Studies on Miscibility of Dehydrated Castor Oil Epoxy Blend with Poly(methyl methacrylate)

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ABSTRACT: Oil epoxies can be used as plasticizers in the processing of hard polymers. For this purpose dehydrated castor oil epoxy (DCOE), a product from sustainable resource, has been chosen for blending with poly(methyl methacrylate) (PMMA) to investigate the compatibility of this blend pair. Blends of DCOE/PMMA were prepared in the weight ratios 80/20, 60/40, 40/60, and 20/80 through solution method by mixing in dimethylsulphoxide. Freestanding films of the blend were cast and the miscibility of the two components was investigated by viscosity and ultrasonic measurements, which provided valuable informa-

tion on the degree of compatibility of the pairs of blends in solution. The compatibility was also examined by differential scanning calorimetry and scanning electron microscopy. All the studies revealed that DCOE was immiscible with PMMA. However, the appearance and texture of the films were not found to show any visible change over several months, which indicates stability of this blend system. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3094–3100, 2006

Key words: poly(methyl methacrylate); dehydrated castor oil epoxy; sustainable resource; missibility; blend

INTRODUCTION

Blending of polymers has been actively investigated for improving the physical and mechanical properties of commercial polymers and has found a place in several reviews and monographs.[1–3] Blends are expected to show superior properties to the component polymers.[4] Since blending is a physical technique it is simpler and more cost effective. Performance of the blend depends upon the miscibility/compatibility of the blend components. The development of final properties of the blend is related to the degree of miscibility of blend components. Although even incompatible or semicompatible blends have found commercial applications, the compatibility of components or homopolymers in a blend is most desirable because of homogeneous mixing on the molecular level resulting in superior properties and uniform change in physical and mechanical properties with changes in composition. The examination of miscibility of any pair of polymers, therefore, is a necessary step in the search of a polymer for the modification of the properties of a commercial polymer. It is all the more important because most polymer pairs have been found to be immiscible.[5]

Poly(methyl methacrylate) (PMMA) is foremost an optical material. However, it has poor impact resis-

tance and high brittleness. Considerable attempts have been made to improve upon its undesirable mechanical properties, while retaining its high optical characteristics, through the formation of miscible and compatible blends.[6,7] As immiscibility of any blend component with PMMA will cause impairment of its transparency, the investigation of miscibility of any polymer with PMMA is, therefore, required in the first place.

Miscibility of PMMA has been extensively investigated with polymers; a few typical examples of polymers showing compatibility or miscibility and conditional miscibility are nitrocellulose,[8] polyvinylidine fluoride,[8] and poly(styrene-*co*-acrylonitrile).[8] A large number of polymers and copolymers, for example, poly(vinylacetate),[8] poly(isobutene),[8] poly(methystyrene),[8] poly(ethylene-*co*-vinylacetate),[8] and poly(butadiene-*co*-styrene)[8] have been found to show immiscibility. Lately, the miscibility of PMMA has been investigated with poly(styrene-*co*-acrylonitrile),[9,10] poly(α-methylstyrene-*co*-acrylonitrile),[11] poly(*p*-methylstyrene-*co*-acrylonitrile),[12] and poly(*p*-methylstyrene-*co*-methacrylonitrile).[13] The first polymer showed miscibility while the others showed miscibility windows. Poly(bisphenolA-carbonate), which possesses high ductility and glass transition temperature, has been extensively investigated for blending with PMMA to improve its mechanical and thermal properties.[14–16] It has been found to provide miscible blend only in tetrahydrofuran.

Alternative attempts have also been made to overcome the problem of immiscibility by blending hard

polymers with smaller molecules, such as plasticizers, which is one of the important and effective techniques to improve the toughness, flexibility, and tensile strength of commercial polymers.[17] The use of petroleum-based plasticizers, such as dibutyl sebecate, dioctyl phthalate, and tricrysyl phosphate to modify the properties of poly(vinyl chloride) and other commercial polymers[18] is a case in point. Unlike macromolecules, these additives or plasticizers with low molar mass are required to be miscibile for being effective in modifying the properties of the commercial polymer and also for obviating the migration of the former.

The concern for safety of environment and the conservation of petroleum has brought about the priority and significance of polymers and additives synthesized from renewable resources, particularly from vegetable oils–a sustainable resource. Lactose,[19] starch acetate,[20] and starch cinnamate[21,22] have been used to modify the properties of poly(vinylchloride), PMMA, and other polymers. Epoxy derived from soyabean oil has widely been used as plasticizer.[23]

In view of the commercial significance of poly(methyl methacrylate), we have attempted to study its miscibility with dehydrated castor oil epoxy, a material of low molar mass derived from a sustainable resource, by the methods of viscosity and ultrasonic measurement in solutions and scanning electron microscopy and differential scanning calorimetry in films. The improvement in the properties of PMMA upon blending with dehydrated castor oil epoxy (DOCE) may lead to the utilization of renewable resource into useful commercial products.

EXPERIMENTAL

Materials

Dehydrated castor oil (DCO) was 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 it before use. PMMA was synthesized from methylmethacrylate monomer (Aldrich) in the laboratory by a standard method. Molecular weight of the polymer was determined by viscosity measurement. Molecular weight of PMMA was found to be 2.3 $\times 10^5$ Da. PMMA was further purified by a solvent–nonsolvent method. DCOE was prepared after a reported method,[24] which yielded DCOE of epoxy equivalent 260. This shows 6.1% epoxidation of DCO.

Blending

The blends of DCOE with PMMA were prepared by mixing the epoxy and the polymer in weight ratios DCOE : PMMA, 80 : 20, 60 : 40, 40 : 60, 20 : 80, and 0 : 100 by taking the requisite amounts of the of two components to obtain 100 mL of 6, 4, and 2 wt % solutions of the blend in dimethyl sulfoxide (DMSO) (Merck, A.R. Grade).

All solutions were thoroughly mixed by agitation on a magnetic stirrer for 2 h. Selected samples were kept for over 1 week. Appearance of turbidity or precipitation was not noticed in any case.

Film preparation

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

Experimental investigations of the blend systems

Blends were studied experimentally by viscosity measurement, ultrasonic velocity measurement, differential scanning calorimeter (DSC), and scanning electron microscopy (SEM). DSC thermograms were recorded on differential scanning calorimeter, model Dupont 910 TA Instruments, USA, in N_2 atmosphere at a heating rate of 10°C min^{-1}. Viscosity of the blend solutions was measured at temperatures 20, 30, and 40°C (accuracy ±0.05°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, 30, and 40°C 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 were measured at the above temperatures by a pycnometer. The morphology of a cross section of the cryogenically fractured blend films was examined by the 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 measurement

Kulshrestha et al.[25] and Mamza and Folaranmi[26] have observed that the plot of the relative viscosity of the blend solutions against their composition is linear when the components are compatible or completely miscible. When the plots are nonlinear or S-shaped, the components are incompatible with reversal of phase at intermediate composition. Figure 1 shows that the variation of relative viscosity of 2 and 4 wt % solutions of blends of PMMA with DCOE against blend composition. The plot appears to be S-shaped
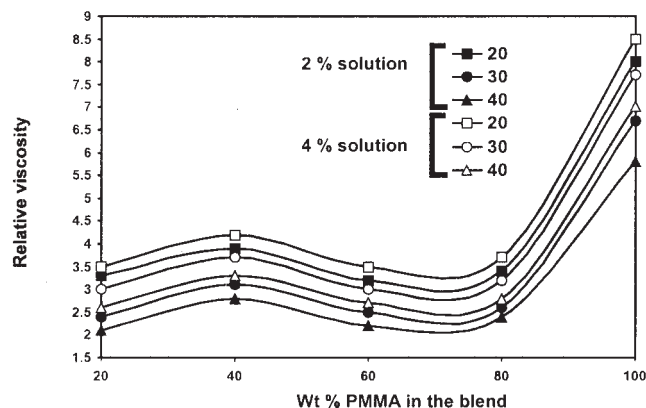
Figure 1 Effect of varying compositions of DCOE : PMMA blend on the relative viscosity of 2 and 4 wt % solutions.

for both 2 and 4 wt % blend solutions. DCOE, therefore, makes an immiscible pair with PMMA. In the temperature range 20–40°C, the shapes of the curves in Figure 1 are similar, which indicates that the nature of interactions, definitely repulsive, between two components, remain same.

The miscibility of the DCOE with PMMA can 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.

Williamson and Wright[27] and Paladhi and Singh[28,29] have observed that the reduced viscosity of blend compositions follows the simple additive rule of mixture when the polymers are miscible. Figures 2 (a) and 2(b) show the plots of calculated and observed reduced viscosity against varying compositions of blends of concentrations of 2 and 6 wt %, respectively. At both the concentrations observed values of reduced viscosity are higher than the calculated values of the reduced viscosity for the blends with 20–50 wt % of PMMA, but beyond this composition for blends with higher weight percent of PMMA, the observed values of reduced viscosity are lower than the calculated ones. The above behavior clearly shows phase inversion in the blend system and their mutual immiscibility. Since in the blend with higher wt % of DCOE observed values of reduced viscosity are higher than the calculated values, it appears that some interaction occurs between the two components. Paladhi and Singh[29] observed a similar deviation of the observed values of reduced viscosity from the calculated values in poly(ethylene oxide) and poly(vinyl alcohol) in water[29] and also in poly(acrylic acid) and poly(vinyl pyrrolidone/polyvinyl alcohol).

It is interesting to compare the observed and calculated values of reduced viscosity of the same blend composition against varying concentrations of its solutions (Figure 3(a and a′), (b and b′), and (c and c′).
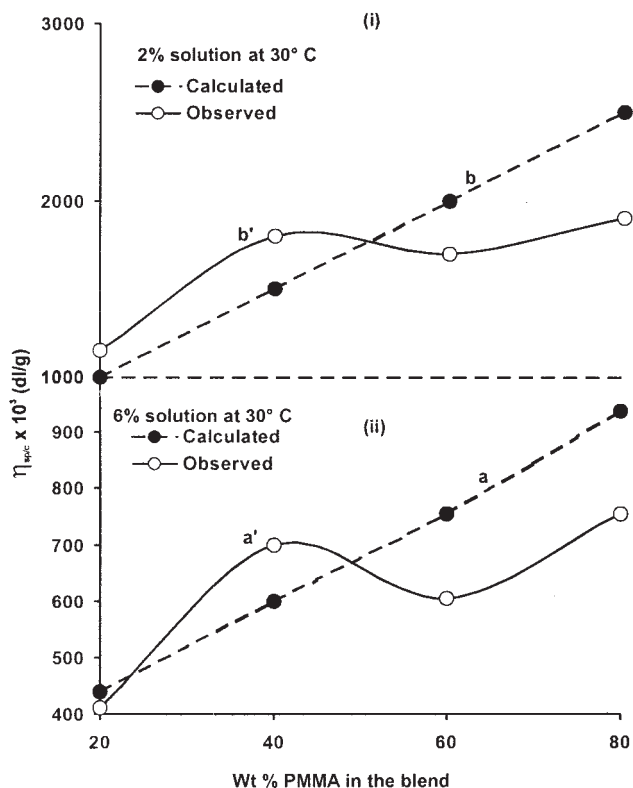

Figure 2 Variation of reduced viscosity with composition of blend.

For blend compositions DCOE : PMMA, 80/20 and 60/40, the observed values of reduced viscosity are higher than the calculated values but, for the blend composition DCOE : PMMA, 40/60, the behavior is reversed. This shows crossover of reduced viscosity with a change in the composition of the blend, signifying phase inversion and immisciblity of the DCOE with PMMA.

Ultrasonic velocity measurements

The miscibility of DCOE : PMMA blends has also been investigated by ultrasonic velocity measurements. Fig-
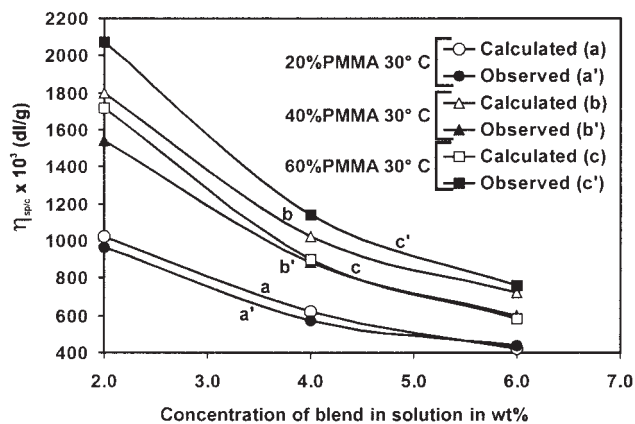

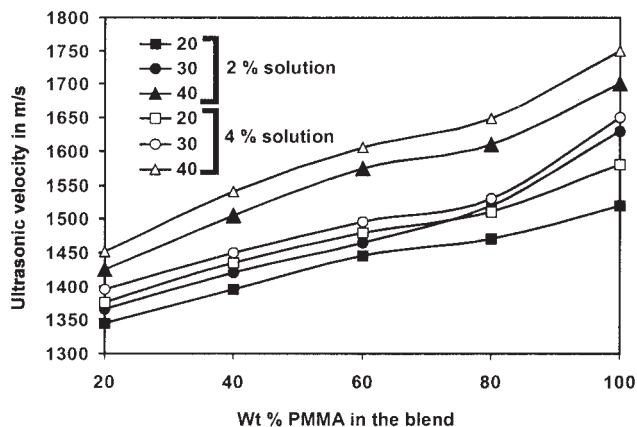**Figure 3** Variation of reduced viscosity of the concentration of the blend.

Figure 4 Effect of varying compositions of DCOE : PMMA blend on the ultrasonic velocity of 2 and 4 wt % solutions.

Figure 6 Variation of ΔH_{mix} with composition of the blend.

ure 4 shows the plots of ultrasonic velocity against different compositions of DCOE : PMMA blend in 2 and 4 wt % solutions at 20, 30, and 40°C. All of the plots in Figure 5 are nonlinear. It is well established that, for a miscible solution, the ultrasonic velocity varies linearly with compositions at all concentrations and temperatures.[28,30,31] Since the plots in Figure 6 at different concentrations and temperatures are nonlinear, the DCOE : PMMA blend pair is immiscible. At blend composition DCOE : PMMA, 60/40, steep inflection occurs in all the plots in Figure 6, which is evidence of phase inversion/phase separation. Thakore et al.[20] have also observed the nonlinear relationship between ultrasound velocity and compositions for the immiscible starch cinnamate/PVC blend.

We notice in Figure 7 that density of the blend solution increases sluggishly in more or less linear fashion with the increase in wt % PMMA in the blend. This behavior will cause the ultrasound velocity to increase more or less in a similar fashion with increasing wt % of PMMA in the blend. Compared to this
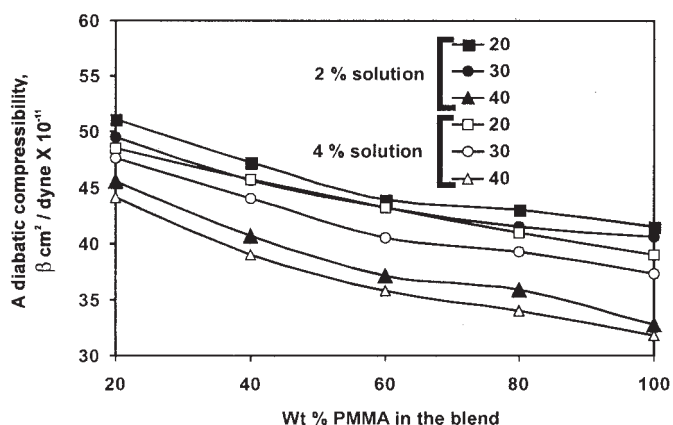
behavior, the ultrasound velocity increases more steeply and at blend composition DCOE : PMMA, 60/40, an inflection occurs in all cases in Figure 4. It can, therefore, be concluded that structural features of the blend markedly influence the ultrasound velocity and beyond the inflection point the structural features of the blend change, which indicates phase separation or phase inversion.

Using ultrasound velocity, adiabatic compressibility of the system can be calculated by the following equation:[32]

$$\beta = \frac{1}{v^2 \rho}$$

where β is the 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.[33] Figure 5 shows the variation of adiabatic compressibility in the DCOE : PMMA blend with increasing wt % of PMMA in the blend. Figure 5 shows more than

Figure 5 Effect of varying compositions of DCOE : PMMA blend on the adiabatic compressibility of 2 and 4 wt % solutions.
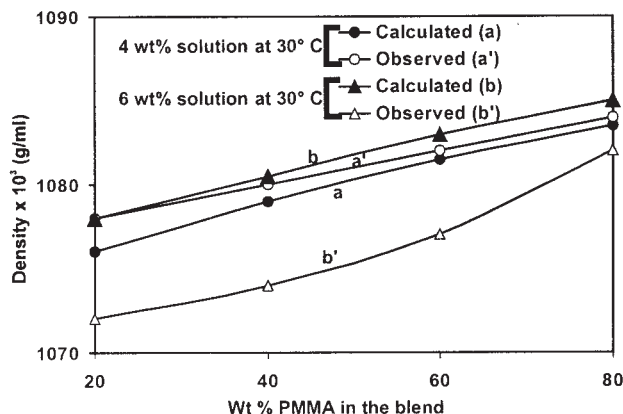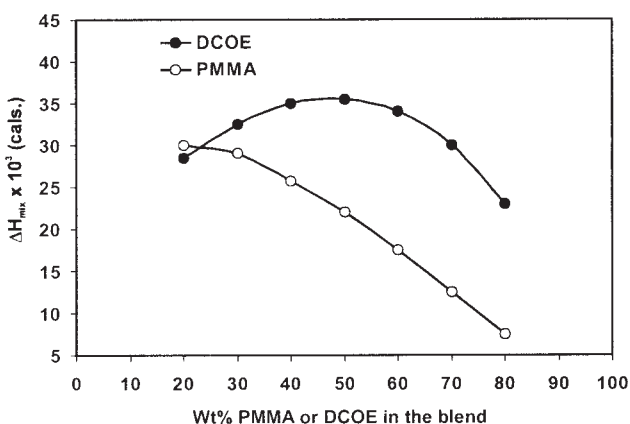

Figure 7 Variation of density with composition of the blend in solution.

one inflection in all cases, but the one is more pronounced at composition 60/40, DCOE : PMMA. This indicates the change in the structural features of the blend with changes in the blend composition, leading to the conclusion that phase inversion or phase separation occurs in this blend system.

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[20,34] or to be lower than the latter.[18,19] Those of miscible blends have been found to be up to 5% larger than the calculated densities.[35] Higher observed densities than the calculated ones show mutual interaction and consequently miscibility. Figure 7 shows the plots of calculated and observed densities of DCOE : PMMA blends against composition in 2 and 6 wt % solutions at 30°C. In 2 wt % solutions, the observed densities are insignificantly higher than the calculated densities (<0.5%) while, in 6 wt % solution, the former is lower than the latter. The density measurement therefore also shows immisciblity of the DCOE with PMMA.

Film study

DCOE : PMMA films of composition DCOE : PMMA, 1 : 0.66 (40% PMMA), DCOE : PMMA, 1 : 1.5 (60% PMMA), and DCOE : PMMA, 1 : 4 (80% PMMA) were cast on transparency sheets from solutions of the blends in DMSO. Films of blend with 40% PMMA were found to be opaque, hard, and tough. Blend with 60% PMMA gave film that was found to be opaque, hard, and brittle. The toughness (manual observation) of the film of this composition was found to be less than the previous composition. The films of the blend containing 80% PMMA were found to be opaque and highly brittle. Its toughness was also found to be less than that of the films of the previous compositions. It appears that the toughness of the film decreases as the ratio of PMMA increases.

It is noticed that the blends having as high as 60% DCOE show good toughness. We have also noticed that the films do not show any change in texture and physical properties on storage over several months.

Heat of mixing, ΔH_{mix}

The two components in the blend will be thermodynamically miscible if ΔG_{mix} is negative. Since entropy of mixing of polymers has insignificant value, ΔG_{mixing} therefore depends upon ΔH_{mixing}. The latter may, therefore, be taken to approximate the former.[36] The ΔH_{mixing} values are therefore indicative of miscibility
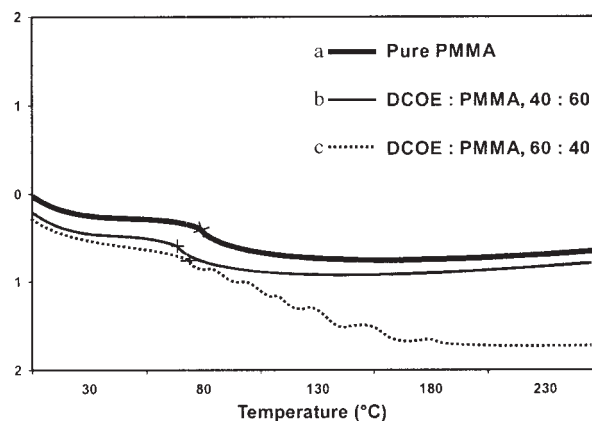

Figure 8 DSC thermogram of the DCOE : PMMA blend.

of blend components. ΔH_{mix} can be calculated using Schneier's equation:[37]

$$\Delta H_{mix}\left\{x_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 \right.$$

$$\left. \times \left[\frac{x^2}{(1-x_2)M_2\rho_2 + (1-x_1)M_1\rho_1}\right]^2\right\}^{1/2}$$

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. The value of solubility parameter δ for PMMA, 9.25, has been taken from Brandrupp and Emergut,[38]; that of DCOE has been calculated using cohesive energy values of different structural units as given by Hoy[39] and was found to be 8.04. The densities of PMMA and DCOE were found to be 1.19 and 0.995 g/cm³, respectively. The molar mass of DCOE was taken to be that of one epoxidized fatty acid chain, equal to 308.6 g to normalize the molar mass of DCOE with that of a repeating unit of PMMA. Using these values, the ΔH_{mix} was calculated with PMMA and DCOE alternately as component 1 for different compositions of the blend and the same were plotted against increasing wt % of PMMA/DCOE as component 1 of the blend in Figure 7. It was observed by Schneier[37] that the components were miscible if ΔH_{mix} was lower than 10×10^{-3} cal uniformly for all compositions. Figure 6 shows that ΔH_{mix} values for different compositions of the blend are higher than 10×10^{-3} cal except for compositions with 70 wt % or higher of PMMA or DCOE as component 1. The blend composition showing ΔH_{mix} values lower than 10×10^{-3} cal are found to show ΔH_{mix} values much higher than 10×10^{-3} cal when the order of the components in the calculation is reversed. The above observations conform with the immiscibility of the
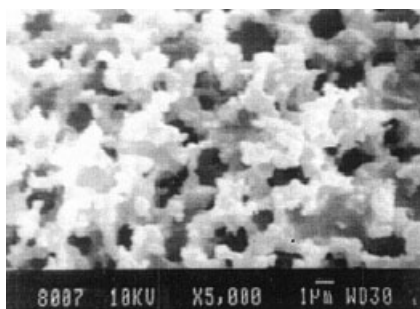
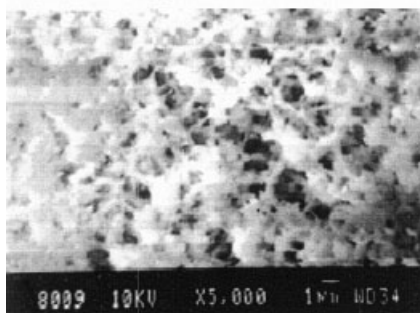Fig. 9. (a) SEM micrograph of the blend DCOE : PMMA, 60 : 40

Fig. 9. (b) SEM micrograph of the blend DCOE : PMMA, 40 : 60

Figure 9 (a) SEM micrograph of the blend DCOE : PMMA, 60 : 40. (b) SEM micrograph of the blend DCOE : PMMA, 40 : 60.

DCOE with PMMA, which has also been observed by viscometric and ultrasonic velocity studies.

Thermal analysis

The DSC thermogram of pure PMMA, as seen in Figure 8(a), shows a tiny inflection at about 80°C, which can be taken as the glass transition temperature of the pure polymer. No thermal event is observed up to almost 230°C. The DSC thermogram of blend composition with 60% PMMA, Figure 8(b), shows a T_g event at about 77°C. The DSC thermogram of the blend composition with 40% PMMA, Figure 8(c), shows a T_g event at about 78°C and several relatively insignificant endothermic events. The disposition of this thermogram clearly shows the complex structure of the blend and the presence of closely related phases/structures engendering numerous endothermic events. It also indicates the largely heterogeneous structure of the blend. We notice little variation in glass transition temperature of the blends, indicating incompatibility of the components in solid phase.

Morphological studies

The SEM micrograph of the fractured surface of the film of the blend DCOE : PMMA, 60 : 40, Figure 9(a), at magnification ×5,000 shows large agglomerates of a polymer phase lying over the layers of a different phase of the polymer agglomerates (appearing white

and dark in the SEM micrographs). The agglomerates extend to several microns. The structure is therefore heterogeneous and incompatible in the solid phase. The macrodomains of the two phases in the blend appear to be responsible for the intricate DSC profile of this blend. The macrodomains are also responsible for the opaqueness of the blend films as well as their stiffness. The SEM micrograph of fractured surface of the film of the blend DCOE : PMMA, 40:60, Figure 9(b), shows two phases in the blend, one appearing white and the other gray in the micrograph. In this case the agglomerates are of smaller sizes and the two phases in this blend appear to be uniformly dispersed. The macrodomains in this case are of a few micron sizes and are much smaller than the domains observed in the previous composition. The SEM micrographs clearly show the heterogeneity of the phases and hence the immiscibility of DCOE with PMMA.

CONCLUSIONS

Blends of PMMA with DCOE were found to be immiscible in solution by viscosity and ultrasonic velocity measurements. It was found that the toughness of these blends decreased with the increasing amount of PMMA. Thermal analysis as well as morphological investigations indicate that the blends are immiscible in solid phase. The films of the blend of different compositions were not found to undergo any change in appearance, texture, and physical properties over a long storage period, showing that the structure/microstructure of these blends is stable.

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