

Miscibility of Polymethylmethacrylate and Polyethyleneglycol Blends in Tetrahydrofuran

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ABSTRACT: The miscibility of polymethylmethacrylate (PMMA) and polyethyleneglycol (PEG) blends in tetrahydrofuran (THF) has been investigated by viscosity, density, refractive index, and ultrasonic velocity studies. Various interaction parameters such as 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 THF in the entire composition range. The

study also revealed that variation in the temperature does not affect the miscibility of PMMA and PEG blends in THF significantly. The presence of hydrogen bonding in the blends in the solid state has also been indicated by FTIR studies. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 452–460, 2009

Key words: polymer solutions; ultrasonic velocity; viscosity; interaction parameter; polymer blends; miscibility; PMMA; PEG; THF

INTRODUCTION

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 with a large number of techniques.^{5–9} A review of literature suggested that no previous studies have been done on the miscibility of polymethylmethacrylate (PMMA) and polyethyleneglycol (PEG) in tetrahydrofuran (THF). Hence, as a part of our research program on polymer blends and solutions,¹⁰ we present in this article, miscibility behavior of PMMA and PEG blends in THF. The choice of the polymers is due to their pharmaceutical, biomedical, and industrial applications.^{11,12} Further, it may also be noted that the polymers containing polar groups with a suscep-

tibility 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 PEG with its terminal —OH groups functioning as weak proton donors, one may expect hydrogen bonding interactions leading to miscibility in PMMA/PEG blends.

EXPERIMENTAL

Materials

PMMA (molecular weight 75,000; Alfa Aesar) and PEG (molecular weight 6000; Alfa Aesar) were used as received. THF (Merck) was distilled before use.

Preparation of polymer solutions

Dilute solutions of 2% (w/v) PMMA and PEG in THF were prepared separately in different stoppered conical flasks. Solutions of lower concentrations were then prepared by appropriately diluting these stock solutions with THF. Similarly, different blend compositions were prepared by mixing appropriate quantities of stock solutions of PMMA and PEG. From each composition of the blend, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, and 2.25% (v/v) concentrations were prepared in THF.

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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 THF traces.

Solution and solid state property measurements density

The densities of individual and blend polymer solutions in THF were measured with a Mettler Toledo Digital density meter model Densito 30 PX. The temperature of the measurement was within an uncertainty of $\pm 0.1^\circ\text{C}$. The instrument was calibrated with standard density water supplied with the instrument. The estimated error in the density measurement was within $\pm 0.05\%$.

Viscosity

Dilute solution viscosities of PMMA, PEG, and their blend solutions were measured at different temperatures using a Ubbelohde viscometer with an accuracy of $\pm 0.1\%$. 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 $\pm 0.1^\circ\text{C}$.

Ultrasonic velocity

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 $\pm 0.1\%$. 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 $\pm 0.1^\circ\text{C}$.

Refractive index

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 and DSC studies

FTIR measurements of the polyblend films were carried out at room temperature using a NICOLET AVATAR 330 FTIR spectrometer. The DSC measurements to determine the glass transition temperature (T_g) of the samples were done on a DSC SP Model instrument from Rheometric Scientific, Ashtead, UK. Measurements were performed over a temperature range of 25–300°C at a heating rate of 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Solution property studies

Viscosity of the blend solutions were measured at 293, 298, 303, 308, and 313 K for three different PEG/PMMA blend compositions at 30 : 70, 50 : 50, and 70 : 30 ratio, along with the pure polymer solutions in THF at nine concentrations, namely, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, and 2.25% (v/v) of the blends as well as pure components. Density, refractive index, and ultrasonic velocity of the polymer solutions were measured at five different temperatures indicated above for PEG/PMMA compositions of 0/100, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10, and 100/0 at a concentration of 2% (v/v).

From viscosity data, relative and reduced viscosities of the polymer solutions have been calculated and plotted against composition/solution concentration (Figs. 1 and 2). The plot of relative viscosity versus blend composition (Fig. 1) was linear for the entire composition range. This behavior is a characteristic of a miscible blend system.^{13–15} The plots of reduced viscosities of the component polymers and their blend compositions versus concentrations at different temperatures (Figs. 1 and 2) were also linear without any crossover indicating that the blends are miscible. A sharp crossover in the plots of reduced viscosity versus concentration is generally shown by immiscible blends.³ The steady increase of reduced viscosities of the solutions and also the absence of any irregular or intricate changes in the reduced viscosities of the blend solutions at a given temperature and with increase of solution concentration suggests the presence of positive specific interactions such as hydrogen bonding in the blend. The variation of reduced viscosity values with temperature on varying blend compositions of polymers has been found to be very little indicating very little influence of temperature on reduced viscosity in the studied system. The interaction parameter of the component polymers and their blend compositions have been found out from the plots of the reduced

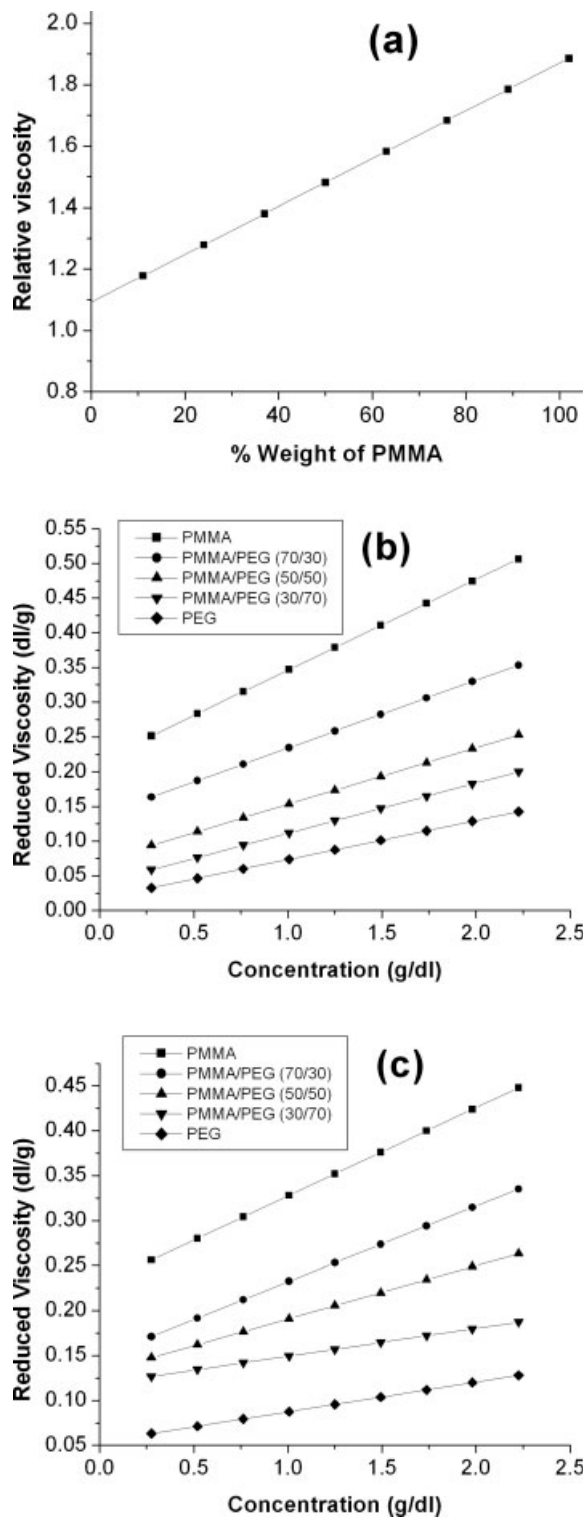


Figure 1 (a) Relative viscosity versus composition of PMMA/PEG blends at 303 K. (b) Reduced viscosity versus concentration of PMMA/PEG blends at 293 K. (c) Reduced viscosity versus concentration of PMMA/PEG blends at 298 K.

viscosity versus concentration and are given in Table I. The slope of the curve gives the corresponding interaction parameter value, which has been evaluated on the basis of classical Huggins equation.^{16,17} Krig-

baum and Wall interaction parameter Δb of the blends^{13,18} has been obtained from the difference between the experimental and theoretical values of the interaction parameters b_{12} and b_{12}^* . Polymer 1-

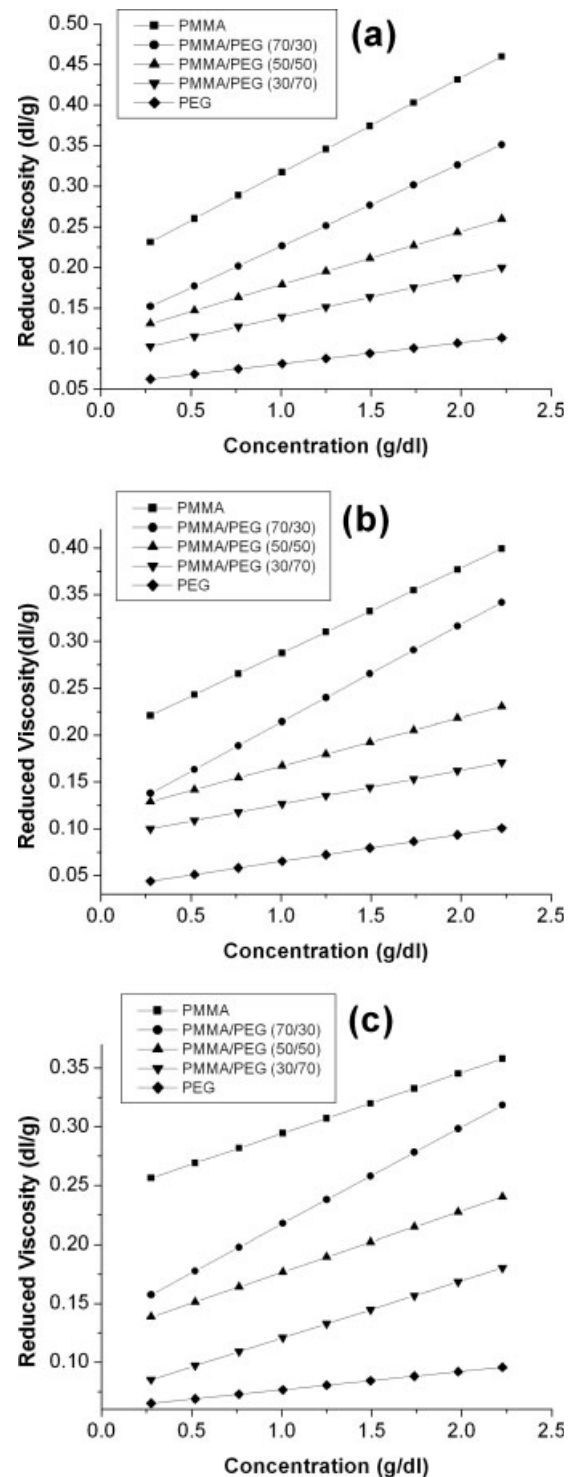


Figure 2 (a) Reduced viscosity versus concentration of PMMA/PEG blends at 303 K. (b) Reduced viscosity versus concentration of PMMA/PEG blends at 308 K. (c) Reduced viscosity versus concentration of PMMA/PEG blends at 313 K.

TABLE I
Slope of Reduced Viscosity Versus Concentration Plots of PEG/PMMA Blends and Individual Solutions at Different Temperatures

PEG/PMMA (v/v)	b_m				
	293 K	298 K	303 K	308 K	313 K
100/0	0.056	0.014	0.026	0.017	0.044
70/30	0.072	0.045	0.062	0.044	0.115
50/50	0.081	0.058	0.070	0.065	0.128
30/70	0.097	0.080	0.094	0.077	0.107
0/100	0.118	0.092	0.127	0.090	0.193

polymer 2 interaction parameter Δb can be calculated as follows:

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

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,

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

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 that 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,

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

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

$$\Delta b = (b_{12} - 2b_{12}^*) \quad (4)$$

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 II) for all blend compositions and at all studied temperatures. This suggests that the blends are miscible in the studied range. If η_1 and η_2 are sufficiently apart, a more effective parameter

μ , defined by Chee⁷ can be used to predict the compatibility. The relation is given by

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

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 III. The results show that the μ values for the system under study are all positive and sufficiently high, indicating the miscibility of the blends. 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:

$$\alpha = K_m - \frac{K_1 [\eta_1]_2^2 W_2^2 + 2\sqrt{K_1 K_2} [\eta_1]_1 [\eta_2]_2 W_1 W_2}{\{[\eta_1]_1 W_1 + [\eta_2]_2 W_2\}^2} \quad (6)$$

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 III. The positive values at all temperatures indicate that the blends are miscible. Further, we have also carried out calculations to identify the miscibility of blends based on

TABLE II
 Δb and Δk_{AB} Values for the PEG/PMMA Blends at Different Temperatures

PEG/PMMA (v/v)	293 K		298 K		303 K		308 K		313 K	
	Δb	Δk_{AB}	Δb	Δk_{AB}	Δb	Δk_{AB}	Δb	Δk_{AB}	Δb	Δk_{AB}
30/70	0.07	0.48	0.02	0.04	0.03	0.33	0.02	0.55	0.03	-0.43
50/50	0.05	0.40	0.01	0.06	0.007	0.58	0.03	0.14	0.02	-0.19
70/30	0.02	0.33	0.03	0.06	0.01	0.10	0.10	0.15	0.05	-0.01

TABLE III
 μ and α Values for the PEG/PMMA Blends at Different Temperature

PEG/PMMA (v/v)	293 K		298 K		303 K		308 K		313 K	
	μ	α	μ	α	μ	α	μ	α	μ	α
30/70	1.8	2.0	0.62	0.12	1.54	0.31	0.89	0.24	1.49	0.63
50/50	1.3	1.1	0.31	0.13	0.36	0.40	1.34	0.24	0.99	1.12
70/30	0.5	1.5	0.93	0.34	0.51	0.24	4.48	0.92	0.24	2.17

Huggins constant. The Huggins constant is a parameter that could also be used to express the interaction between unlike polymers.²⁰ The k_{AB} value was concerned with b_{AB} as shown in the equations

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

and

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

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

$$k_{AB,t} = (k_A k_B)^{0.5} \quad (9)$$

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

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

The positive Δk_{AB} value indicates that the polymer mixture in solution-state is miscible. Table II shows the Δk_{AB} values for our system, which are positive for all the compositions up to 308 K indicating the miscibility of the blends in this temperature range. The negative value for the blends at 313 K shows that the blends are not miscible at this temperature. This may be due to the loss of specific interactions between the polymer and solvents at such relatively high temperatures compared with room temperature.

The heat of mixing (ΔH_m) was also used as a measure to study²¹⁻²³ the blend compatibility. According to Schneier,²² ΔH_m of the polymer blends is given by

$$\Delta H_m = \left\{ W_1 M_1 \rho_1 \left(\delta_1 - \delta_2 \right)^2 \left[\frac{W_2}{(1 - W_2)} M_2 \rho_2 + (1 - W_1) M_1 \rho_1 \right]^2 \right\}^{1/2} \quad (11)$$

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 [$9.1 \text{ (cal/cm}^3)^{1/2}$] and PEG [$5.1 \text{ (cal/cm}^3)^{1/2}$] were taken from the literature,²⁴ and these

values were used to calculate ΔH_m with eq. (12). Figure 3 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. This behavior further confirms that the blend solutions are miscible in the studied range of compositions and temperature. The slight deviation of the plot from linearity may be due to the large difference in the molecular weights of PMMA and PEG samples used; causing initial increase in heat of mixing on increase of PMMA content in the blend. Further, the heat of mixing calculated at different temperatures did not vary significantly with temperature and in fact, as is seen in Figure 3, the ΔH_m values for various temperatures are overlapping. This behavior shows that the effect of temperature on miscibility of the blends is not very significant and that the specific interactions that make the blends miscible are also very weak.

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 parameters (χ_i) have been computed from Flory-Huggins theory²¹ with

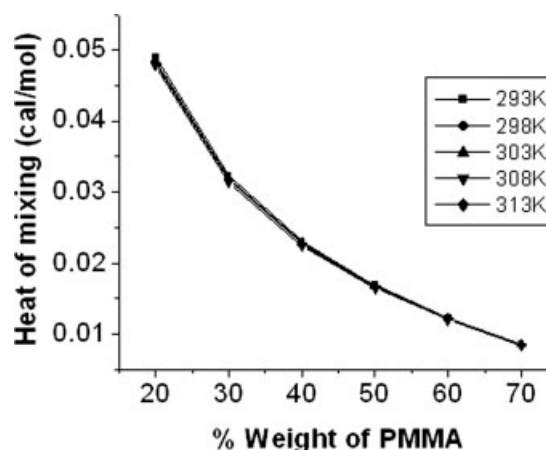


Figure 3 Heat of mixing of PMMA/PEG blends at different temperature.

TABLE IV
Polymer–Polymer Interaction Parameters for PMMA and PEG in the Blend

Temperature (K)	Polymer	χ_i calculated from eq. (12)
293	PMMA	0.02
	PEG	2.92
298	PMMA	0.02
	PEG	2.88
303	PMMA	0.01
	PEG	2.85
308	PMMA	0.01
	PEG	2.84
313	PMMA	0.01
	PEG	2.83

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

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 additively relationship,

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

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 IV, whereas the blend–solvent interaction parameters are given in Table V. From these data, we 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 kinds of conclusions have also been reported by Aminabhavi and coworkers²⁷ in the case of PMMA/polyvinyl alcohol blends in dimethyl formamide.

To confirm the miscibility behavior 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

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

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. 4–6) and they are found to be linear. For incompatible blend solutions, these plots are nonlinear showing distinct phase inversion at intermediate compositions.^{27,28} 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 and DSC studies

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

TABLE V
Blend–Solvent Interaction Parameters at Different Temperatures

Temperature (K)	PMMA/PEG (v/v)	δ calculated from eq. (13)	χ_i calculated from eq. (12)
293	20/80	5.7	1.9
	30/70	6.1	1.5
	40/60	6.6	1.1
	50/50	7.0	0.8
	60/40	7.4	0.5
298	70/30	7.8	0.3
	20/80	5.7	1.9
	30/70	6.1	1.5
	40/60	6.6	1.1
	50/50	7.0	0.8
303	60/40	7.4	0.5
	70/30	7.8	0.3
	20/80	5.7	1.9
	30/70	6.1	1.4
	40/60	6.6	1.1
308	50/50	7.0	0.8
	60/40	7.4	0.5
	70/30	7.8	0.7
	20/80	5.7	1.8
	30/70	6.1	1.4
313	40/60	6.6	1.1
	50/50	7.0	0.8
	60/40	7.4	0.5
	70/30	7.8	0.3
	20/80	5.7	1.8

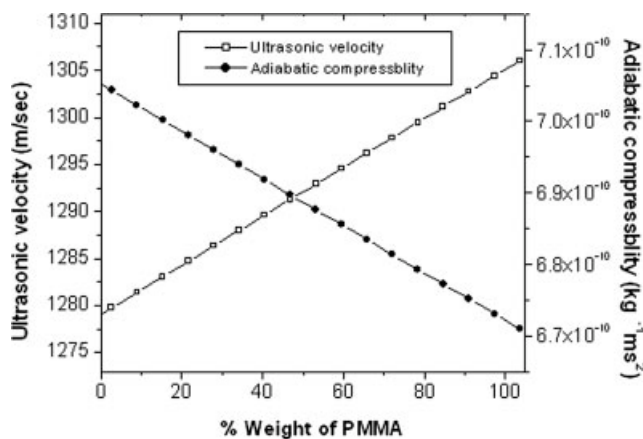


Figure 4 Ultrasonic velocity and adiabatic compressibility versus composition of PMMA/PEG blends at 303 K.

typical chemical changes, FTIR spectroscopy is very sensitive to the formation of hydrogen bond.²⁹ If the groups involved in the hydrogen bond formation in a blend system are carbonyl and hydroxyl moieties, then the vibration frequencies of both the groups are expected to show a red shift due to hydrogen bond formation compared with the noninteracting group frequencies. In the present case, the carbonyl frequency of pure PMMA (Fig. 7) at 1749 cm^{-1} decreased to 1746 cm^{-1} in the 50 : 50 PMMA/PEG blend (Fig. 8) indicating the formation of a weak hydrogen bond between component polymers, which can contribute to the miscibility of the blends. However, we observed an increase in the hydroxyl group frequencies from 3452 cm^{-1} in pure PEG (Fig. 9) to 3632 cm^{-1} in the 50 : 50 PMMA/PEG blend, contrary to the expectation. This enhancement in the —OH stretching frequencies may be attributed to the presence of intra- and intermolecular hydroxyl–hydroxyl as well as hydroxyl–ether oxygen hydrogen bonding interactions in PEG that occur at lower frequencies (3452 cm^{-1}) and the same being changed

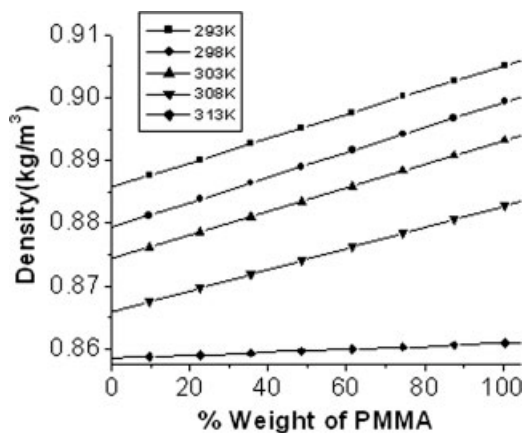


Figure 5 Variation of density of PMMA/PEG blend solutions with PMMA blend composition at different temperatures.

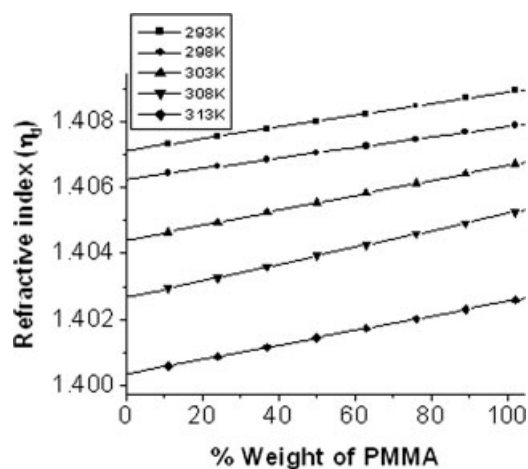


Figure 6 Variation of refractive index of PMMA/PEG blend solutions with PMMA blend composition at different temperatures.

to intermolecular hydroxyl–carbonyl hydrogen bonding interactions that occur at higher frequencies in the blend system. Similar observations have also been reported in the case of miscible blends of polyvinylalcohol and polyvinylpyrrolidone.^{30,31} The intensity of —OH stretching band in the PEG–PMMA blend is also less compared with that in the pure PEG sample. This may be indicative of weaker hydrogen bonding tendencies in the blend.^{31–34} These results also suggest that the interaction forces that exist in the blends are mainly dipole–dipole forces and weak hydrogen bonding interactions. Further, DSC analysis of the blend films also exhibited single endothermic peaks (not shown) and were intermediate of the T_g values of pure PMMA and PEG. The T_g values of the blend films also increased regularly on increase of PMMA content in the blends (Fig. 10). Such a systematic variation of T_g in the blends is indicative of miscibility of the components in the blends. Immiscible blends would show

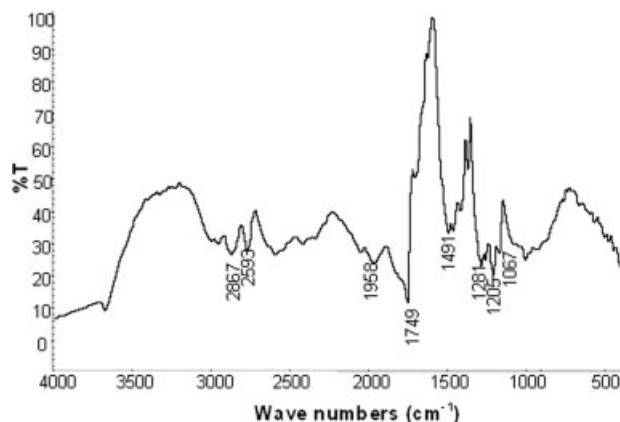


Figure 7 FTIR spectrum of PMMA.

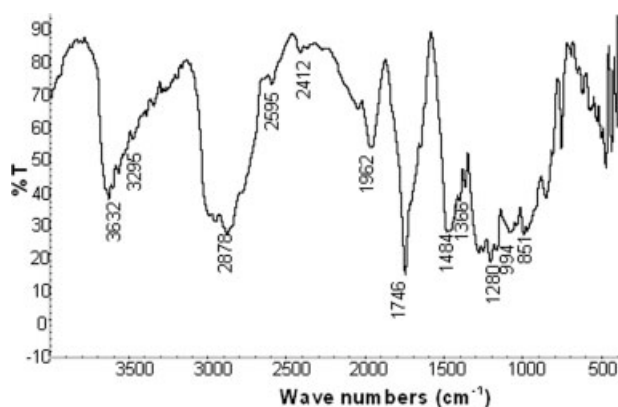


Figure 8 FTIR spectrum of (50/50) PMMA/PEG blend.

more than one T_g peak in the DSC and also in a nonsystematic pattern.²⁷ Hence, the FTIR spectral and DSC study results also compliment the results obtained by solution studies, ascertaining the presence of specific interactions and miscibility of the of the blend system studied.

CONCLUSIONS

The miscibility behavior of PMMA and PEG blends in THF has been studied in the temperature range 298–313 K. The miscibility has been analyzed by solution viscosity, ultrasonic velocity, and refractive index measurement of the blend solutions and calculating various interaction parameters based on these data. The results indicated the presence of positive interactions in the system and that the blends are miscible in the entire composition range between 298 and 308 K. The Δk_{AB} interaction parameter test indicated that blends are immiscible at 313 K. The heat of mixing estimations of the blends indicated that the effect of temperature on the miscibility of the blends is not very significant. The FTIR studies

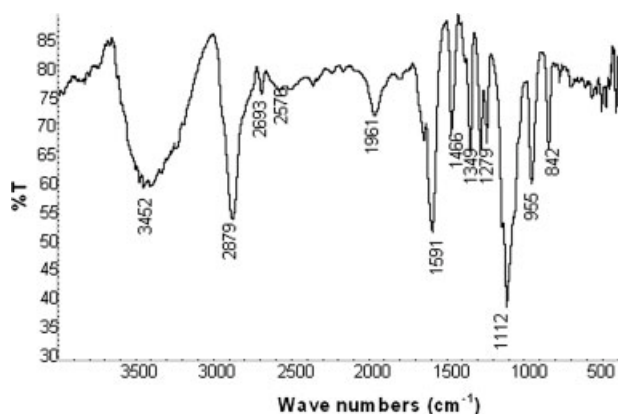


Figure 9 FTIR spectrum of PEG.

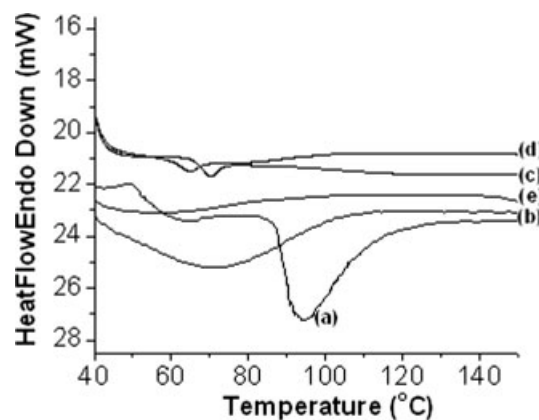


Figure 10 DSC scans of PMMA/PEG blends; (a) Pure PMMA, (b) PMMA/PEG(70/30), (c) PMMA/PEG(50/50), (d) PMMA/PEG(30/70), (e) Pure CAB.

of the blend films also indicated the presence of weak specific interactions supporting the results of solution studies.

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