPEA and LOPEA were immiscible with PVA in solution. In solid phase the DCPEA and PVA were found to be partially miscible whereas LOPEA and PVA were found to be completely immiscible. Films of the blend DCPEA:PVA:80:20 were found to be the toughest. Blends of all compositions showed lower absorption of moisture than pure PVA. In view of the toughness of its films, low moisture uptake and high content of sustainable

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resource based polymer, DCPEA:PVA, 80:20 blend holds potential for commercial application.

Keywords: blend, dehydrated castor oil polyesteramide, linseed oil polyesteramide, miscibility, poly(vinylalcohol)

INTRODUCTION

Polymer blends were actively investigated for many decades past [1–4]. Polymer modification through blending is a means of obtaining materials with balanced combinations of specific properties. Various attempts have been made to improve one or the other property of most commercial polymers through blending [5]. For maximum development of the properties in these systems the component polymers should be miscible on molecular scale. The miscible blends have their commercial significance in the versatility they exhibit in their physical and mechanical properties. However, immiscible ones that make heterogeneous phase have also found commercial application [6].

For improvement in the properties of a polymer of high molar mass, blending is normally done with another polymer of a large molar mass. However, the improvement in toughness, tensile strength and flexibility of the former can also be achieved by blending with a substance of lower molar mass. Dibutyl sebacate, tricrisyl phosphate, and dioctyl phthalate have been used for improving the properties of poly(vinyl chloride) and other commercial polymers [7]. Low molar mass materials from vegetable resource like lactose [8] and starch cinnamate [9] have been used to modify the properties of poly(vinyl chloride), poly (methyl methacrylate), and other polymers.

Improvements in the physical and mechanical properties of commercial polymers by blending with natural counterparts of high molar mass have also been attempted. The blend is also called bioartificial polymer. Poly(vinyl alcohol), among other polymers, which makes tough but water sensitive film has been variously used with lignin [10], chitosan [11], polysachharides [12], collagen [13] and gelatin [12] to obtain blends of desired physical and mechanical properties. Most studies are focused at the investigation of miscibility of the components in the blend and the transport and mechanical properties of the latter.

Vegetable oils constitute a major resource of several polymers, namely alkyds, polyesters, polyurethanes, epoxies, and others [14–15]. Polyvinyl alcohol can be used to modify the properties of the polymers from vegetable oil resource and vice versa. Polyesteramides are an easily synthesized product from vegetable oils that have been investigated for their surface coating properties [14,16]. They do not make free standing films in ambient conditions. These polymers, synthesized from different vegetable oils, will have fatty acid chains of different unsaturation and will expectedly show different behavior in the interaction with their synthetic counterparts with regard to the miscibility of the components and the modification of their physical and mechanical properties.

In the present communication the authors have chosen dehydrated castor oil (DCPEA)-and linseed oil-polyesteramide (LOPEA), the former having 87% linoleic, 3% linolenic, and 8% oleic acid and the latter having 17% linoleic, 51% linolenic, and 22% oleic acid [17], for blending with PVA to obtain a product with improved mechanical and physical characteristics over the original components. The authors have first attempted to investigate the miscibility of the two polymers, both in solution and solid phase, using techniques of viscosity, ultrasonic velocity measurement, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). Moisture absorption by films of the blends of various compositions has also been investigated.

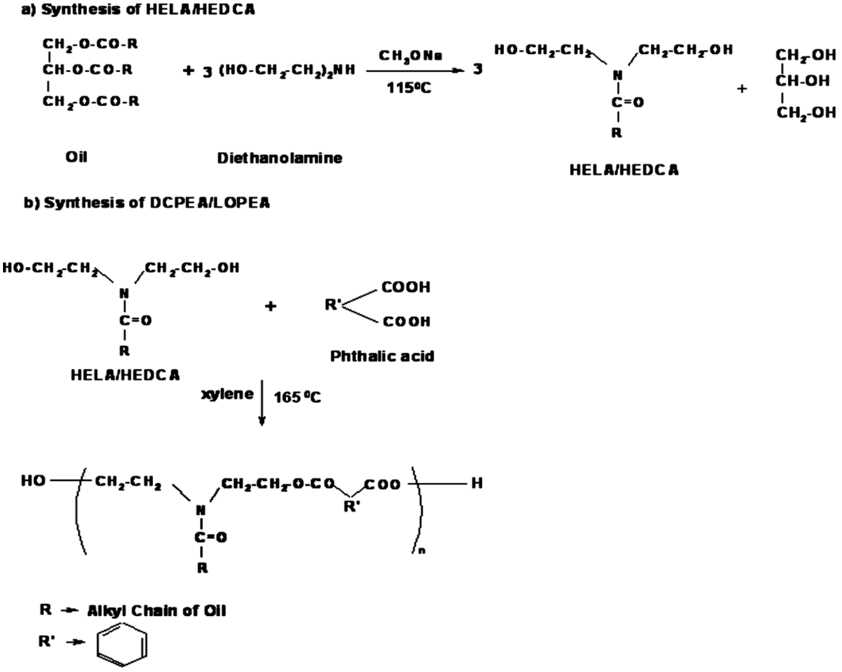
EXPERIMENTAL

Materials

Linseed oil and dehydrated castor oil were purchased from M/s Atul Chemicals Pvt. Ltd. Delhi. The oils were dewaxed by keeping them in a refrigerator at 15°C overnight and filtering before use PVA ($\overline{M_w} = 125,000$) (s.d. Fine Chemical, India) was used without further purification. The DCPEA and LOPEA were prepared by a reported method [12].

Synthesis of Polyesteramides

Briefly, the method consists in taking 0.1 mol of dehydrated castor oil (DCO)/linseed oil (LO) and heating with diethanolamine (0.3 mol) and sodium methoxide (0.007 mol) at 115°C. The reaction product N,N bis(2-hydroxy ethyl) linseed oil fatty amide (HELA)/dehydrated castor oil fatty amide (HEDCA) was recovered from an ethereal layer by treating the reaction product with ether and washing with NaCl solution and removing the solvent in a rotary vacuum evaporator. HELA/HEDCA (0.05 mol) is converted into LOPEA/DCPEA by reacting it with phthalic acid (0.08 mol) in xylene at 165°C for 4 h



REACTION SCHEME 1 Synthesis of polyesteramide.

(See Reaction Scheme 1). Final product is recovered from the solvent in a rotary vacuum evaporator and purified by the solvent-nonsolvent method.

Blending

The Blends of LOPEA and DCPEA with PVA were prepared by mixing them in the weight ratios, DCPEA/LOPEA:PVA, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80 in dimethyl sulphoxide (Merck,AR, India) to obtain 2 wt% and 4 wt% solutions of the blend of each composition. The total volume of the solution was kept at 100 ml. All the solutions were thoroughly mixed for 4 h by agitation on a magnetic stirrer. Three samples of each blend systems were kept under ambient condition for a week. Appearance of turbidity or precipitation was not noticed in any case in the aforementioned period, but beyond this period, separation of phases was noticed in LOPEA:PVA blends followed by DCPEA:PVA blends.

Film Preparation

A few ml of 6 wt% solution of selected compositions of the blends in DMSO were poured on a transparency sheet and allowed to dry under ambient conditions. It was found that these behaved the same way with regard to the viscosity and ultrasound velocities as 2 wt% and 4 wt% solutions while it gave better films in a lesser time (10 days). The films so obtained were further dried in vacuum at 60°C for 8 h.

Investigations of the Blends

DCPEA:PVA and LOPEA:PVA blends were characterized by viscosity method, ultrasonic velocity measurements, DSC and SEM techniques. DSC thermograms were recorded on differential scanning calorimeter, Dupont 910 (TA Instruments, New Castle, USA) in N_2 atmosphere at a heating rate of $20^{\circ}C\,min^{-1}$. Viscosity of the blend solutions was measured at temperatures of 20 and 30°C (accuracy = ±0.05°C) in a thermostatic bath using an Ubbelhode suspended level viscometer. The ultrasonic velocity of the blend solutions was measured by an ultrasonic interferometer (Model MX-20, Mittal Enterprises, New Delhi, India) at the aforementioned temperatures. The temperature in the sample cell was maintained by circulating water from a thermostatic bath through the outer jacket of the sample cell with a thermal stability of ±0.1°C. The densities of the solutions of different compositions of DCPEA:PVA and LOPEA:PVA blends at $30 \pm 0.2^{\circ}C$ were measured by a pycnometer. The morphology of a cross-section of the cryogenically fractured blend films was examined by scanning electron microscopy, 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 of the blends was studied using a standard technique. Weighed pieces of the perfectly dried films were exposed in a dessicator containing saturated $NaNO_3$ solution (maintaining 65% relative humidity) at 20°C until a constant weight was reached. From the weight gain the uptake of moisture (wt%) was calculated.

RESULTS AND DISCUSSION

Viscosity Measurements

The variation of relative viscosity with change in the composition of DCPEA:PVA and LOPEA:PVA blends has been plotted in Figure 1 (a, a′, b, b′, c, c′, d, and d′) for 2 wt% and 4 wt% blend solutions at 20°C and 30°C. Kulshreshta et al. [18–19] and Mamza et al. [20] have

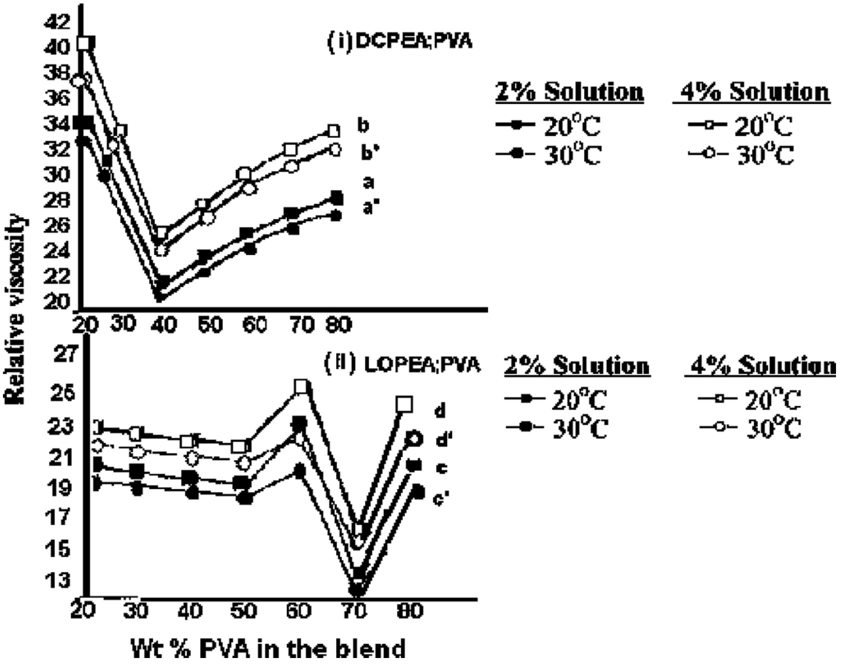


FIGURE 1 Effect of varying composition of (i) DCPEA:PVA, (ii) LOPEA:PVA blend on the relative viscosity of 2% and 4% solution at 20°C and 30°C.

observed that the plot of the relative viscosity against composition is linear at all concentrations and temperatures if the components are miscible with each other, whereas if these plots are nonlinear at any of these concentrations and temperatures, the components are immiscible or partially miscible depending on the extent of nonlinearity. Figure 1 (a, a′, b, and b′) shows that the relative viscosity plot against composition for DCPEA:PVA blend is grossly nonlinear with phase inversion at 40 wt% PVA in the blend. There is some linearity in the portion of the plot before phase inversion but beyond it, the plot is nonlinear. Because of the overall nonlinearity of the plot the components are considered to be immiscible with each other. Precipitation has also been observed in the blend solutions in over two weeks, which also indicates the mutual immiscibility of the two components. Before the composition of phase inversion one can assume that PVA is dispersed in DCPEA phase. The decrease in the relative viscosity till the earlier composition (40 wt% PVA) shows the increase in the compactness of the blend structure as the amount of the former goes up in the blend. This indicates some specific interaction between PVA and DCPEA through hydrogen bonding or dipole–dipole interaction. However, because of structural incompatibility of the two components, as the amount of PVA in the blend reaches the point of phase inversion, the reversal of phases occurs and DCPEA is now dispersed in PVA phase. Consequently the DCPEA:PVA composite molecules also undergo structural change and they become more loose and expanded as is shown by the increase in relative viscosity after the composition of phase inversion. Because the solutions of the blends were prepared in dimethyl sulphoxide that has a high dipole moment as does the PVA, the interaction between the two is much stronger than that between PVA and DCPEA molecules. The frictional force of flow of DCPEA:PVA composite molecules increase as more and more PVA is incorporated in the blend that also causes the enhancement in the relative viscosity values as has been observed in the Figure 1 (a, a′, b, and b′).

Figure 1 (c, c′, d, and d′) shows the variation of relative viscosity with composition of the LOPEA:PVA blend system in 2 wt% and 4 wt% solutions at 20 and 30°C. The variation of relative viscosity is highly nonlinear with multiple inflections against the increasing amount of PVA in the blend at the two concentrations and temperatures studied. All the curves show phase inversion at 40, 60, and 70 wt% PVA corresponding to the points of inflections. LOPEA has fair amount of pendant fatty acid chains of high, medium, and low unsaturation which together, cause complexity in the interaction of LOPEA with PVA molecules leading to multiple phase inversions. In this system the initial decrease in the relative viscosity is much less than in the case of DCPEA, Figure 1 (c, c′, d, and d′). The interaction of LOPEA molecules with PVA is, therefore, also weaker in this composition range. The earlier observations establish high immiscibility of LOPEA with PVA. These blend solutions were found to be highly unstable as compared to those of DCPEA:PVA blend system as precipitation occurred in solutions in them in a week.

Ultrasonic Velocity Measurements

Figure 2 (a, a′, b, and b′) and Figure 2 (c, c′, d, and d′) show, respectively, the variation of ultrasonic velocity measurements with varying amounts of PVA in DCPEA:PVA and LOPEA:PVA blends in 2 wt% and 4 wt% solutions at 20 and 30°C. It has been well established that for a compatible and miscible blend the ultrasonic velocity in solution varies linearly with composition at all concentrations and temperatures [21–23]. The nonlinearity in ultrasonic velocity-composition plots shows immiscibility or partial miscibility of the components

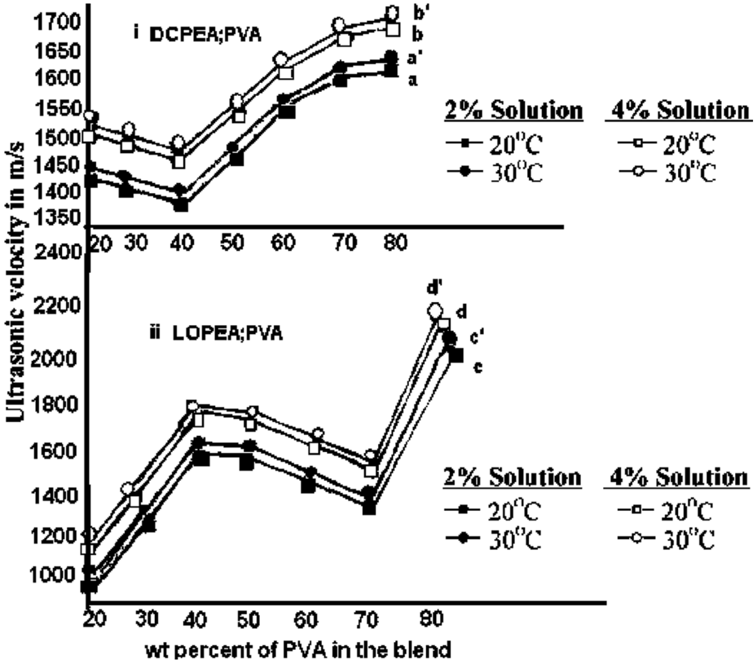


FIGURE 2 Effect of varying composition in DCPEA:PVA and LOPEA:PVA blend on the ultrasonic velocity of 2 wt% and 4 wt% solution at 20°C and 30°C.

depending on the extent of nonlinearity. In DCPEA:PVA blend system, it is observed that the ultrasound velocity composition plots are highly nonlinear (Figure 2 a, a′, and b, b′) with an inflection at 40 wt% PVA in the blend indicating immiscibility of DCPEA with PVA. It coincides with the inflection at 40 wt% PVA in the blend in viscosity-composition plots and is indicative of the reversal of phases that has been explained in the previous section.

The curves reveal that the structure of the blend undergoes drastic change beyond the composition of phase inversion whereas below it the ultrasound velocity shows sluggish decrease with the increase of PVA in the blend. Between the composition 20–40 wt% of PVA in the blend it can be considered to be dispersed in DCPEA phase. Although the compactness of the DCPEA:PVA composite molecules increases in the above composition range, as has been explained in the case of viscosity, some structure breaking of the medium (DMSO) also take place simultaneously, bringing about a decrease in the ultrasound velocity. After the point of phase inversion, ultrasound velocity is found to go up with the increase of PVA content in the blend.

The blend structure undergoes a drastic change in this region. The DCPEA molecules are now dispersed in the PVA phase. The phase inversion exposes the PVA molecule more extensively to DMSO, causing greater interaction between the two as both have high dielectric constant. This effect will lead to a more compact structure of the medium causing enhancement in the ultrasound velocity. The authors therefore, notice that structural information obtained from viscosity measurements are corroborated by ultrasound velocity measurements.

In LOPEA:PVA system also, Figure 2 (c, c′, d, and d′), the ultrasound velocity-composition plots are grossly nonlinear with inflection at 40 wt% PVA and 70 wt% PVA, which coincide with the inflections obtained in case of relative viscosity-composition curves in Figure 1 (c, c′, d, and d′). The ultrasonic velocity measurements also establish the immiscibility of LOPEA with PVA. LOPEA molecules have more pendant alkyl chains of higher unsaturation that will cause complexity in their interaction with PVA molecules, causing multiple phase inversions. Figure 2 (c, c′, d, and d′) shows that the structure of the LOPEA:PVA blend is composition dependent and has three different structures in at least three composition regions spurred by phase inversions/phase separations. Ultrasound velocity measurement thus too reveals marked difference in the interactions of LOPEA and DCPEA with PVA. In other words, the extent and nature of the unsaturation in the fatty acid chains in the polyesteramides determine the nature of their interaction with PVA and the extent of miscibility of the two polymers.

Density Measurements

The densities of the solutions of blends of different compositions calculated on the basis of additivity of the density values of pure components values and compared with the corresponding observed densities, provides evidence of miscibility or immiscibility of components in the blend. In case of immiscible blend the observed densities have been found to agree with the calculated densities or to be lower than those [24–25]. Observed densities in the miscible blends were found to be higher up to 5 wt% than the calculated densities [26]. Figure 3 (a and a′) shows the plots of calculated and observed density values of different compositions of LOPEA:PVA blend at 30°C. It is noticed that the observed density varies nonlinearily with the composition of the blend and also shows an inflection at 40 wt% PVA. This inflection coincides with the ones observed at 40 wt% PVA in the blend in the viscosity and ultrasound velocity versus composition plots in Figure 1 (c, c′ and d, d′) and Figure 2 (c, c′ and d, d′). Moreover, the

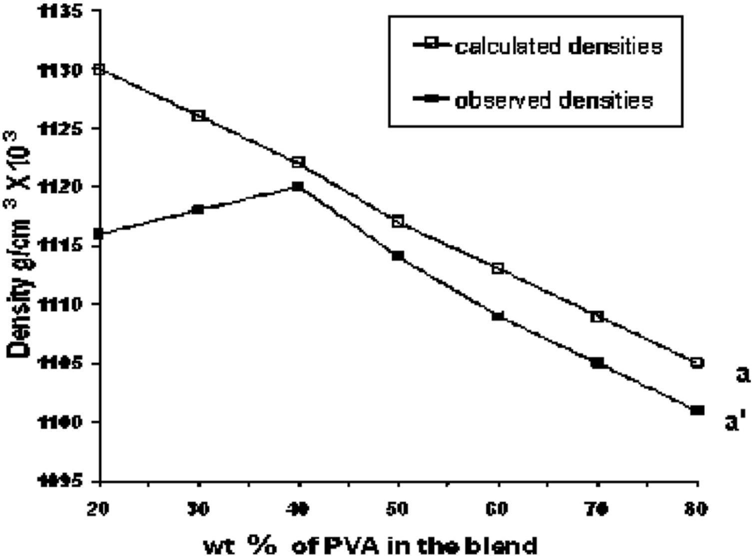


FIGURE 3 Calculated and observed densities of 2 wt% solutions of different compositions of LOPEA:PVA blend at 30°C.

observed density values of solutions of different compositions were found to be lower than the corresponding values of the calculated densities. These observations clearly establish that the LOPEA and PVA are immiscible with each other in solution.

Since the densities of 2 wt% solutions of DCPEA and PVA are quite close to each other, being, respectively, 1.155 and 1.140 g/cm^3, no meaningful information could be derived from the observed and calculated density plots in the case of DCPEA:PVA blends and hence they are not provided.

Film Study

Films of different compositions of DCPEA:PVA and LOPEA:PVA blends were prepared. Film of DCPEA:PVA blend with 20 wt% PVA was found to be transparent, highly stiff and flexible (manual observation). Film of composition 40 wt% PVA was also found to be transparent, flexible, and highly stiff but is stiffness was less than the previous composition. Films with 70 wt% PVA was brownish, transparent, flexible with less stiffness (manual observation) and were also sticky. Stickiness is presumably caused by the oozing of DCPEA. The decrease in stiffness beyond 20 wt% PVA is attributed to the phase inversion at 40 wt% PVA in the blend.

In case of LOPEA:PVA blends, the films of the blend with 20 wt% PVA was opaque, light brown, and stiff (manual observation). Film of blend having 40 wt% PVA was also opaque, brown but less stiff. A film of the blend with 60 wt% PVA was opaque and dark brown with poor stiffness. A blend with 80 wt% PVA did not yield well-formed film. The viscosity of the solution of this composition was so high that it could not be spread evenly on the transparency sheet and as a result it yielded a thick, poorly formed film of no merit.

The aforementioned observations in case of LOPEA:PVA films reveal the immiscibility of the two components. Because of the reversal of phases and phase separations, films of poor stiffness and high opaqueness are obtained even with high amount of PVA in the blends.

Thermal Analysis

The DSC thermogram of pure PVA indicates glass transition, T_g, at 70°C (Figure 4a). A small melting endotherm is also observed between temperatures 155°C and 210°C. The DCPEA:PVA:80:20 blend gives glass transition temperature at 35°C (Figure 4b). T_g of pure PVA is not observed in this thermogram. This shows miscibility of the two components. Because SEM micrograph reveals a microstructure indicating fair miscibility of the two components (see following section) the authors also infer the same from DSC measurements. The blend

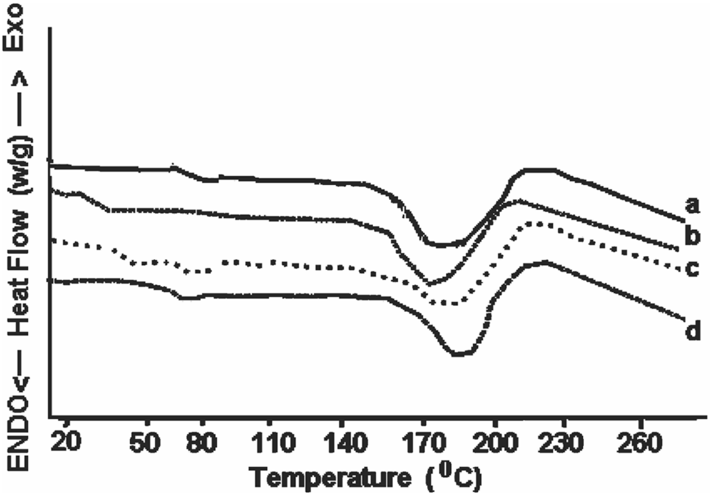


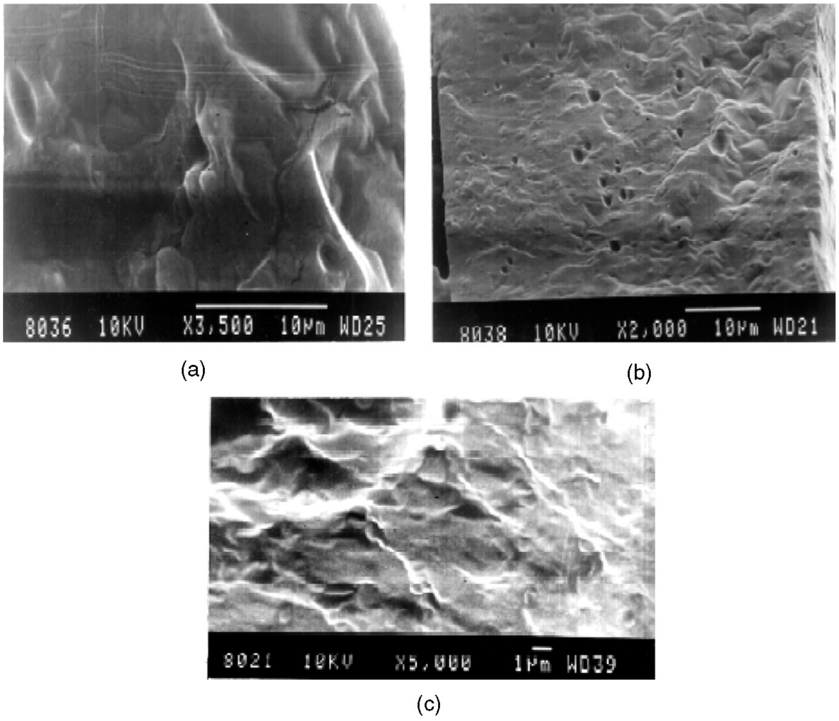
FIGURE 4 DSC thermogram of DCPEA/LOPEA:PVA blends (a) pure PVA, (b) DCPEA:PVA 80:20, (c) DCPEA:PVA 40:60, (d) LOPEA:PVA 80:20.

DCPEA:PVA:40:60 exhibits a T_g at 45°C and another T_g at 70°C for PVA (Figure 4c) indicating two immiscible phases. Using the information from SEM micrograph we can infer semi- miscibility of the two components.

The DSC themogram of the LOPEA:PVA:80:20 blend shows T_g at 70°C (Figure 4d) which coincides with T_g of pure PVA. This indicates the presence of a heterogeneous phase and the immiscibility of LOPEA with PVA. The T_g of LOPEA:PVA:40:60 blends is found at 70°C (not shown in Figure 4) indicating the presence of a heterogeneous phase in the blend and the immiscibility of two components.

Morphological Studies

The SEM micrograph of the film of DCPEA:PVA:80:20 blend observed at the magnification 3500× (Figure 5a) shows white lamellae



(a) (b)

(c)

FIGURE 5 SEM micrograph of (a) DCPEA:PVA:80:20, (b) DCPEA:PVA: 40:60, (c) LOPEA:PVA:80:20.

emerging from the major domains and also enclosing some domains. The micrograph reveals predominantly a single phase with discrete appearance of another phase. Because the films of this composition are also transparent, the blend of this composition can be considered to be fairly miscible in the solid state as was observed from the DSC thermogram. More revealing is the SEM micrograph of the blend DCPEA:PVA:40:60 (Figure 5b). In this case too, the authors see domains appearing as light black color enclosed by lamellae appearing white. The microstructure comprises of one dominant phase with another phase in scant amount. In this blend the components appear to be semi miscible in the solid phase. The authors thus observe that while in solution the DCPEA and PVA are mutually immiscible, partial miscibility is found in solid state as has also been observed from DSC measurements.

Figure 5c gives the SEM micrograph of LOPEA:PVA:80:20 blend that shows extended sheet structure with profuse separation of white

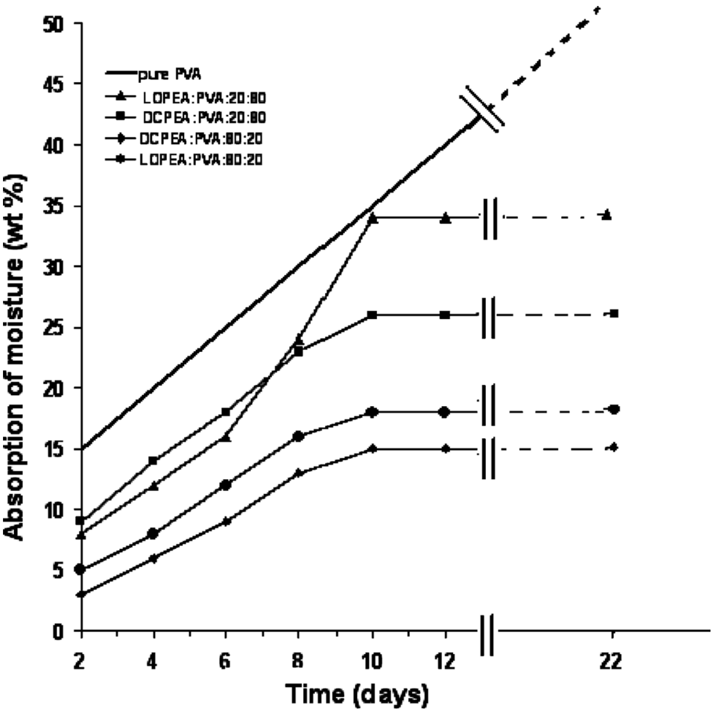


FIGURE 6 Moisture absorption of (i) DCPEA:PVA, (ii) LOPEA:PVA blends.

lamellae of another phase. The later appear to be merging into each other and making larger domains. The microstructure is indicative of a heterogeneous phase structure and hence LOPEA and PVA are immiscible in solid state.

Moisture Absorption Studies

The moisture absorption by blends in wt% (Figure 6) was found to be significantly lower than that for pure PVA. The latter shows water-vapor absorption of about 45 wt% in about two weeks while LOPEA:PVA and DCPEA:PVA blends containing 80 wt% PVA exhibits saturated absorption of about 34 wt% and 26 wt%, respectively, in the same period. A maximum of 13 wt% and 18 wt% moisture was absorbed, respectively, by DCPEA/LOPEA:PVA:80:20 blends (Figure 6). With the increase in the ratio of DCPEA/LOPEA:PVA in the blend, the intake of moisture was found to decrease appreciably. The blending of LOPEA/DCPEA with PVA was thus found to significantly reduce the absorption of water vapors, which is an important aspect of the commercial utility of these blends. It is noteworthy that while pure PVA shows continuous increase in the absorption of moisture with time, it tends to level off in the blends of all composition in two weeks.

CONCLUSION

1. DCPEA and LOPEA were found to be immiscible with PVA in solution but the later polyesteramide, having higher unsaturation in its fatty acid chains, was found to be more immiscible with PVA than the former polyesteramide.
2. DCPEA showed some miscibility with PVA in the solid state, but LOPEA was found to be immiscible with the later in the solid state.
3. Films of DCPEA with PVA were tough and flexible but the toughness of the films of all composition of the blend decreased as the amount of polyvinyl alcohol in the blend increased. The films of all the blends of PVA with the polyesteramide of linseed oil were weak in strength.
4. All the blends of DCPEA and LOPEA with PVA showed lower absorption of moisture than the pure PVA. The blends having 80 wt% DCPEA and LOPEA showed the lowest moisture absorption of 13 wt% and 18 wt%, respectively.
5. The blend composition DCPEA:PVA:80:20 holds applicational promise in view of the high ratio of sustainable resource based polymer in it, toughness of its films and lower water vapor absorption.

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