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Polymer 40 (1999) 7167–7171

polymer

Polymer Communication

Studies on the compatibility and specific interaction in cellulose acetate hydrogen phthalate (CAP) and poly methyl methacrylate (PMMA) blend

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Received 4 March 1999; received in revised form 30 April 1999; accepted 30 April 1999

Abstract

Compatibility of cellulose acetate hydrogen phthalate (CAP) and poly methyl methacrylate (PMMA) has been investigated by solution viscometric, ultrasonic and differential scanning calorimetric (DSC) methods. From viscosity measurements, Krigbaum and Wall polymer–polymer interaction parameter is evaluated. Ultrasonic velocity and adiabatic compressibilites versus blend composition are plotted, and found to be linear. T_g values are calculated using Gordon–Taylor and Fox equations. The results obtained reveal that CAP forms a miscible blend with PMMA in the entire composition range. Compatibility may be due to the formation of hydrogen bond between the carbonyl group of PMMA and the free hydroxyl group of CAP. Compatibility is further predicted from dielectric measurements. © 1999 Elsevier Science Ltd. All rights reserved.

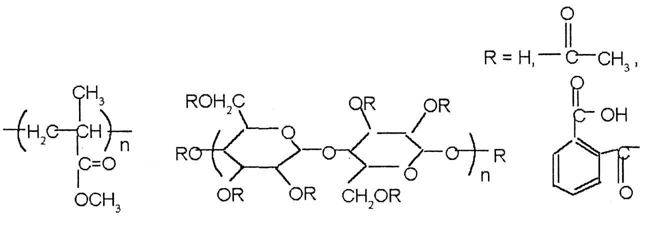
Keywords: Polymer blend; Compatibility; Interaction parameter

1. Introduction

Polymers containing proton donor groups are found to be miscible with those containing proton acceptor groups due to a specific interaction like hydrogen bonding. PMMA is miscible with many polymers like PVC, PEO, PVDF, SAN etc [1–4]. In PMMA–PVC blend, Schurer et al. [5] has reported that ester group in PMMA is a proton acceptor, and PVC is a weak proton donor via hydrogen, and the interaction involved is hydrogen bonding. There are few reports on the studies of interactions of PMMA with other polymers. Hence, in this paper we report a new miscible blend system of PMMA and CAP, and make an attempt to study the interactions involved in blending PMMA with a proton donor polymer. PMMA and CAP are chosen for the present study because of their pharmaceutical applications [6,7].

2. Experimental

Polymers used for the present study, CAP and PMMA, were obtained from commercial sources. The viscosity average molecular weight ($\bar{M}_V$) of CAP and PMMA are 70 000 and 101 000, respectively. The structure of CAP and PMMA are as follows:



Polymethyl methacrylate(PMMA) Cellulose acetate hydrogen phthalate(CAP)

(Phthalate content : 30-40%, Acetyl content : 19-24%, Hydroxyl content : 36-51%.)

For viscometric studies, dilute polymer solutions (2% w/v) were used. Stock solutions of CAP and PMMA and their different blend compositions 30/70, 50/50 and 70/30 were prepared in a common solvent DMF. Viscosity measurements were made using Ubbelohde Viscometer at 31°C with an accuracy of ±0.2%.

Ultrasonic velocity of the blend solutions of 3% w/v were measured at 30°C using ultrasonic pulse echo interferometer (SD UI-003) with a measuring frequency of 10 MHz. The accuracy of measurement was ±0.5%. For DSC studies, thin films of component polymers and their blends with thickness in the order of microns were prepared by solution casting using DMF as the common solvent. Films were dried in vacuum for 48 h and were found to be transparent. DSC

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PII: S0032-3861(99)00311-0

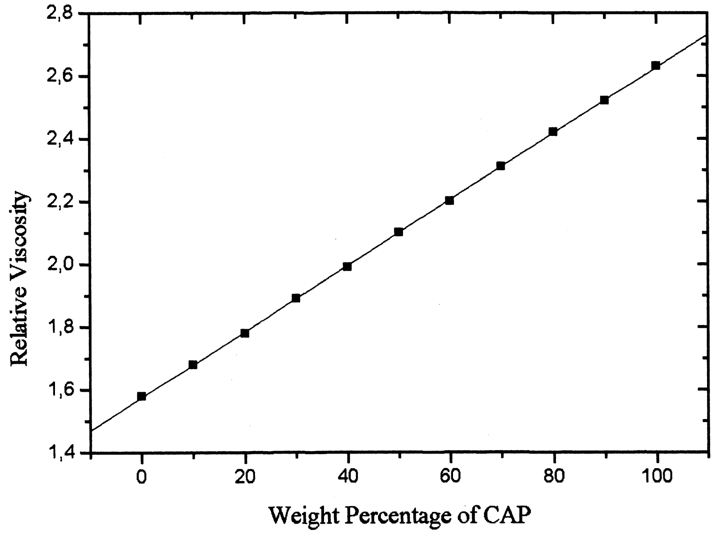

Fig. 1. Relative viscosity versus composition of CAP–PMMA blends.

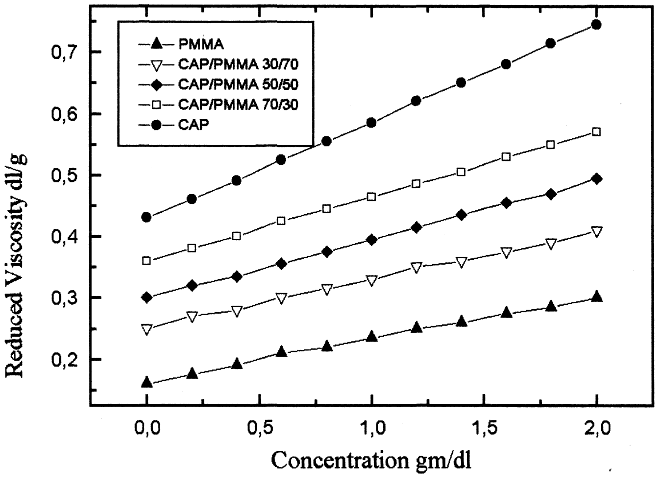

Fig. 2. Reduced viscosity versus concentration of CAP–PMMA blends.

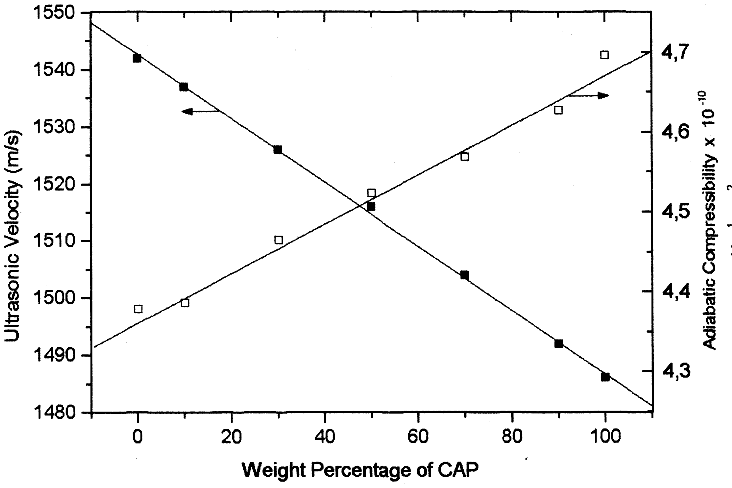

Fig. 3. Ultrasonic velocity and adiabatic compressibility versus composition of CAP–PMMA blends.

measurements were done in Shimadzu DSC-50 and the scan rate was 10 K/min.

3. Results and discussion

From viscometric measurements, relative and reduced viscosities of homopolymers and their blends are found out. A plot of relative viscosity versus blend composition (Fig. 1) is found to be linear for the entire composition range, which is characteristic of a compatible blend system [8–10]. Reduced viscosities of the component polymers and their 30/70, 50/50 and 70/30 blend compositions are plotted against concentrations (Fig. 2). The plots are linear and no cross-over is seen showing that the blends are compatible. A sharp cross-over in the plots of reduced viscosity versus concentration is shown by incompatible blends [11]. The intercept of the plots gives the intrinsic viscosity of the corresponding polymer and their blends, and are presented in Table 1. The experimental intrinsic viscosity values thus obtained are compared with their weighed average values and found to be slightly higher than the theoretical values (Table 1). For an immiscible blend system, it has been observed that the intrinsic viscosity always shows a negative deviation due to the repulsive interaction between polymers [12].

The interaction parameter *b* of the component polymers and their blend compositions are found out from the plots of the reduced viscosity versus concentration and is given in Table 1. The slope of the curve gives the corresponding *b* value. Evaluation of *b* is done on the basis of classical Huggins equation [13,14].

Krigbaum and Wall interaction parameter Δb of the blends [15] was obtained from the difference between the experimental and theoretical values of the interaction parameters b_{12} and b^*_{12}. Polymer1–polymer2 interaction parameter Δb can be calculated as follows:

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

where C_m is the total concentration of polymers $C_1 + C_2$ and $(\eta)_m$ is the intrinsic viscosity of blend. $(\eta)_m$ can be theoretically defined as:

$$(\eta)_m = [\eta]_1 X_1 + [\eta]_2 X_2. \tag{2}$$

(for non-interacting system), where X_1 and X_2 are weight fractions of polymer1 and polymer2, respectively. b_{12} is the interaction parameter which is defined by the equation

$$b_m = X_1^2 b_{11} + 2X_1X_2b_{12} + X_2^2 b_{22} \tag{3}$$

where b_m defines the global interaction between all polymeric species. b_{12} may be obtained experimentally by Eqs. (1) and (3)

$$b^*_{12} = (b_{11}b_{22})^{1/2}, \tag{4}$$

$$\Delta b = (b_{12} - b^*_{12}) \tag{5}$$

Table 1
Intrinsic viscosity and interaction parameter of CAP–PMMA blends

Blend comp of CAP/PMMA	Intrinsic viscosity		Slope of red viscosity vs. concentration curve	Experimental b_{12} value	Theoretical b^*_{12} value	Δb	μ
	Experimental (dl/g)	Theoretical (dl/g)					
0/100	0.16	0.16	0.05	—	—	—	—
30/70	0.25	0.241	0.0875	0.117	0.088	0.028	0.386
50/50	0.30	0.295	0.100	0.0968	0.088	0.008	0.116
70/30	0.36	0.349	0.123	0.0986	0.088	0.010	0.141
100/0	0.43	0.43	0.156	—	—	—	—

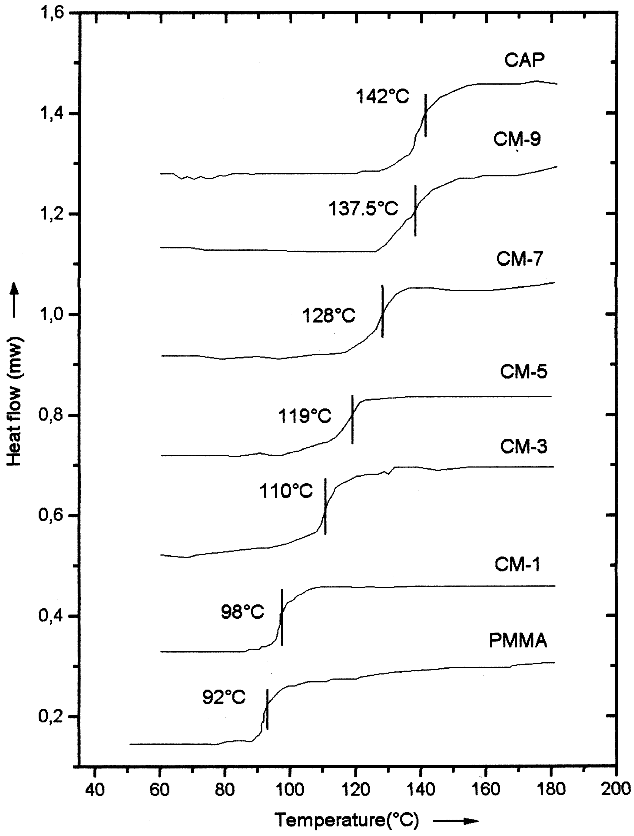

Fig. 4. DSC thermograms of CAP–PMMA blends.

(* means theoretical value) $\Delta b > 0$ signifies miscibility and $\Delta b < 0$ indicates phase separation. It is found that Δb values are positive for all blend compositions predicting compatibility (Table 1). If η_1 and η_2 are sufficiently apart, a more effective parameter μ can be used to predict the compatibility

$$\mu = \frac{\Delta b}{(\eta_2 - \eta_1)^2}. \tag{6}$$

High value of μ may be due to specific interaction of hydrogen bonding between the polymers. The value of μ are found to be positive (Table 1).

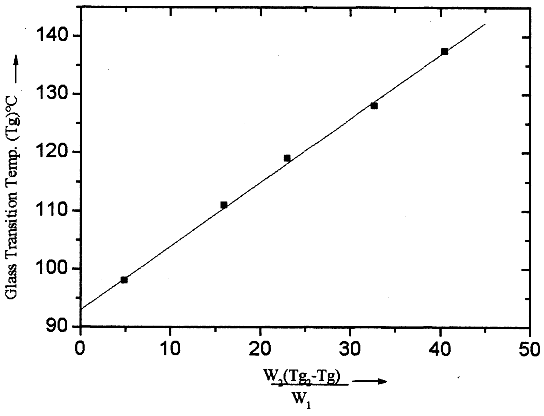

Fig. 5. Verification of Gordon–Taylor equation for CAP–PMMA blends.

Ultrasonic velocity, density and adiabatic compressibility values of blends are found out. Adiabatic compressibility is calculated using the formula

$$\beta_{\text{ad}} = \frac{1}{v^2 \rho} \tag{7}$$

where v is the ultrasonic velocity and ρ the density. Ultrasonic velocity of blends is plotted against blend compositions (Fig. 3) and found to be linear. For incompatible blend solutions, ultrasonic velocity versus composition curve is non-linear showing distinct phase inversion at intermediate composition [16]. Adiabatic compressibility also varies linearly with blend composition (Fig. 3).

The glass transition temperature (T_g) of homopolymers and their blends are recorded from DSC endotherms (Fig. 4) and given in Table 2. Blends exhibit single T_g, intermediate to those of CAP and PMMA. The T_g of miscible blend can be predicted using Fox equation (Eq. 8) [17] and Gordon–Taylor equation (Eq. 9) [18].

$$\frac{1}{T_g} = \frac{X_1}{T_{g1}} + \frac{X_2}{T_{g2}}, \tag{8}$$

$$T_g = \frac{X_1 T_{g1} + k X_2 T_{g2}}{X_1 + k X_2} \tag{9}$$

where X_1, X_2, T_{g1} and T_{g2} are the weight fractions and glass

Table 2
Experimental and theoretical glass transition temperatures of CAP–PMMA blend

Blend composition of CAP/PMMA	Experimental T_g values (°C)		Theoretical T_g values	
	DSC	Dielectric measurement	Neilson equation	Fox equation
0/100	92	89	—	—
10/90	98	—	97	96
30/70	110	108	107	103
50/50	119	117	117	112
70/30	128	127	127	122
90/10	137.5	—	137	135
100/0	142	142	—	—

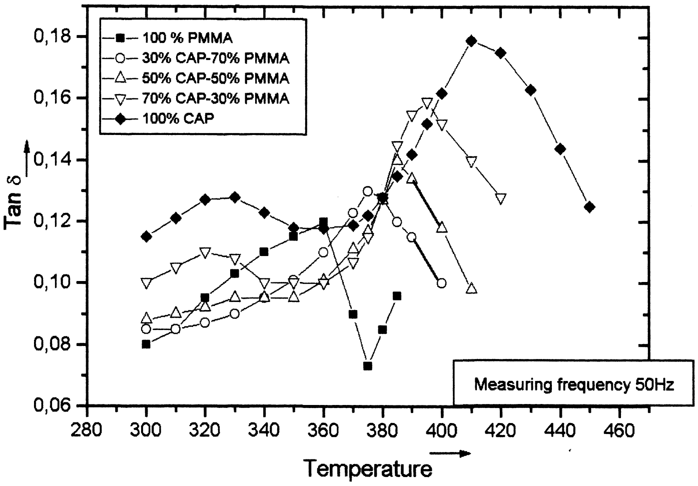

Fig. 6. Dielectric loss as a function of temperature (K) for different compositions of CAP–PMMA blends.

transition temperatures corresponding to polymer1 and polymer2, respectively. *k* is a constant which gives a semi-quantitative measure of degree of the interaction between two polymers. T_g values calculated from Fox equation and their theoretical values obtained from Neilson equation [19] are shown in Table 2. The blends show a positive deviation from Fox equation implying an intermolecular interaction between the polymers. Slope (*k*) of the straight line obtained from Gordon–Taylor equation (Fig. 5) is found to be 1.1. Higher the value of *k*, higher is the interaction. The intercept of Gordon–Taylor equation curve is found to be 93°C which is the T_g of pure PMMA.

Compatibility has been further confirmed from dielectric measurements [20]. In blends, dielectric loss as a function of temperature displayed a single peak in the region between that of the two polymers, corresponding to the T_g. The T_g values obtained from dielectric measurements agree well with those obtained from DSC (Table 2). At very low frequency, a β-relaxation peak is also observed for pure CAP and for blends with a higher content of CAP i.e. at 52°C, but not for blends with a lower content of CAP and pure PMMA (Fig. 6).

The β-relaxation may be due to the orientation of polar OH group in CAP. In blends with low percentage of CAP, this peak disappears because all the free OH groups may be involved in hydrogen bonding with the CO group of PMMA. From the structure of CAP and PMMA, it is clear that in blends with higher percentage of CAP, even though OH groups are involved in hydrogen bond formation, there may be free OH groups, and this contributes to the β-relaxation peak, in blends with a high content of CAP and in pure CAP.

All these observations show that there is a specific interaction between CAP and PMMA, and CAP forms a compatible blend with PMMA in the entire composition range. The compatibility of the system may be due to the formation of a hydrogen bond between the carbonyl group of PMMA and the free hydroxyl group of CAP.

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