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Studies on the Miscibility of Poly(2-hydroxyethyl methacrylate) and Poly(ethylene oxide) Blends

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Studies on the Miscibility of Poly(2-hydroxyethyl methacrylate) and Poly(ethylene oxide) Blends

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Miscibility characteristics of poly[2-hydroxyethylmethacrylate] (PHEMA) and poly[ethylene oxide] (PEO) have been investigated by solution viscometry, ultrasonic and differential scanning calorimetric (DSC) methods. The interaction parameters were obtained using the viscosity data. Ultrasonic velocity and adiabatic compressibility vs. blend composition have been plotted and are found to be linear. A single glass transition temperature was observed by differential scanning calorimetry. Variation of glass transition temperature (T_g) with composition follows Garden-Taylor equation. T_g values have also been calculated from the Fox equation. The results obtained reveal that PHEMA forms a miscible blend with PEO in the entire composition range.

Keywords: polymer blends; miscibility; poly[2-hydroxyethylmethacrylate]; poly[ethylene oxide]

1 Introduction

Polymer blends are a physical mixture of structurally different polymers that are interacting through secondary forces with no covalent bonding (1). The importance of blending has increased recently because of their superior properties over homopolymers and can be compared to those of alloys over metals. The superior properties of polymer blends depends upon the miscibility of its components at the molecular scale. Miscibility in polymer blends is assigned to specific interactions between polymeric components, which usually give rise to a negative free energy of mixing in spite of the high molecular weight of polymers. There are many experimental and theoretical methods, such as thermal analysis (2), electron microscopy (3), dynamic mechanical studies (4). All these techniques, though sophisticated are costly and time consuming. Hence, simple, low cost and rapid techniques are of great importance in recent years. Several researchers used a viscometric technique (5–8) Ante et al. (5) used the dilute solution viscosity to probe the miscibility and molecular interactions in polymer mixtures composed of polystyrene and poly(ethylene-co-propylene), polystyrene and poly(dodecyl methacrylate), as well as polystyrene and poly(octadecyl methacrylate). Ultrasonic measurements (9, 10) have also been used to investigate the polymer–polymer miscibility in solution. Recently, Pai and coworkers (10) have used ultrasonic techniques for the study of the miscibility of polymers. In this article, as a part of our studies on polymeric materials (11–13), we report on the miscibility of a new blend system of poly[2-hydroxyethylmethacrylate] (PHEMA) and poly(ethyleneoxide) (PEO). PHEMA and PEO have been selected for the present study due to their pharmaceutical applications (14, 15). Polyethylene oxide (PEO) is a biodegradable hydrophilic polymer having many applications in the medical and food industry (16).

2 Experimental

Polymers used in the present study, PHEMA($M_w = 130000$) and PEO ($M_w = 10000$) were commercially supplied by Aldrich Chemical Company, Inc. *N,N*-dimethylformamide (DMF) was AR grade and used as received.

For viscometric studies, dilute polymer solutions (2% w/v) were used. Stock solutions of PHEMA and PEO and blend solutions at different compositions of 30/70, 50/50 and 70/30 were prepared in a common solvent DMF. Viscosity measurements were made using a Ubbelohde viscometer at 30°C.

Ultrasonic velocity of the blend solutions of 3% w/v were measured at 30°C using ultrasonic pulse echo interferometer (SD UI-003).

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

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solvent. Films were dried in vacuum for 48 h and found to be transparent. The DSC measurements were made on a Mettler TA 4000 DSC in nitrogen atmosphere. The instrument was calibrated with an indium and zinc standard for lower and higher temperature, respectively.

3 Results and Discussions

The viscometric measurement is a good method to investigate polymer–polymer interaction in solution. Viscometric analysis of polymer–polymer miscibility in dilute solution is based on the Huggins equation, which reflects the relationship between specific viscosity and polymer concentration. Fortunately, by studying binary polymer mixtures in solution and in the solid state, Christopoulou et al. (17) have shown that there is a very close relation between their behavior in solution and in the solid state. The compatibility found in solution would remain even when the solvent is absent. The phenomenon is called the "memory effect" (18, 19). When a common solvent is used and when the molecular masses of the mixture polymers are high and comparable, the films obtained present a good mixing. Therefore, this viscometric technique which is effective, quick and inexpensive, is widely used for many polymer pairs to determine their miscibility. The measured values of viscosity, reduced viscocities of the homopolymers and their blends are discovered. A plot of reduced viscosities of the component polymers and their 30/70, 50/50, and 70/30 blend compositions is found to be linear and no cross over is seen, indicating that the blends are compatible (Figure 1) (20, 21). A sharp cross over in the plots of reduced viscosity vs. concentration is shown by incompatible blends (21).

The interaction parameter ΔB of the blends was calculated using the Chee (20) expression when the polymers are mixed in weight fractions of w_1 and w_2 as:

$$\Delta B = \frac{b - \bar{b}}{2w_1w_2} \tag{1}$$

where $\bar{b} = w_1\, b_{11} + w_2\, b_{22}$

where b_{11} and b_{22} are the slopes of the viscosity curves for the pure components.

The coefficient b is related to the Huggins coefficient K_H as:

$$b = \mathbf{K}_H[\eta]^2 \tag{2}$$

For the ternary system, the coefficient b is also given by:

$$b = w_{12}b_{11} + w_{22}b_{22} + 2w_1w_2b_{12} \tag{3}$$

If η_1 and η_2 are sufficiently separate, a more effective parameter μ can be used to predict the compatibility.

$$\mu = \frac{\Delta B}{([\eta]_2 - [\eta]_1)^2} \tag{4}$$

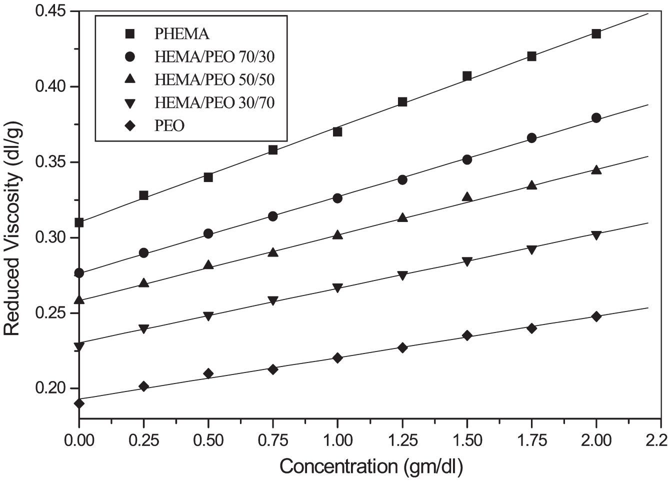

Fig. 1. Reduced viscosity vs. concentration of PHEMA-PEO blends.

$\mu > 0$ signifies miscibility and $\mu < 0$ indicates phase separation. It is found that μ values are positive for all blend compositions predicting compatibility (Table 1).

Recently, Sun et al. (21) suggested a new equation by considering the long range hydrodynamic interactions for the determination of miscibility of polymers as follows:

$$\propto = k_m - \frac{k_1\eta_1^2w_1^2 + k_2\eta_2^2w_2^2 + \sqrt{2k_1k_2}[\eta]_1[\eta]_2w_1w_2}{\{[\eta]_1w_1 + [\eta]_2w_2\}^2} \tag{5}$$

where k_1, k_2 and k_m are the Huggins constants for individual pure components 1, 2 and blend, respectively. Sun et al., suggested that a blend will be miscible if $\propto\ \geq 0$ and immiscible when $\propto < 0$. In the present study, ∝ values are positive for all blend compositions indicating that blends are miscible (Table 1).

The ultrasonic sound waves offer a useful technique for investigating the miscibility of polymer blend in solution, the variation of ultrasonic velocity vs. blend compositions is linear for compatible blends and nonlinear for non-compatible (22). Ultrasonic velocity, density and adiabitic compressibility values of blends were discovered. Adiabitic compressibility is calculated using the formula:

$$\beta_{ad} = \frac{1}{\nu^2\rho} \tag{6}$$

Table 1. Miscibility parameters μ^a and α^b

Blend composition PHEMA/PEO	μ	α
0/100	—	—
30/70	0.2549	0.2191
50/50	0.2608	0.2624
70/30	0.2104	0.2300
100	—	—

[a] Using Chee (17) expression.
[b] Using Sun (18) expression.

Where ν is the ultrasonic velocity and ρ is the density. Ultrasonic velocity of blends is plotted against blend compositions (Figure 2) and found to be linear, which is the characteristic of compatible blends (23). For incompatible blend solutions, ultrasonic velocity versus composition curve is non linear showing distinct phase inversion at intermediate composition. Adiabitic compressibility also varies linearly with blend composition (Figure 2).

In order to confirm the correct nature of the blend under consideration, DSC analysis also carried out. The glass transition temperature (T_g) of homopolymers and their blends are recorded from DSC endotherms (Figure 3) and given in Table 2. Blends exhibit single T_g intermediate to those of PHEMA and PEO. The T_g of miscible blend can be predicted using the Fox equation (24), Equation (7) and the Gordon-Taylor Equation (25) Equation (8).

$$\frac{1}{T_g} = \frac{X_1}{T_{g1}} + \frac{X_2}{T_{g2}} \tag{7}$$

$$T_g = \frac{X_1 T_{g1} + kX_2 T_{g2}}{X_1 + kX_2} \tag{8}$$

Where X_1, X_2, T_{g1} and T_{g2} are the weight fractions and glass transition temperatures corresponding to polymer 1 and polymer 2, respectively, k is a constant which gives a semi-quantitative measure of degree of the interaction between two polymers. T_g values calculated from the Fox equation and their theoretical values calculated from the rule of mixtures 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 (Figure 4) is found to be 1.12. Higher the value of 'k' higher is the interaction.

Table 2. Experimental and theoretical glass transition temperatures

Blend composition PEO/PHEMA	Experimental Tg (°C) values by DSC	Theoretical Tg (°C) values	
		Additive behaviour	Fox equation
0/100	385	—	—
10/90	372	371.6	365.5
30/70	346.2	344.8	331.8
50/50	320.6	319	303.88
70/30	293	291.2	280.26
90/10	267.4	264.4	260
100/0	251	—	—

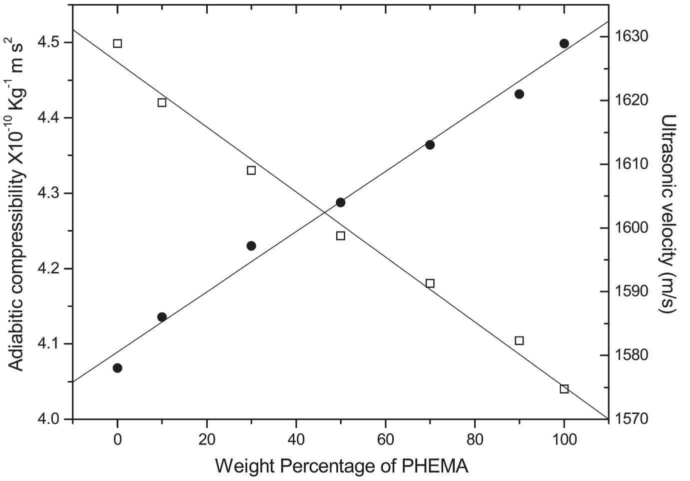

Fig. 2. Ultrasonic velocity and Adiabatic compressibility vs. blend composition.

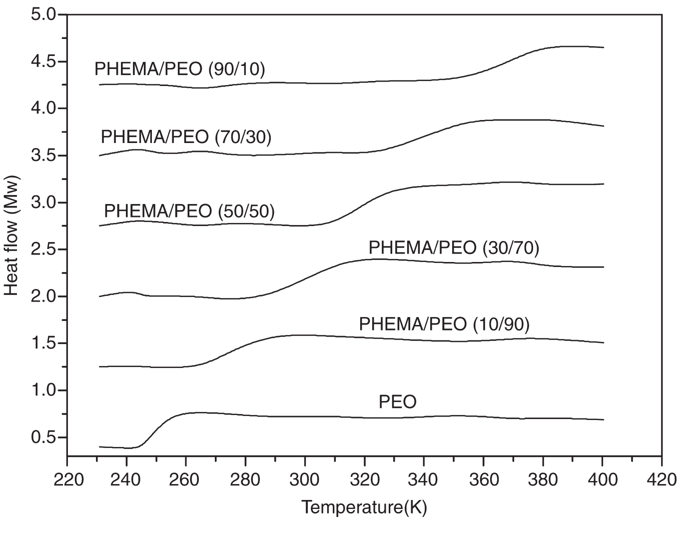

Fig. 3. DSC thermograms of PHEMA-PEO blends.

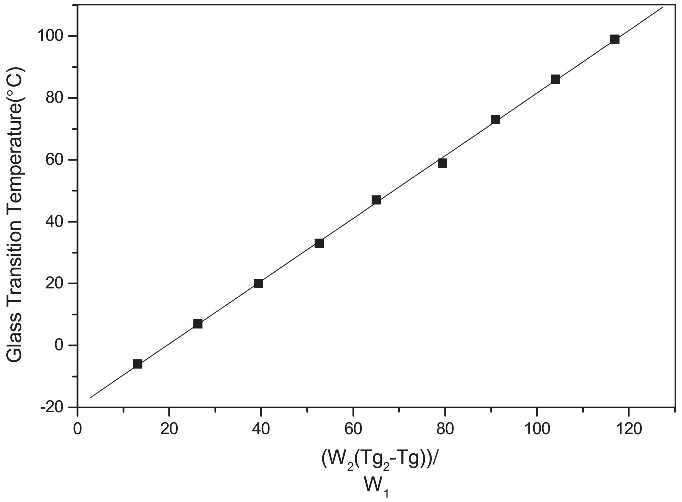

Fig. 4. Verification of Gordon-Taylor equation for PHEMA-PEO blends.

5 Conclusions

The miscibility of poly(2-hydroxyethylmethacrylate)/poly (ethyleneoxide) blends was investigated by viscosity, ultrasonic velocity and differential scanning calorimetry and it was found that PHEMA/PEO blend system is miscible in the entire composition range. The estimated values of the thermodynamic parameter α and interaction parameter μ of this system indicated that the blend (PHEMA/PEO) is compatible. These results confirm that viscometry, a non-expensive technique can be applied to evaluate the existence of attractive interactions of polymer systems in solution. Ultrasonic velocity, density and adiabitic compressibility values of blends were found to be linear which, is the characteristic of compatible blends. The results obtained by and differential scanning calorimetry provide a clear indication that blends of are miscible in the solid state over the whole composition range. The blends show a positive deviation from Fox equation implying an intermolecular interaction between the polymers

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