Miscibility of poly(methylmethacrelate) and cellulose acetate butyrate blends in dimethyl formamide

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The miscibility of poly(methylmethacrelate) (PMMA) and cellulose acetate butyrate (CAB) blends in dimethyl formamide (DMF) have been investigated by viscosity, density, refractive index and ultrasonic velocity studies. The polymer-solvent and blend-solvent interaction parameters and heat of mixing have been calculated using the viscosity, density and ultrasonic velocity data. The results indicated the existence of positive interactions in the blend polymer solutions and that they are miscible in dimethyl formamide in the entire composition range between 303-323 K. The study also revealed that variation in the temperature does not affect the miscibility of PMMA and CAB blends in DMF significantly. The presence of hydrogen bonding in the blends in the solid state has also been indicated by FTIR studies. SEM images also supported the miscibility of blends.

Keywords: Polymer solutions, Ultrasonic velocity, Viscosity, Interaction parameter, Polymer blends, Miscibility, PMMA, CAB, DMF

The study of miscibility and interactions present in polymer and solvent in a polymer blend solution system is of great significance for engineering applications of polymers. They also provide substantial information on the processes involving polymer production and their uses[1,2]. Polymer blends are physical mixtures of structurally different polymers or copolymers, which interact through secondary forces with no covalent bonding that are miscible at molecular level. The basis of polymer-polymer miscibility may arise from any specific interaction, such as hydrogen bonding, dipole-dipole forces or charge transfer interactions in the system[3,4]. Polymer blend miscibility has been studied widely using a large number of techniques[5-9].

A review of literature suggested that no previous studies have been done on the miscibility of poly(methylmethacrelate) (PMMA) and cellulose acetate butyrate (CAB) in dimethyl formamide (DMF). Hence as a part of research program on polymer blends and solutions[10,11], miscibility behaviour of PMMA and CAB blends in DMF has been presented in this paper. The choice of the polymers is due to their pharmaceutical, biomedical and industrial applications[12,13]. Further, it may also be noted that the polymers containing polar groups with a susceptibility to act as proton donors were found to be miscible with those having a tendency to act as proton acceptors due to a specific interaction like hydrogen bonding. With the $-CO-$ group in PMMA which can function as a proton acceptor and CAB with its $-OH$ group functioning as weak proton donors, one may expect miscibility in PMMA/CAB blends. The structures of PMMA and CAB are shown in Fig. 1.

Experimental Procedure

Materials

PMMA (molecular weight, 75000; Alfa Aesar) and CAB (molecular weight, 70,000; Alfa Aesar) were used as received. DMF (Merck) was distilled before use.

Preparation of polymer solutions

Dilute solutions of 2% (*w/v*) PMMA and CAB in DMF were prepared separately in different stoppered conical flasks. Solutions of lower concentrations were then prepared by appropriately diluting these stock solutions with DMF. Similarly different CAB/PMMA
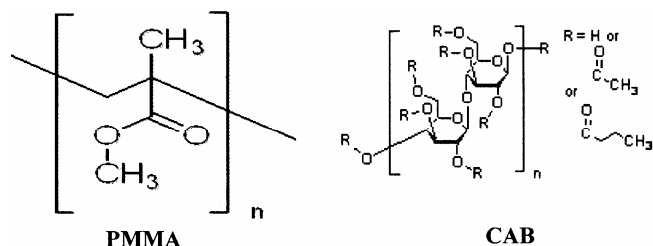

Fig. 1 — Structures of PMMA and CAB

blend compositions of 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10 ratio, along with the pure polymer solutions in DMF at nine concentrations between 0.05 to 1.2% (*v/v*) of the blends as well as pure components were prepared by mixing appropriate quantities of stock solutions of PMMA and CAB.

Preparation of the blend films

The blend solutions prepared as stated above were cast on clean teflon dish. Films were dried initially at room temperature and were then kept in a vacuum oven at 40°C for 48 h to remove any residual DMF traces. The complete removal of DMF has also been confirmed by FTIR spectra of the films. The absence of N−C=O bending and C-N stretching frequencies at 600 and 1300 cm^{-1} respectively indicate the absence of DMF in the blend film.

Solution and solid state property measurements

The densities of individual and blend polymer solutions in DMF were measured with a Mettler-Toledo Digital density meter model Densito 30 PX. The temperature of the measurement was within an uncertainty of ±0.1°C. The instrument was calibrated with standard density water supplied with the instrument. The estimated error in the density measurement was within ±0.05%. Dilute solution viscosities of PMMA, CAB and their blend solutions were measured at different temperatures using an Ubbelhode viscometer with an accuracy of ±0.1%. Solution viscosities at different temperatures were determined by equilibrating the viscometer tube in a thermostat maintained at a desired temperature for about 10 min before the flow time measurement. The temperature of the bath was kept constant within an accuracy of ±0.1°C. Ultrasonic velocity measurements were carried out on a fixed frequency continuous wave ultrasonic interferometer (Model F81, Mittal Enterprises, New Delhi) operating at 2 MHz using the standard procedure. The error in the measurement of ultrasonic velocity was within ±0.1%. Measurements at different temperatures were carried out by circulating water at required temperatures from a thermostatic bath, inside the double walled jacket covering the interferometer cell. The accuracy of temperature maintenance was within ±0.1°C. The refractive index values of polymer solutions were measured with a Mettler Toledo Refractometer model Refracto 30 GS. The uncertainty in the values was within ±0.0001 units at all the temperatures. At least three independent readings of

all the physical properties were taken for each mixture. The average of these values was used for the data analyses.

FTIR, SEM and differential scanning calorimetry (DSC)

FTIR measurements of the polyblend films were carried out at room temperature using a NICOLET AVATAR 330 FTIR spectrometer. SEM images of the blend films were recorded on a JEOL Scanning electron microscope. DSC measurements were carried out on a DSC SP model instrument (Rheometric Scientific, Ashtead, UK) on the fabricated films of PMMA, CAB, and their blends. Measurements were performed over a temperature range of 25-150°C at a heating rate of 10°C/min under the nitrogen atmosphere.

Results and Discussion

Solution property studies

Viscosity of the blend solutions were measured at 303, 313 and 323K for different CAB/PMMA blend compositions of 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10 ratio, along with the pure polymer solutions in DMF at nine concentrations between 0.05 to 1.2% (*v/v*) of the blends as well as pure components. Density, refractive index and ultrasonic velocity of the polymer solutions were measured at three different temperatures indicated above for all the CAB/PMMA compositions at a concentration of 1% (*v/v*).

From viscosity data, relative and reduced viscosities of the polymer solutions have been calculated and plotted against composition/solution concentration (Figs 2-3). The plot of relative viscosity versus blend composition (Fig. 2) was linear for the
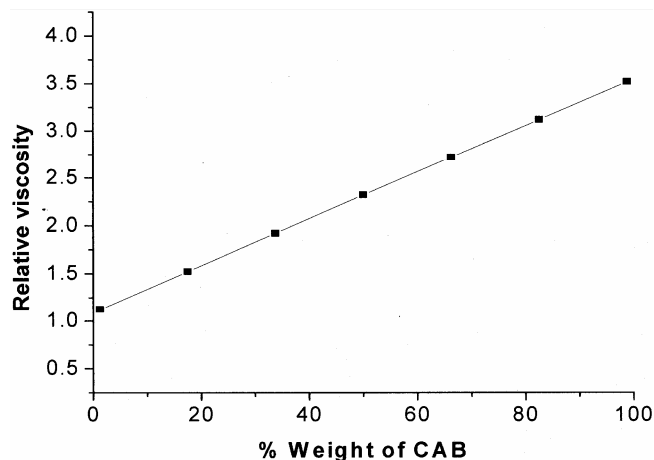
Fig. 2 — Relative viscosity versus composition of PMMA/CAB blends at 303 K

entire composition range. This behaviour is characteristic of a miscible blend system[14-16]. The plots of reduced viscosities of the component polymers and their blend compositions versus concentrations at different temperatures (Fig. 3) were also linear without any cross over indicating that the blends are miscible. A sharp cross over in the plots of reduced viscosity versus concentration is generally shown by immiscible blends[3].

The interaction parameter of the component polymers and their blend compositions have been found out from the plots of the reduced viscosity versus concentration and are given in Table 1. The slope of the curve gives the corresponding interaction parameter value, which has been evaluated on the basis of classical Huggins equation[17,18]. Krigbaum and Wall[14] interaction parameter Δb of the blends has been obtained from the difference between the experimental and theoretical values of the interaction
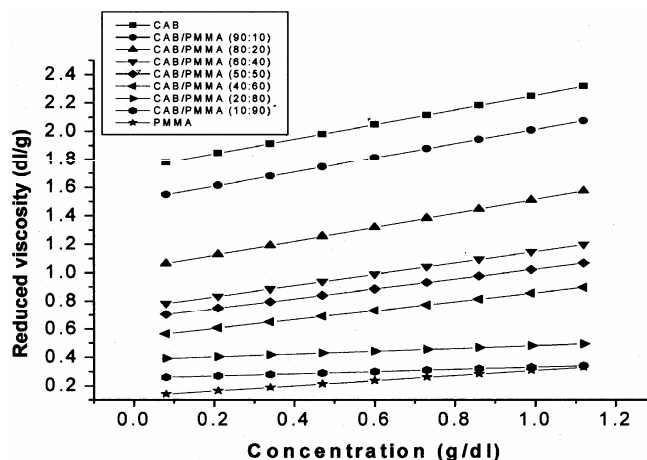
parameters b_{12} and b_{12}^*. Polymer 1-polymer 2 interaction parameter Δb can be calculated as follows:

$$\frac{(\eta_{sp})_m}{C_m} = (\eta)_m + b_m C_m \qquad \ldots(1)$$

where C_m is the total concentration of polymers $C_1 + C_2$, $(\eta_{sp})_m$ is the specific viscosity and b_m represents the global interaction between all polymeric species defined by the equation,

$$b_m = X_1^2 b_{11} + 2 X_1 X_2 b_{12} + X_2^2 b_{22} \qquad \ldots(2)$$

where X_1 and X_2 are weight fractions of polymer 1 and polymer 2 respectively, b_{12} is the interaction parameter of the blend system which can be calculated from Eq. (2) and b_{11} and b_{22} are respective individual interaction parameters. The interaction parameters b_{11}, b_{22} and b_m have been calculated from the slopes of the plot of reduced viscosity versus concentration[16]. The interaction parameter b_{12}^* was then calculated theoretically by using equation,

$$b_{12}^* = (b_{11}b_{22})^{1/2} \qquad \ldots(3)$$

The difference (Δb) calculated from the theoretical b_{12}^* from Eq. (3) and the experimental b_{12} with Eq. (2) is given as,

$$\Delta b = (b_{12} - b_{12}^*) \qquad \ldots(4)$$

If $\Delta b > 0$, blends are miscible; and if $\Delta b < 0$ phase separation occurs. It has been found that Δb values are positive (Table 2) for all blend compositions and at all studied temperatures. This suggests that the blends are

Fig. 3 — Reduced viscosity versus concentration of PMMA/CAB blends at 313 K

Table 1 — Intrinsic viscosity and slope of reduced viscosity versus concentration plots of PMMA/CAB blends and individual solutions at different temperatures

CAB/PMMA (v/v)	Intrinsic viscosity (dl/g) at 303K	Slope of red viscosity vs. concentration curve at 303K	Intrinsic viscosity (dl/g) at 313K	Slope of red viscosity vs. concentration curve at 313K	Intrinsic viscosity (dl/g) at 323K	Slope of red viscosity vs. concentration curve at 323K
0/100	0.209	0.030	0.113	0.076	0.213	0.040
10/90	0.392	0.026	0.168	0.191	0.412	0.030
20/80	0.502	0.082	0.379	0.121	0.419	0.098
40/60	0.665	0.238	0.541	0.318	0.537	0.345
50/50	0.909	0.200	0.676	0.349	0.634	0.408
60/40	0.998	0.387	0.750	0.399	0.702	0.445
80/20	1.449	0.616	1.063	0.559	0.951	0.525
90/10	1.639	0.679	1.552	0.417	1.116	0.543
100/0	1.953	0.752	1.736	0.517	1.190	0.693

completely miscible in the studied range.

Table 2 — Δb and Δk_{AB} values for the PMMA/CAB blends at different temperatures

CAB/PMMA	303 K		313 K		323 K	
(v/v)	Δb	Δk_{AB}	Δb	Δk_{AB}	Δb	Δk_{AB}
0/100	-	-	-	-	-	-
10/90	0.02	0.09	0.10	0.16	0.09	0.38
20/80	0.05	0.25	0.26	0.33	0.09	0.22
40/60	0.06	0.09	0.41	0.41	0.02	0.15
50/50	0.06	0.23	0.52	0.52	0.30	0.20
60/40	0.23	0.28	0.94	1.12	0.21	0.27
80/20	1.25	1.09	1.25	1.84	0.09	0.40
90/10	1.32	1.14	2.14	2.08	0.27	0.51
100/0	-	-	-	-	-	-

Table 3 — μ and α values for the PMMA/CAB blends at different temperatures

CAB/PMMA	303 K		313 K		323 K	
(v/v)	μ	α	μ	α	M	α
0/100	-	-	-	-	-	-
10/90	0.01	0.50	0.19	0.25	0.20	0.23
20/80	0.01	0.59	0.02	0.28	0.03	0.36
40/60	0.02	0.74	0.14	0.18	0.34	0.32
50/50	0.03	0.12	0.15	0.85	0.34	0.19
60/40	0.02	0.13	0.18	0.52	0.31	0.13
80/20	0.08	0.08	0.43	0.11	0.28	0.24
90/10	0.07	0.09	0.47	0.10	0.14	0.06
100/0	-	-	-		-	-

If η_1 and η_2 are sufficiently apart, a more effective parameter μ, defined by Chee[7] can be used to predict the compatibility. The relation is given by,

$$\mu = \frac{\Delta b}{(\eta_2 - \eta_1)^2} \qquad \ldots(5)$$

where η_1 and η_2 are intrinsic viscosities of pure component solutions. The blend is miscible when $\mu \geq 0$ and immiscible if $\mu < 0$. The values of μ, calculated with aforementioned expression at different temperatures for the present system have been presented in Table 3. The results show that the μ values for the system under study are all positive and sufficiently high, indicating the miscibility of the blends in the entire composition range. High value of μ may also be due to specific interaction of hydrogen bonding between the polymers.

Recently, Sun et al.[19] have suggested a new formula for the determination of polymer miscibility as follows:

$$\alpha = K_m - \frac{K_1 [\eta_1]_2^2 W_2^2 + 2\sqrt{K_1 K_2} [\eta]_1 [\eta]_2 W_1 W_2}{\left\{ [\eta]_1 W_1 + [\eta]_2 W_2 \right\}^2} \quad \ldots(6)$$

where K_1, K_2, and K_m are the Huggins's constants for individual components 1 and 2 and the blend, respectively. The long-range hydrodynamic interactions are considered while deriving this equation. They have also suggested that a blend will be miscible when $\alpha \geq 0$ and immiscible when $\alpha < 0$. The α values for the present system at various temperatures have been listed in Table 3. The positive values at all temperatures indicate that the blends are

miscible. Further, to identify the miscibility of blends based on Huggins[17] constant, calculations have also been done. The Huggins constant is a parameter which also could be used to express the interaction between unlike polymers[20]. The k_{AB} value was concerned with b_{AB} as shown in the equations

$$b_{AB} = k_{AB} [\eta]_A [\eta]_B \qquad \ldots(7)$$

and

$$k_{AB} = \frac{b_m - \left(b_A W_A^2 + b_B W_B^2 \right)}{2 [\eta]_A [\eta]_B W_A W_B} \qquad \ldots(8)$$

The factor $k_{AB,}$ is a theoretical value derived from the geometric means of k_A and k_B as

$$k_{AB,t} = \left(k_A k_B \right)^{0.5} \qquad \ldots(9)$$

The deviation from the theoretical value also provides information about the interaction between unlike polymers as shown in

$$\Delta k_{AB} = k_{AB} - k_{AB,t} \qquad \ldots(10)$$

The positive Δk_{AB} value indicates that the polymer mixture in solution-state is miscible. Table 2 shows the Δk_{AB} values for present system, which are positive for all the compositions between 303 and 323 K indicating the miscibility of the blends in this temperature range. Further, the low positive values of Δk_{AB} may also be an indication of the presence of only weak specific interactions in the blend system.

The heat of mixing (ΔH_m) was also used as a measure to study[21-23] the blend compatibility.

According to Schneier[22], ΔH_m of the polymer blends is given by

$$\Delta H_m = \left\{ W_1 M_1 \rho_1 \left(\delta_1 - \delta_2 \right)^2 \right.$$

$$\left. \times \left[\frac{W_2}{(1-W_2)} M_2 \rho_2 + (1-W_1) M_1 \rho_1 \right]^2 \right\}^{1/2} \quad \ldots(11)$$

where W, M, and ρ are the weight fraction of the polymer, the monomer molecular weight, and the polymer density respectively, and δ represents the solubility parameter of the polymer. The δ values of PMMA [9.1(cal/cm^3)$^{1/2}$] and CAB [12.4 (cal/cm^3)$^{1/2}$] were taken from the literature[24], and these values were used to calculate ΔH_m with Eq. (11). Figure 4 shows the variation of ΔH_m versus blend composition. It is evident from the figure that the variation follows almost a linear pattern, without any reversal (increase followed by decrease or vice-versa) in the trend. However, variation of ΔH_m with composition shows slightly deeper change up to 20% CAB composition, compared to other values. This change may be due to the presence of a small component of thermodynamic immiscibility in this region. Further, the heat of mixing calculated at different temperatures did not vary significantly and in fact, as is seen in Fig. 4, the ΔH_m values for various temperatures are overlapping. This behaviour shows that the effect of temperature on miscibility of the blends is not very significant.

Polymer/polymer and polymer blend/solvent interactions

The interaction parameters between polymer and polymer and polymer blend and solvent are a measure of miscibility. The polymer-solvent interaction
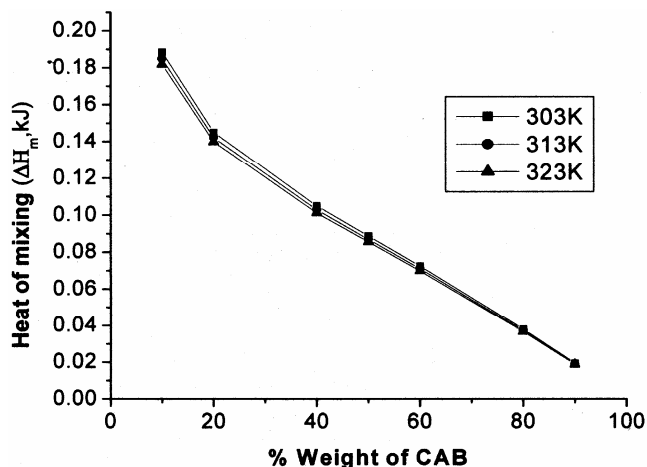
Fig. 4 — Heat of mixing of PMMA/CAB blends at different temperatures

parameters (χ_i) have been computed from Flory-Huggins theory[21] with

$$\chi_i = \left(\frac{V_i}{RT} \right) (\delta_2 - \delta_1)^2 \quad \ldots(12)$$

where δ_1 and δ_2 are the solubility parameter of solvent and polymer, respectively, and V_i, R, and T are the molar volume of the solvent, universal gas constant, and temperature (K), respectively. The same expression has also been used for the calculation of interaction parameter between polymers in polymer blends[25,26]. The blend/solvent interaction parameters have also been calculated according to the method adopted by Singh and Singh[18]. The solubility parameters of the blend (δ) was calculated from the additivity relationship,

$$\delta = X_1 \delta_1 + X_2 \delta_2 \ldots \quad (13)$$

where X_1 and X_2 are the mass fractions and δ_1 and δ_2 are the solubility parameters of the component polymers in the blend system. The interaction parameters of the polymer-polymer blend systems have been presented in Table 4, whereas the blend-solvent interaction parameters are given in Table 5. From these data, it is observed that the net polymer-polymer interactions were higher than those observed for blend-solvent interactions for all the blend compositions at all the temperatures. Such a difference between polymer-polymer interactions and blend-solvent interactions suggested the compatible nature of the blends in the studied range. Similar kind of conclusion has also been drawn by Aminabhavi et al.[27] in the case of PMMA/Polyvinyl alcohol blends in dimethyl formamide.

To confirm the miscibility behaviour of the blends further, the ultrasonic velocity, adiabatic compressibility, density and refractive index values of the blend solutions have been measured at five different temperatures. Adiabatic compressibility has been calculated by using the formula,

Table 4 — Polymer-polymer interaction parameter (χ_i) for CAB and PMMA in the blend

Temperature (K)	Polymer	χ_i calculated from Eq. (12)
303	CAB	0.01
	PMMA	1.16
313	CAB	0.01
	PMMA	1.14
323	CAB	0.01
	PMMA	1.11

$$\beta_{ad} = \frac{1}{v^2 \rho} \qquad \qquad \qquad \ldots(14)$$

Table 5 — Blend-solvent interaction parameters at different temperatures

Temperature (K)	CAB/PMMA (v/v)	δ calculated from Eq. (13)	χ_i calculated from Eq. (12)
303	10/90	9.43	0.92
	20/80	9.76	0.70
	40/60	10.4	0.36
	50/50	10.7	0.23
	60/40	11.0	0.13
	20/80	11.7	0.01
	10/90	12.0	0.01
313	10/90	9.43	0.90
	20/80	9.76	0.69
	40/60	10.4	0.35
	50/50	10.7	0.23
	60/40	11.0	0.13
	20/80	11.7	0.01
	10/90	12.0	0.01
323	10/90	9.43	0.88
	20/80	9.76	0.67
	40/60	10.4	0.34
	50/50	10.7	0.22
	60/40	11.0	0.12
	20/80	11.7	0.01
	10/90	12.0	0.01

where v is the ultrasonic velocity and ρ is the density. Ultrasonic velocity, adiabatic compressibility, density and refractive index of the blend solutions have been plotted against blend compositions at different temperatures (Figs 5-7) and they are found to be linear. For incompatible blend solutions, these plots are non-linear showing distinct phase inversion at intermediate compositions[27-29]. Hence these results provide further supporting evidence for miscible nature of the studied blends in the entire composition range. The miscibility may be due to the presence of intermolecular interactions such as hydrogen bonding between the blend polymers.

FTIR Spectroscopy

To confirm the presence of hydrogen bonding in the blends and hence the miscibility of blends in the solid state, FTIR spectra of the individual and blend polymer films have been measured at room temperature. Although the changes in energies, bond lengths, and electron densities with the formation of hydrogen bonds are actually quite small and about two to three orders of magnitude smaller than typical chemical changes, FTIR spectroscopy is very

sensitive to the formation of hydrogen bond[29,30]. If the groups involved in the hydrogen bond formation in a blend system are carbonyl and hydroxyl moieties,
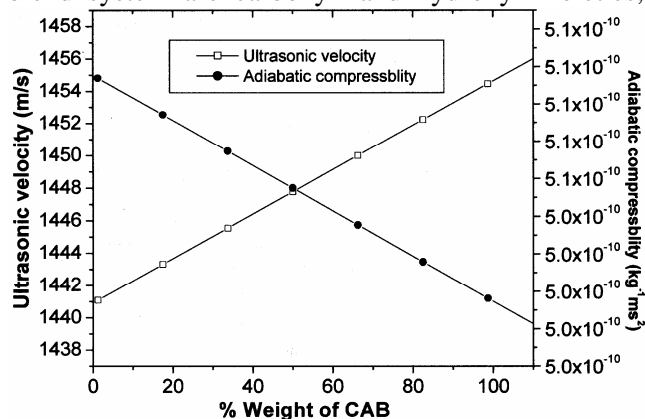

Fig. 5 — Ultrasonic velocity and adiabatic compressibility versus composition of PVC/CAB blends at 303 K
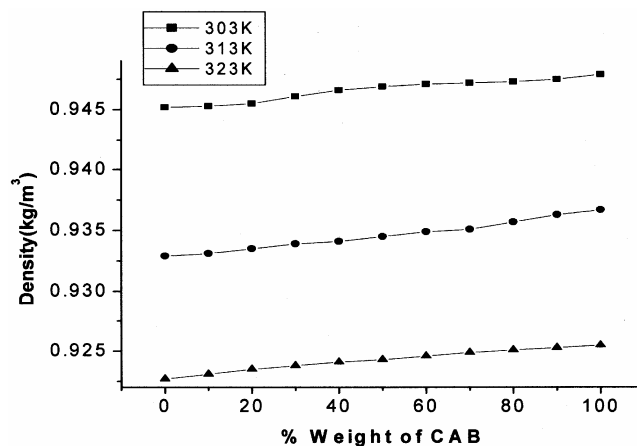

Fig. 6 — Effect of temperature on the variation of density with the composition of 2% (w/v) of PMMA/CAB blend in solution
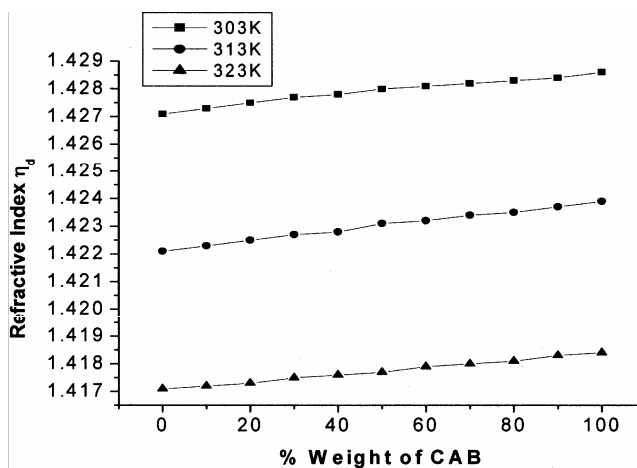
Fig. 7 — Effect of temperature on the variation of refractive index with the composition of 2% (*w/v*) of PMMA/CAB blend in solution at different temperatures.
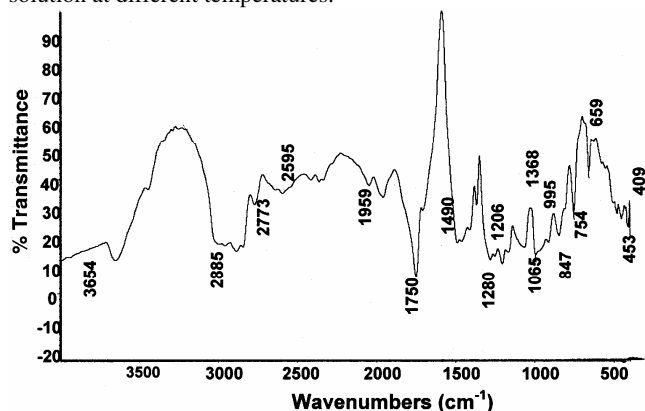

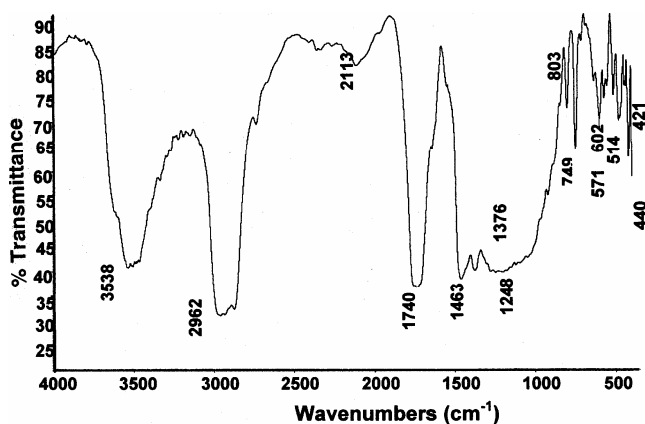Fig. 8 — FTIR spectrum of polymethylmethacrelate

Fig. 9 — FTIR spectrum of (50/50) PMMA/CAB blend

exhibit a single T_g and the T_g values are also intermediate the T_g s of the pure blend components. Such a behaviour is indicative of the miscibility of the blends[27,32].
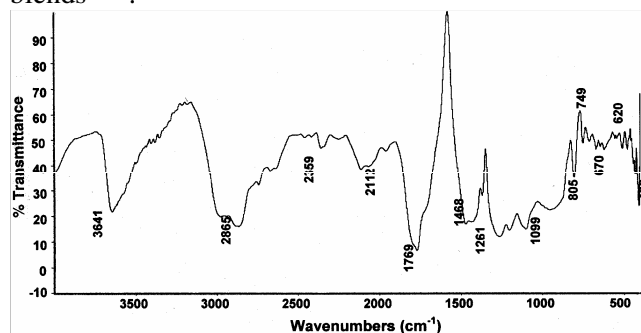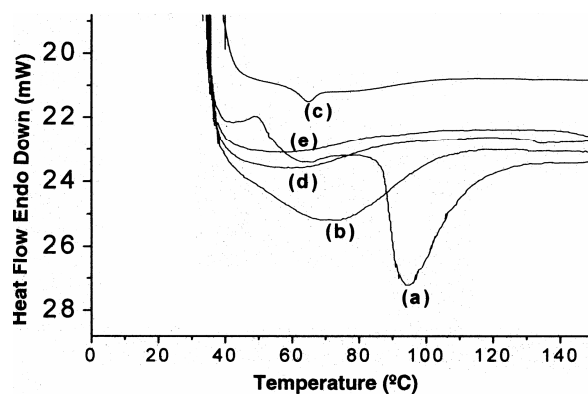

Fig. 10 — FTIR spectrum of CAB

Fig. 11 — DSC thermograms: (a) pure PMMA, (b) 70:30 PMMA/CAB, (c) 50:50 PMMA/CAB, (d) 20:80 PMMA:CAB, and (e) pure CAB
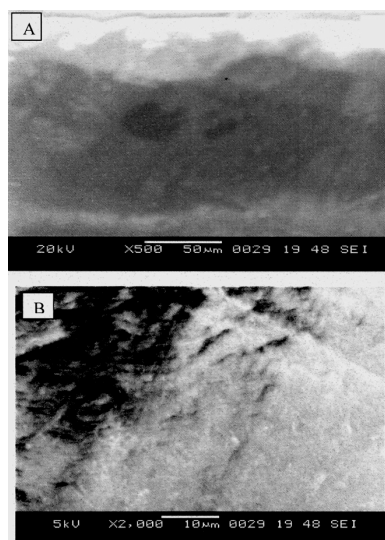
then the vibration frequencies of both the groups are expected to show a red shift due to hydrogen bond formation compared to the non-interacting group frequencies. In the present case, the carbonyl frequency of pure PMMA (Fig. 8) at 1750 cm^{-1} decreased to 1740 cm^{-1} in the 50:50 PMMA/CAB blend (Fig. 9) indicating the formation of a hydrogen bond between component polymers, which can contribute to the miscibility of the blends. A decrease in the hydroxyl group frequencies from 3641 cm^{-1} in pure CAB (Fig. 10) to 3538 cm^{-1} in the 50:50 PMMA/CAB blend is also observed. Hence, the FTIR spectral results also compliment the results obtained by solution studies, ascertaining the presence of specific interactions and miscibility of the of the blend system studied[29-31]. Figure 11 displays the DSC thermograms of few CAB/PMMA blends. The blends

Fig. 12 — SEM images of 50:50 PMMA/CAB blend: (A) low magnification and (B) high magnification

SEM Study

Figure 12 shows SEM images of 50:50 PMMA/CAB blend. As can be seen from the images, the blend exhibits uniform morphological features without any phase separation or aggregation indicating the miscibility of the blend[27].

Conclusions

The miscibility behaviour of PMMA and CAB blends in DMF has been studied in the temperature range 303-323 K. The results indicated that the blends are miscible in the entire composition range between 303-323 K. The FTIR study of the blend films also indicated the presence of specific interactions such as hydrogen bonding, supporting the results of solution studies. The SEM images of the blend film showed uniform morphological features indicating complete blend miscibility.

Acknowledgment

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