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Miscibility of polymethyl methacrylate / polyether sulfone blend by viscisoty, ultrasonic velocity and polarized optical microscopic methods

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Abstract

The solutions of blends of polymethyl methacrylate/ polyether sulfone were prepared in different proportions in a common solvent. The miscibility of these blends was probed by solution techniques such as viscosity and ultrasonic velocity and a solid state technique such as polarized optical microscopy. Using viscosity data, the interaction parameters of these blends of different compositions were computed with the relevant equations. The immiscible nature of these blends as indicated by the viscosity data was confirmed by the ultrasonic velocity and polarized optical microscopic methods. The immiscible nature of these blends suggests that these two polymers are favourable for preparing polymer alloys using a suitable compatibiliser.

Keywords: Polymer blends, Polymethyl methacrylate, Polyether suflone, Miscibility, Ultrasonic velocity, Viscosity, Optical microscopy.

INTRODUCTION

When two or more polymer or copolymers are physically mixed, polymer blends are resulted. These polymer blends often exhibit properties that are superior to any one of the component polymers. In recent years, there is increasing interest in the studies of these polymer systems. However, the manifestation of superior properties depends upon the miscibility of homopolymers at the molecular scale. The mixing results in altogether different morphology of the blends ranging from single – phase system to two phase or multiphase systems. Various techniques are available to study the miscibility of the polymer blends [1]. Chee [2] and Sun et al. [3] used the viscosity method for the study of the polymer – polymer miscibility. Singh and Singh [4] used ultrasonic velocity and viscosity methods for investigating polymer – polymer miscibility. They showed that the variation of ultrasonic velocity and viscosity with blend composition is linear for miscible blends and non – linear for immiscible blends. Varada Rajulu et al. [5-9] used viscosity, ultrasonic velocity, refractive index and density measurements for probing the miscibility of several polymer blends. In the present study, we used these techniques to investigate the miscibility of polymethyl methacrylate (PMMA) / polyether sulfone (PES) blend. We selected these polymers as PMMA is an amorphous tough polymer with many optical applications and PES is engineering plastic, which finds many applications as separation membrane.

MATERIALS AND METHODS

The blends of PMMA/ PES of different compositions were prepared by mixing solutions of polymers in DMF. PMMA (M/s. Rishab Polymers, India; $\overline{Mn} = 60000$) and PES (M/s Aldrich, $\overline{Mn} = 100000$) were used in the present study. The total weight of the two components was always maintained at 2g/dl. The ultrasonic velocities of the blend solutions were measured by ultrasonic interferometric technique as described elsewhere [5-9]. The relative viscosities of the blend solutions were measured at 35 ^{0}C using an USLV. The polarizing micrograms of the blend films cast for all compositions were recorded using a microprocessor controlled Carl Zeiss Polarizing Microscope.

RESULTS AND DISCUSSION

The measured values of reduced viscosity for PMMA, PES and PMMA/ PES (blend in which the weight fraction of PMMA and PES each is 0.5) in DMF at 35 ^{0}C are presented in Table 1.

Table 1. Reduced viscosities of PMMA, PES and their blend (0.5: 0:5 composition) in DMF at 35 ^{0}C

Concentration (g/dl)	Reduced Viscosity $(\eta_{sp}/C)\,(dl/g)$		
	PMMA	PES	PMMA/PES
1.43	0.5089	0.4340	0.4912
1.54	0.5027	0.4807	0.5120
1.67	0.5111	0.4661	0.5114
1.82	0.4938	0.5770	0.4840
2.00	0.5187	0.5683	0.4571

The Huggin's plot for this blend in which the weight of both the components was maintained at 0.5 is presented in Fig. 1. In the same figure, the Huggin's plots for the constituent homopolymers are also presented.

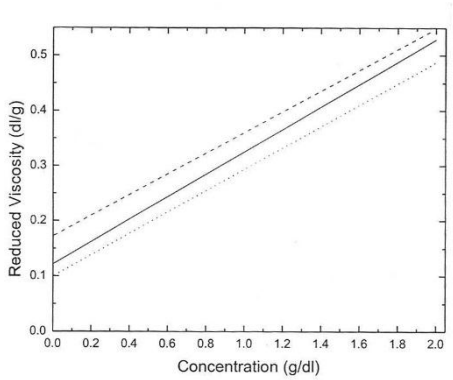

Fig. 1 Huggin's plot of PMMA, PES and PMMA (0.5)/PES (0.5) blend (----- PES; -- PMMA/ PES Blend an d ... PMMA)

In the same figure, the Huggin's plots for the constituent homopolymers are also presented. In order to probe the miscibility of the PMMA/ PES blends, the equations suggested by Chee [2] and Sun et al. [3] (Eqns. 1 and 2 respectively) were utilized and the interaction parameters μ and α were calculated.

$$\mu = \frac{\Delta B}{\left\{ [\eta]_2 - [\eta]_1 \right\}^2} \quad ..(1)$$

Here $\Delta B = W_1^2 b_{11} + W_2^2 b_{22} + 2 W_1 W_2 b_{12}$ in which W_1 *and* W_2 are the weight fractions of the two polymers, b_{11} *and* b_{22} *and* b_{12} are the slopes of the Huggin's plots of the two polymers and b_{12} is that of the blend. $[\eta]_1$ *and* $[\eta]_2$ are intrinsic viscosities for pure component solutions.

$$\alpha = K_m - \frac{K_1 [n]_1^2 W_1^2 + K_2 [\eta]_2^2 W_2^2 + 2 (K_1 K_2)^{1/2} [\eta]_1^2 [\eta]_2^2 W_1 W_2}{\left\{ [\eta]_1 W_1 + [\eta]_2 W_2 \right\}} \quad ...(2)$$

Where K_1, K_2 *and* K_m are the Huggin's constants for individual components 1, 2 and blend respectively. While deriving this equation [Eq. (2)], the long range hydrodynamic interactions are taken into account. Sun et al. [3] suggested that the blend would be miscible if $\alpha \geq 0$ and immiscible when $\alpha < 0$.

The μ *and* α values for blends of different compositions are presented in Table 2.

Table 2. Interaction parameters μ *and* α for PMMA/ PES blends of different compositions

Weight fraction of PMMA/ PES Blend	μ	α
0.2/0.8	-1.550	-0.468
0.4/0.6	-1.131	-0.508
0.5/0/5	-2.266	-0.379
0.6/0.4	-0.547	-0.935
0.8/0.2	-1.534	-4.854

From this table, it can be seen that μ *and* α for PMMA/ PES blends of all compositions are negative. This indicates that the blends under investigation are immiscible in nature. In order to further probe the miscibility of the polymer blends under study, the ultrasonic velocity of the polymer blend solutions was measured. The measured values of ultrasonic velocity of PMMA/ PES polymer blends are presented in Tables 2. The variation of ultrasonic velocity of PMMA/ PES polymer blends with composition is depicted in Fig. 2.

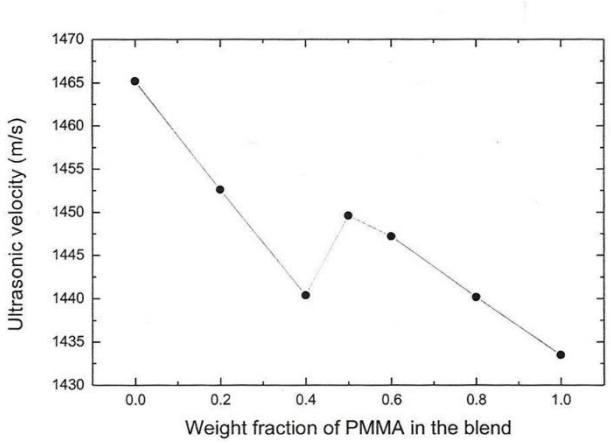

Fig. 2 The variation of ultrasonic velocity with weight fraction of PMMA in PMMA/ PES Blend in DMF at 35 ^{0}C

From this figure, it is clearly evident that the variation is non-linear for the system under study showing multiphase nature in the blend. Singh and Singh [4] have also attributed the non-linear variation of ultrasonic velocity with blend compositions to the immiscible nature of several blends.

In order to further probe the miscibility or otherwise of PMMA/PES blend, the authors used the solid – state technique, viz., polarized optical microscopy. The micrograms of the PMMA/PES blends of different compositions are presented in Fig. 3.

From these micrograms, it is evident that the components of PMMA and PES exist as two phases in the blend. This clearly indicates that the blends is immiscible in nature. Chattopadhaya and Benerjee [10] also used polarizing microscopic technique to confirm the miscibility or otherwise of the blends in film form. These studies provide us a clue that the combination of PMMA and PES can be converted in to a polymer alloy by suitable compatibilisation.

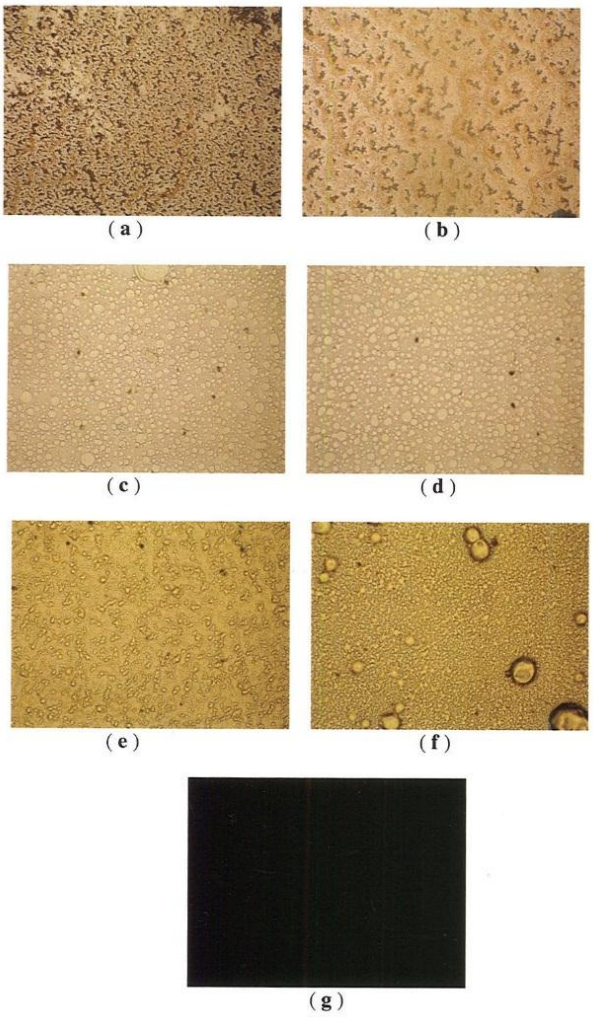

Fig. 3 Polarized Optical Micrographs of PMMA/ PES blends with the weight fraction of PMMA – (a) 0.0; (b) 0.2; (c) 0.4; (d) 0.5; (e) 0.6; (f) 0.8 ; (g) 1.0.

In order to explain the immiscible nature of PMMA/ PES blend basing on thermodynamics, the solubility parameters were calculated using Van Krevelen [11] group additive method. The computed values of solubility parameters PMMA and PES are found to be $19.1\ J^{1/2}/cm^{3/2}$ *and* $21.5\ J^{1/2}/cm^{3/2}$ respectively. The difference between these two values is found to be 2.5 $J^{1/2}/cm^{3/2}$ (i.e. 2.5 H). As per thermodynamic criterion, the components in a mixture are miscible only when the difference in their solubility parameters is less than 2H. As in the present case, the value exceeded 2H, the blend became an immiscible one.

CONCLUSIONS

From the viscosity, ultrasonic velocity and polarized optical microscopic techniques, the blends of PMMA/PES were found to be immiscible. The computed solubility parameters (Hildebrand parameters) also confirmed the same.

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