

# Miscibility Studies on Linseed Oil Epoxy Blend with Poly(methacrylic acid)

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**ABSTRACT:** With the aim to utilize a vegetable oil epoxy, a product from a sustainable resource, for improving the properties of polymethacrylic acid (PMAA), the blends of the latter with the epoxy of linseed oil were prepared in solution by mechanical mixing of the requisite amounts of the two components in dimethylsulphoxide. Freestanding films of the blend were cast. The miscibility of the two components was investigated by viscosity, ultrasonic, and density measurements which showed that the two components were semicompatible in solution. The compatibility in

solid phase was also examined by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), which revealed that linseed oil epoxy (LOE) and PMAA were incompatible. The films of blend of all compositions were found to be sticky, which was caused by the oozing of LOE. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2512–2519, 2006

**Key words:** linseed oil epoxy; blend; polymethacrylic acid; semicompatible

## INTRODUCTION

Homopolymers do not alone possess the desired mechanical properties for several applications. Efforts have therefore been made to improve upon their properties through blend formation among other methods.<sup>1,2</sup> Blend formation is a physical technique and hence is simpler and cost effective in comparison to other methods. The blends have been classified as compatible, semicompatible, and incompatible based on the extent of miscibility of the two components with each other. The performance of the blend has been found to depend upon the degree of miscibility.<sup>3,4</sup> Compatible blends are therefore most desired, because of homogeneous mixing on molecular level and the development of superior mechanical properties.<sup>5</sup> Considerable effort has been made to obtain the blend of most commercial polymers like poly(methyl methacrylate),<sup>6,7</sup> poly(styrene),<sup>8,9</sup> poly(ethylene),<sup>10,11</sup> poly(vinylchloride),<sup>12,13</sup> and others.

Polymethacrylic acid (PMAA) is a hard, brittle, and transparent material. It is too water sensitive to serve as plastic.<sup>14</sup> Being water soluble, it is biodegradable. Attempt has been made to improve its fracture toughness through complex formation and copolymerization.<sup>15</sup> In comparison to other commercial polymers, studies on blending of PMAA are far less. They are mostly related to inter-polymer complex formation,

the resulting complex being mainly used for obtaining membranes for ultrafiltration,<sup>16</sup> reverse osmosis,<sup>17</sup> dialysis,<sup>18</sup> battery separators, and other applications. PMAA has been reported to form gel with poly(vinylalcohol) at room temperature.<sup>19</sup> Blends of PMAA with poly(2-hydroxy ethyl methacrylate) (PHEMA) has been found to be completely miscible in solid phase on a scale of 5–10 nm for all composition.<sup>20,21</sup> Methacrylic acid was copolymerized with methyl methacrylate as block copolymer—poly(methacrylic acid-block-methyl methacrylate). It showed aggregation in aqueous solution in the course of neutralization.<sup>22</sup> Chatterjee et al.<sup>23,24</sup> have investigated the complex formation of poly(methacrylic acid-co-methacrylamide) with poly(ethyleneimine) in mixed solvents (water + organic solvent) and have observed interpolymer complex as more stable in the mixed solvents as compared to pure organic solvents. Interpolymer complex formation between PMAA and polyethylene glycol has been extensively investigated.<sup>25,26</sup> Likewise, complex formation with poly(ethyleneoxide) at different pH values has also been studied.<sup>27</sup> It was observed that existence of a certain number of undissociated carboxyl group was necessary for stable complex formation.

Blending of commercial polymers with smaller molecules like plasticizers is also an important and effective technique to improve the toughness, flexibility, and tensile strength of these polymers.<sup>28</sup> Petroleum based plasticizers like dibutyl sebecate, dioctyl phthalate, and tricrysl phosphate have been used to modify the properties of poly(vinyl chloride) and other commercial polymers.<sup>29</sup> These additives or plasticiz-

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ers with low molar mass are also required to be miscible for being effective in modifying the properties of the commercial polymer and also for obviating the migration of the former. Lactose,<sup>30</sup> strach acetate,<sup>31</sup> and starch cinnamate<sup>32,33</sup> have been used to modify the properties of polyvinylchloride, polymethyl methacrylate, and other polymers. Vegetable oil based polymers, particularly epoxies and polyesteramides, can also be used as plasticizer with commercial polymers to impart flexibility and toughness to their films and other products.<sup>28</sup> Soybean oil epoxy notably has been used as plasticizer in the processing of poly(vinylchloride).<sup>34</sup>

The use of renewable resources including vegetable oils as a source of polymers to substitute the petroleum based commercial polymer is a pressing need of the time against the expected exhaustion of the petroleum stocks by the end of the twenty first century.<sup>35</sup> We have observed earlier that notable attention has not been paid to improve the brittleness and water sensitiveness of PMAA by methods other than complex formation and copolymerization. One of the methods to improve the toughness and water sensitivity of these polymers could be to blend them with a vegetable oil epoxy. Oils are known to possess varying amounts of more than one fatty acid components as triglycerides with varying unsaturation in their chains. They would show different behavior in their interactions with commercial polymers of different chemical nature, especially with regard to their compatibility with these polymers as well as with regard to the physical, mechanical, and chemical characteristics produced in their blends.

Keeping these facts in mind, we have chosen linseed oil, a commercially available nonedible seed oil of high unsaturation for synthesizing blends with PMAA in different ratios. We have first attempted to investigate the compatibility and miscibility of the two components both in solution and in solid phase, using the techniques of viscosity, ultrasonic velocity measurements, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM).

## EXPERIMENTAL

### 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 filtering before use. PMA was synthesized from methacrylic acid monomer (Aldrich) in the laboratory. Polymer was purified by solvent–nonsolvent method. Molecular weight of the polymer was determined by viscosity measurement. Molecular weight of PMA was found to be  $2.3 \times 10^5$  Da. Linseed oil epoxy (LOE) was prepared after a reported method,<sup>36</sup> which yielded epoxidized oil of epoxy equivalent weight of 260.

### Blending

The blend of LOE with PMAA were prepared by mixing the LOE and the polymer in weight ratios LOE : PMAA of 80/20, 60/40, 40/60, and 20/80, by taking the requisite amounts of the two components to obtain 100 mL of 4 and 2 wt % solutions of the blend in dimethyl sulfoxide (DMSO; Merck, AR). All solutions were thoroughly mixed by agitation on a magnetic stirrer for 2 h. Selected samples were kept for over a week. Appearance of turbidity or precipitation was not noticed in any case.

### Film preparation

Six weight percent solutions of selected composition of the blend in DMSO were cast on 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.

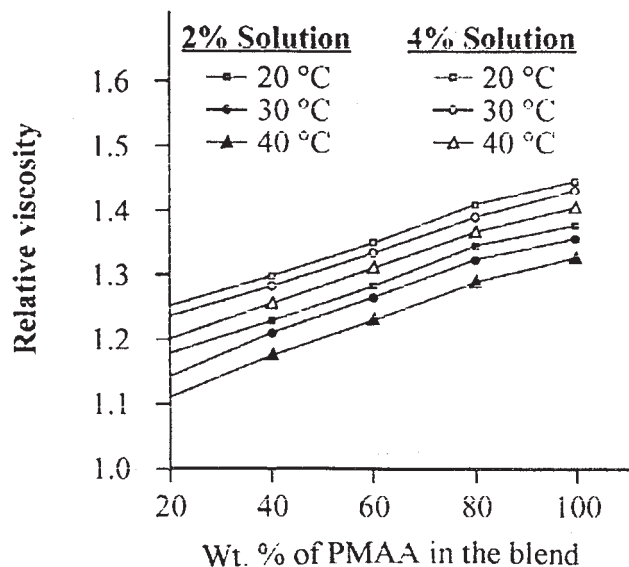
### Experimental investigations of the blends

LOE - PMAA blends were studied experimentally by viscosity measurements, ultrasonic velocity measurements, DSC, and SEM. DSC thermograms were recorded on differential scanning calorimeter Dupont 910, TA Instruments, USA, in N<sub>2</sub> atmosphere, at a heating rate of 10°C min<sup>-1</sup>. Viscosity of the blend solutions was measured at temperatures 20, 30, and 40°C (accuracy =  $\pm 0.05^\circ\text{C}$ ) in a thermostatic bath using an Ubbelohde suspended level viscometer. The ultrasonic velocity of the blend solutions was measured by an ultrasonic interferometer Model MX-20 (Mittal Enterprises, New Delhi). The temperature in the sample cell was maintained at 20, 30, and 40°C by circulating water from a thermostatic bath through the outer jacket of the sample cell, with a thermal stability of  $\pm 0.1^\circ\text{C}$ . 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 were examined by SEM (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.

## RESULTS AND DISCUSSION

### Viscosity measurements

Figure 1 shows the plot of variation of relative viscosity against blend composition in 2 and 4 wt % solutions at 20, 30, and 40°C. The plot shows progressive increase in relative viscosity with the increasing proportion of PMAA in the blends. The plots at 20, 30, and 40°C are almost linear with a small inflection at

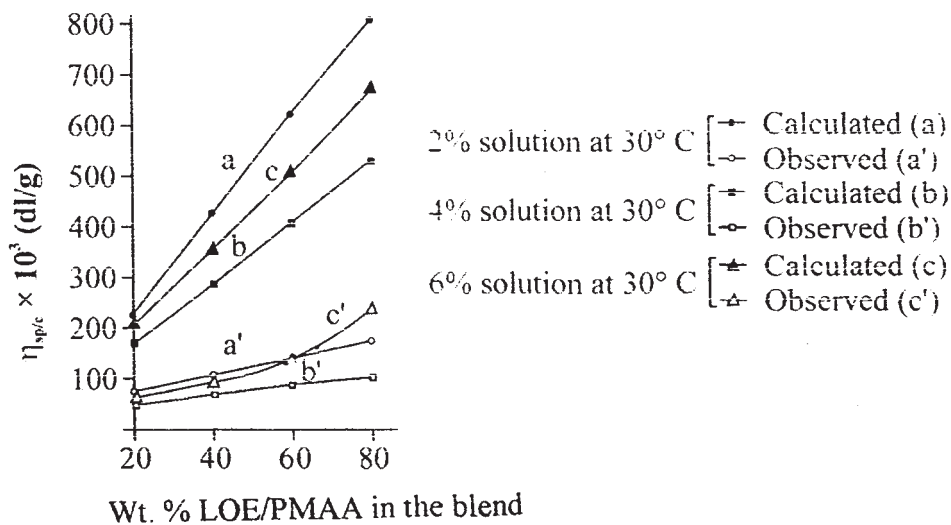


**Figure 1** Effect of varying composition of LOE : PMAA blend on the relative viscosity of 2 and 4% solutions.

the composition 20 and 80% (w/w) PMAA in the blend. We attribute these inflections to phase separation in the blend structure at these compositions. This trend of variation of relative viscosity with composition was found to be the same at 20, 30, and 40°C. The linearity in a wide composition range with deviations at the composition 20 and 80% (w/w) PMAA in the blend indicates semicompatibility of the two components. The ultrasonic velocity measurements also show similar inflection at composition 20 and 80% (w/w) PMAA in the blend. It has been observed by Kulshreshta et al.<sup>37</sup> and Mamza and Folaranmi<sup>38</sup> 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 compatible or completely miscible with each other, while if these plots are not linear at any of the concentrations and temperatures, the components are incompatible or semicompatible, depending upon the extent of non-linearity. Since the increase in the viscosity is similar at the 20, 30, and 40°C, it can be inferred that the interaction between the components is stable even at relatively higher temperatures. It has also been observed that all the compositions of the blend in the 2 and 4 wt % solution are transparent and, on keeping even for several weeks, no turbidity appeared. This shows that the phase separation that occurs in the solution because of semicompatibility does so at submicrometer scale.

On comparing the observed and calculated reduced viscosities of the blend solutions of different compositions at concentrations 2, 4 and 6 wt % [Fig. 2 (a and a', b and b' and c and c', respectively)], we observe that the calculated reduced viscosities are higher than the observed reduced viscosities for all compositions of the blend system. However, the variation of observed reduced viscosities with composition is found to be almost linear in 2 and 4 wt % solutions and nonlinear in 6 wt % solutions. Williamson and Wright<sup>39</sup> and Paladhi and Singh<sup>40</sup> have observed that the reduced viscosity of blend compositions follows the simple additive rule of mixture when the polymers are miscible. The lower values of observed reduced viscosity than the calculated ones show incompatibility of the components. However, from the linear variation of the observed reduced viscosity with composition in solutions of different concentrations, we infer semicompatibility of the two components. In case of immiscible components, the variations in observed reduced viscosity with composition in found to be



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

nonlinear. Paladhi and Singh<sup>41</sup> have observed nonlinear variation of the observed values of the reduced viscosity in case of poly(ethylene oxide) and poly(vinylalcohol) in water and also in case of poly(acrylic acid) and poly(vinyl pyrrolidone/polyvinylalcohol) and concluded for the immiscibility of these pairs. The lower values of the observed reduced viscosities than the calculated values for the same composition show positive interaction between LOE and PMAA and consequently tight binding of the two components and enhanced compactness of the blend structure. The blend of composition 20 wt % PMAA and 80 wt % LOE shows lowest reduced viscosity or the most tightly bound structure.

The miscibility of LOE : PMAA blends has also been investigated by the ultrasonic velocity measurements. Figure 3 shows the plots of ultrasonic velocity against different compositions of LOE : PMAA blend in 2 and 4 wt % solutions at 20, 30, and 40°C. An inflection is observed in all the plots at composition 20 wt % PMAA in the blend. Beyond this composition, the plots are linear in 2 wt % solution. A slight nonlinearity is observed in case of 4 wt % solutions. The inflection at 20 wt % PMAA in the blend can be attributed to phase separation. It is well-established that for a compatible and miscible blend, the ultrasonic velocity varies linearly with compositions at all concentrations and temperatures,<sup>40,42,43</sup> while an S-shaped curve shows incompatibility/immiscibility of the two components. On the basis of the above observations, it can be inferred from ultrasonic measurements also that LOE-PMAA pair is semicompatible in DMSO. The nature of the plots in Figure 3 is same at 20, 30, and 40°C, which further confirms that the forces responsible for blend formation are consistent and stable over a range of

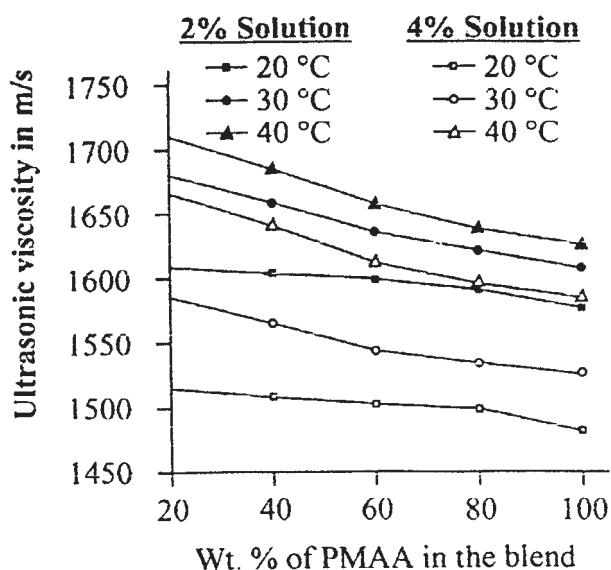


Figure 3 Effect of varying composition of LOE : PMAA blend on the ultrasonic velocity of 2 and 4% solutions.

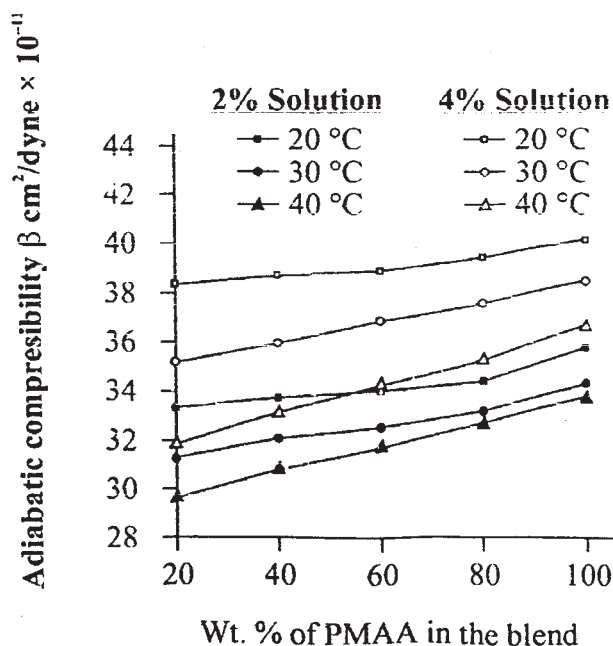


Figure 4 Effect of varying composition of LOE : PMAA blend on the adiabatic compressibility of 2 and 4% solutions.

temperature between 20 and 40°C. It is surprising that 4 wt % solutions of the blend show lower ultrasound velocity than 2 wt % solutions at the same temperature. It appears that because of higher concentration of PMAA in 4 wt % solution, the interaction of DMSO with PMAA would be larger than when the concentration of PMAA blends was 2 wt % in DMSO. This will cause greater structure breaking of DMSO liquid, causing the lowering of ultrasound velocity.

Using ultrasound velocity, adiabatic compressibility of the system can be calculated by the following equation.<sup>44</sup>

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

where  $\beta$  is adiabatic compressibility of the medium,  $v$  is the velocity of the sound waves, and  $\rho$  is the density of the medium. Adiabatic compressibility is inversely proportional to the cohesive energy of the polymer molecules.<sup>45</sup> Figure 4 shows the variations of adiabatic compressibility derived from ultrasound velocity measurements. In this case, an inflection is observed at 20 wt % PMAA in the blend for all cases shown in the Figure 4. Between 20 and 80 wt % PMAA in the blend the plots are linear. At the latter composition, the plots show a wide inflection. The inflection can be attributed to phase separation in the blend system. It may thus be inferred that LOE-PMAA system, as has been observed previously, is semicompatible in solution. The value of adiabatic compressibility is found to be the lowest for the composition, 20 wt % PMAA in the blend, because of the highly compact structure of the



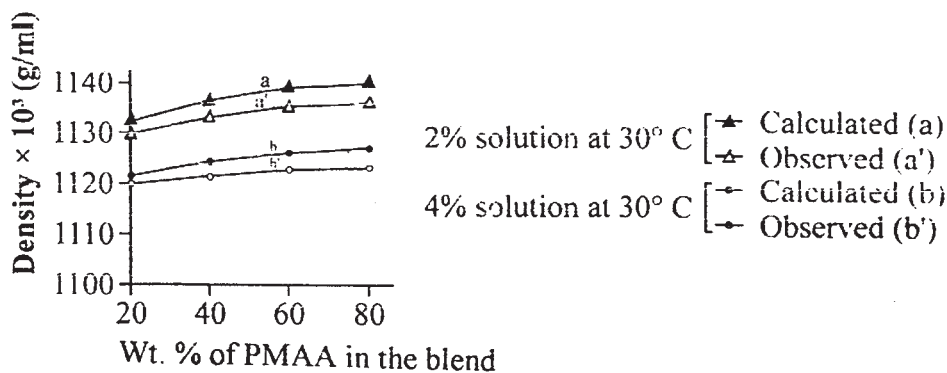


Figure 5 Variation of density with composition of blend in solution.

blend resulting from the highest interaction between the components. Beyond 20 wt % PMAA in the blend, the adiabatic compressibility was found to increase, showing loosening of the blend structure and the decrease in mutual interaction between the components. The same results were also obtained from the reduced viscosity studies (Fig. 2).

### Density measurements

The density of the blends of different compositions calculated on the basis of additivity of volumes and compared with corresponding observed densities provide evidence of miscibility or immiscibility of the blend components. For immiscible blends, the observed densities have been reported to agree with the calculated densities<sup>31</sup> or to be lower than the latter.<sup>29,30</sup> Those of miscible blends have been found to be larger up to 5% than the calculated densities.<sup>46</sup> Figure 5 shows the plots of calculated and observed densities of LOE : PMAA blends against composition in 2 and 4 wt % solutions at 30°C; the two plots appear to be linear and parallel. From the insignificantly lower values of observed densities than the calculated values as well as from the linearity of its plot (Fig. 5a'), it can be inferred that the two components are semicompatible in solution.

### Film study

Film characteristics of the blend of LOE : PMAA of the composition LOE : PMAA of 80 : 20 were cast from its solution in DMSO. The films were found to be slight translucent, brown in color, flexible, and less stiff (manual observation). The films containing 40% PMAA were also slight translucent, brown in color, flexible, and showed poor stiffness. The films with 60 wt % PMAA had the same characteristic as those of the previous case. All films were also found to be slightly sticky. The slight translucency of the films may be due to the similar values of the refractive

indices of LOE and PMAA solutions of the same concentrations. The stickiness of the films can be correlated to the phase separation and exudation of one of the phases. The inter and intramolecular hydrogen bonding in PMAA molecules, which are presumably larger than the hydrogen bond formation between epoxy-PMAA molecules, cause the loosening of the epoxy molecules, which slowly exude out of the films. We can thus infer that the blend is not stable in the solid phase and the components are incompatible.

### Heat of mixing ( $\Delta H_{\text{mix}}$ )

The two components in the blend will be thermodynamically miscible if  $\Delta G_{\text{mix}}$  is negative. Since entropy of mixing of polymers has insignificant value,  $\Delta G_{\text{mix}}$  therefore depends upon  $\Delta H_{\text{mix}}$ . The latter may, therefore, be taken to approximate the former.<sup>47</sup> The  $\Delta H_{\text{mix}}$  values are, therefore, indicative of miscibility of blend components.  $\Delta H_{\text{mix}}$  can be calculated using Schneier's equation.<sup>48</sup>

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

where  $\Delta H_{\text{mix}}$  is the heat of mixing, subscripts 1 and 2 represent the component polymers, and  $x$ ,  $M$ ,  $\rho$  and  $\delta$  respectively, are the weight fraction, molar mass of one repeat unit, density, and solubility parameter of the component polymers. Value of solubility parameter  $\delta$  for PMAA (9.9) has been taken from Brandrupp and Immergut,<sup>49</sup> and that of LOE has been calculated using cohesive energy values of different structural units as given by Hoy<sup>50</sup> and was found to be 8.17. The densities of PMAA and LOE were found to be 1.23 and 0.981 g/cm<sup>3</sup>, 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 PMAA. Using these values, the  $\Delta H_{\text{mix}}$  was calculated with PMAA and

LOE alternately as component 1 for different composition of the blend and the same were plotted against increasing wt % of PMAA/LOE as component 1 of the blend in Figure 6. It was observed by Schneier<sup>48</sup> that the components were miscible if  $\Delta H_{mix}$  was lower than  $10 \times 10^{-3}$  cal, uniformly for all compositions. Figure 6 shows that  $\Delta H_{mix}$  values for different compositions of the blends are higher than  $10 \times 10^{-3}$  cal, except for compositions with higher than 80 wt % of PMAA as component 1. The  $\Delta H_{mix}$  values for different compositions of the blend, with LOE taken as component 1, were found to be higher than  $10 \times 10^{-3}$  cal. The blend composition showing  $\Delta H_{mix}$  values lower than  $10 \times 10^{-3}$  cal are found to show  $\Delta H_{mix}$  values much higher than  $10 \times 10^{-3}$  cal when the order of the components in the calculation is reversed. The above observations confirm incompatibility of the LOE with PMA in solid phase.

### Thermal analysis

The DSC thermogram of pure PMAA [Figs. 7(a-c)] shows a  $T_g$  at 174°C, followed by an endothermic event spanning between 180 and 255°C. The PMAA-LOE blend containing 60% PMAA [Fig. 7(c)] gives  $T_g$  at 174°C. However, the endothermic peak in this case spans over a larger temperature range, from almost 180 to 280°C. This may be due to the presence of LOE with PMAA in the blend. Likewise, in the LOE blend of composition 40% PMAA [Fig. 7(b)], the  $T_g$  is observed at 175°C, while in this case the following endothermic peak extends over the temperature range 180–280°C. It is observed that the glass transition temperature of PMAA does not change on mixing with LOE, showing that the two components are not miscible/compatible in the solid phase.

### Morphological studies

The SEM micrograph of the blend of composition LOE : PMAA, 60 : 40 (40% PMAA), and 40 : 60 (60%

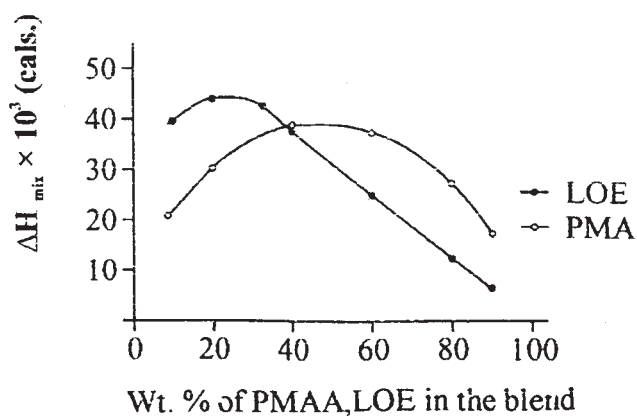
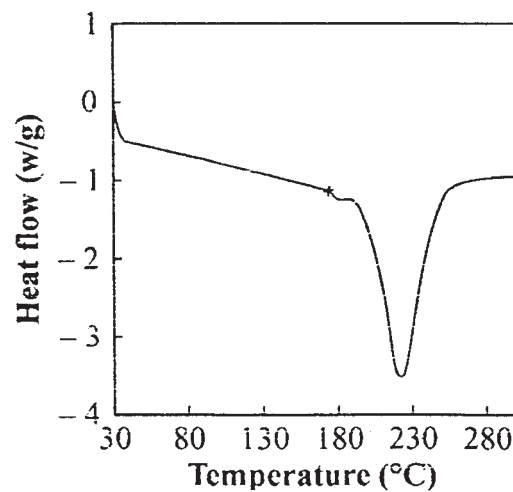
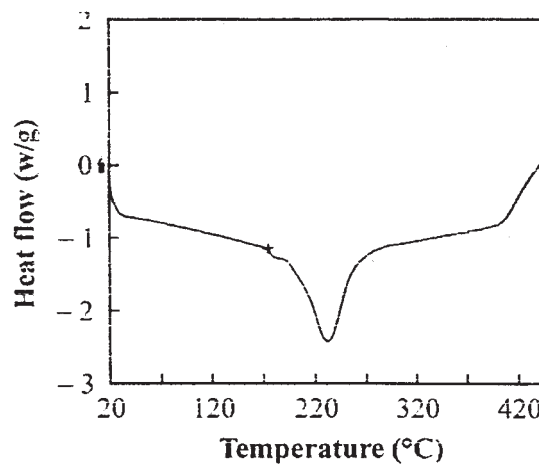


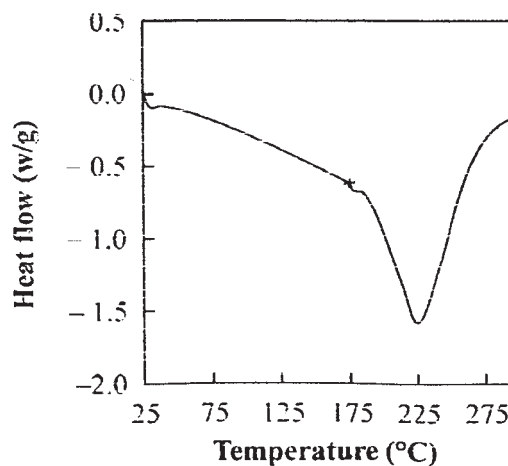
Figure 6 Variation of  $\Delta H_{mix}$  with composition of blend.



(a)

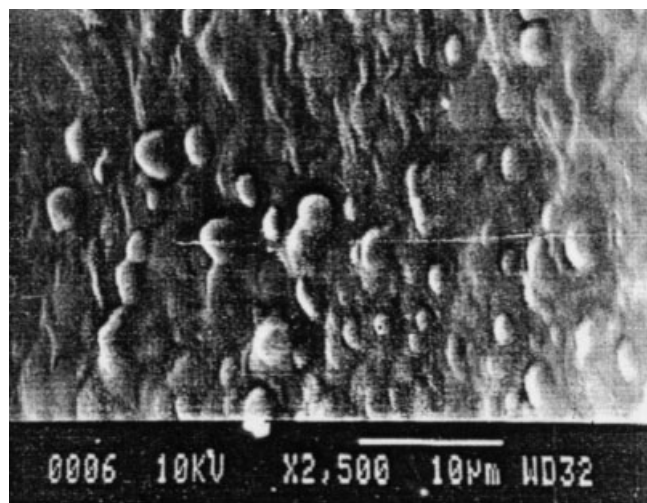


(b)

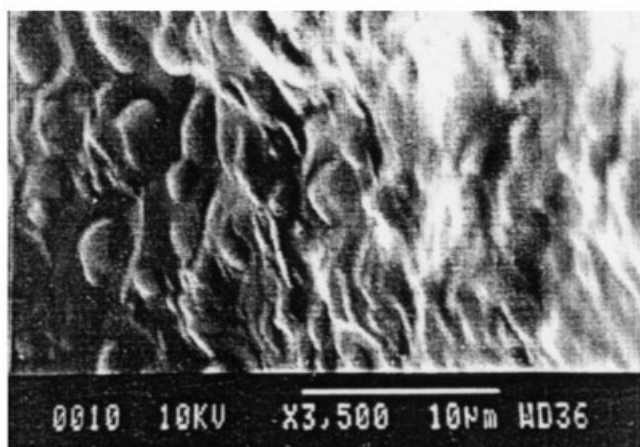


(c)

Figure 7 (a) DSC thermogram of pure PMAA. (b) DSC thermogram of the blend composition LOE : PMAA, 40 : 60. (c) DSC thermogram of the blend composition LOE : PMAA, 60 : 40.



(a)



(b)

**Figure 8** (a) SEM micrograph of the blend composition LOE : PMAA, 60 : 40. (b) SEM micrograph of the blend composition LOE : PMAA, 40 : 60.

PMAA), were recorded. The SEM micrograph of the blend with 40% PMAA [Fig. 8(a)] shows globules of 1–3  $\mu\text{m}$  in size distending and separating from the continuous amorphous phase of the blend. It appears that LOE separates as small globules from a homogeneous phase. The LOE is, therefore, immiscible and incompatible with PMAA in solid phase. We have earlier observed that the films were sticky presumably from oozing out of epoxy from films. It appears that in solid phase, as DMSO evaporates, the PMAA molecules come closer to each other, causing inter- and intramolecular hydrogen bond formation between the PMAA molecules, which is much stronger than the hydrogen bonding or electrostatic interaction between the PMAA and epoxy molecules. This causes the release or oozing of epoxy molecules.

The SEM micrograph of the blend with 60% PMAA [Fig. 8(b)] shows the microstructure more clearly than

the previous one. In this case, the microstructure appears to be consisting of elongated fibers throughout the bulk. The fibers are both straight and tilted. The micrograph clearly shows two phases, indicating that the blend is heterogeneous and incompatible in solid phase. From the above observations, it can be concluded that these blends are incompatible in solid phase, as was predicted from the film study.

## CONCLUSIONS

Blends of LOE with PMAA were found to be semi-compatible in solution phase by ultrasonic velocity, viscosity, and density measurements. The films were slightly translucent, flexible, and sticky, having poor stiffness. Thermal analysis as well as morphological investigations indicates that the blends are incompatible in solid phase.

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