Miscibility Study of Cellulose Acetate/Carboxylated Poly(vinyl chloride) Blend in Cyclohexanone by Viscosity, Ultrasonic Velocity, Refractive Index, and Polarizing Microscopic Methods

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ABSTRACT: The viscosity, ultrasonic velocity, refractive index, and density of cellulose acetate/carboxylated poly(vinyl chloride) (CA/C-PVC) blends in cyclohexanone, a common solvent, were measured at 30°C. After casting films of the blend for a 50:50 composition, polarizing micrographs were taken. Using the viscosity data, the interaction parameters were computed by employing two different equations. These values indicated that the CA/C-PVC blend is miscible. This was confirmed by ultrasonic, refractive index, density, and polarizing microscopic methods. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 557–561, 2001

Key words: polymer blends; ultrasonic velocity; viscosity; refractive index; polarizing microscopy; miscibility

INTRODUCTION

Polymer blends are formed by combining two or more polymers by mechanical or chemical methods of infinite mixing. The resulting polymeric systems often exhibit properties that are superior to any one of the component polymers alone. There has been a great deal of interest in studies of these polymer systems, generally known as polymeric alloys.[1] However, the manifestation of superior properties depends upon the miscibility of homopolymers on a molecular scale. In general, there are three different types of blends, that is, totally miscible, partially miscible, and immiscible. The miscibility results in altogether different morphologies of the blend ranging from a single-phase system to two- or multiphase systems. There have been various techniques for studying the miscibility of polymer blends.[2] Some of these techniques may be complicated, costly, and time-consuming. Hence, it is desirable to identify simple, low-cost, and rapid techniques to study the miscibility of polymer blends. Chee[3] and Sun et al.[4] suggested viscometry for the study of polymer–polymer miscibility. Singh and Singh[5,6] suggested the use of ultrasonic velocity and viscosity measurements for investigating polymer miscibility. Paladhi and Singh[7,8] showed that variation of the ultrasonic velocity and the viscosity with blend compositions is linear for miscible blends. Recently, Varada Rajulu et al.[9] used ultrasonic and refractometric techniques for the study of the

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Table I Ultrasonic Velocity, Density, and Refractive Index of CA/C-PVC Blend Solutions in Cyclohexanone at 30°C

Percent of CA in the Blend	Ultrasonic Velocity (m/s)	Density (g/cc)	Refractive Index
0.0	1398.0	0.9565	1.4445
20.0	1398.4	0.9565	1.4445
40.0	1398.8	0.9565	1.4445
50.0	1399.0	0.9565	1.4445
60.0	1399.2	0.9565	1.4445
80.0	1399.7	0.9565	1.4445
100.0	1400.0	0.9565	1.4445

miscibility of polymers. In the present study, the authors employed some simple and rapid techniques and measured the viscosity, ultrasonic velocity, density, and refractive index and also took polarizing micrograms (for 50:50 composition) of cellulose acetate/carboxylated poly(vinyl chloride) (CA/C-PVC). Varada Rajulu et al.[10] already found that the cellulose acetate/poly(vinyl chloride) (CA/PVC) blend is immiscible. To investigate the miscibility of the CA/C-PVC blend, the present work was undertaken.

EXPERIMENTAL

The blends of CA/C-PVC of various compositions were prepared by mixing solutions of the polymers in cyclohexanone. CA (M/S MACC, India; $\bar{M}_v$ = 1,00,000) with an acetyl content of 56% and C-PVC (M/S Aldrich Chemicals, Milwaukee, WI; $\bar{M}_v$ = 220,000) with a carboxyl content of 1.8% were employed in the present study. The total weight of the two components in solution was always maintained at 1 g/dL. The ultrasonic velocities of the blend solutions were measured by an ultrasonic interferometric technique as described elsewhere.[11] The temperature is maintained at 30°C by circulating water from a thermostat with a thermal stability of ±0.05°C through the double-wall jacket of the ultrasonic experimental cell. The densities of the solutions were measured at 30°C by a specific gravity bottle. The refractive index of the blend solutions was measured with an Abbe's refractometer with a thermostated water-circulation system at 30°C as described elsewhere.[12] The relative viscosities of the blend solutions were measured at 30°C using an Ubbelohde suspended level viscometer. Polarizing micrographs of the cast blend films (for 50:50 composition) were taken using a Carl Zeiss polarizing microscope.

RESULTS AND DISCUSSION

The measured values of the ultrasonic velocity, density, and refractive index of the blend solutions are presented in Table I. Figure 1 shows Huggins' plots for a blend of CA/C-PVC in which the weight fraction of both components was maintained at 0.5. Chee[3] gave the expression for the interaction parameter when the polymers are mixed in weight fractions W_1 and W_2 as

$$\Delta B = \frac{b - \bar{b}}{2W_1W_2} \quad (1)$$

where $\bar{b} = W_1b_{11} + W_2b_{22}$ and where b_{11} and b_{22} are the slopes of the viscosity curves for the com-

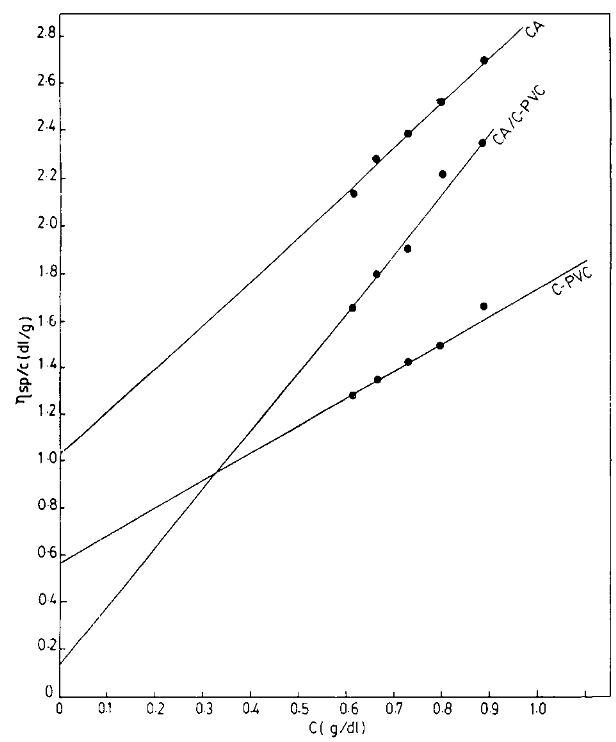


Figure 1 Variation of reduced viscosity with composition in CA/C-PVC (equal weight fraction) blend in cyclohexanone at 30°C.

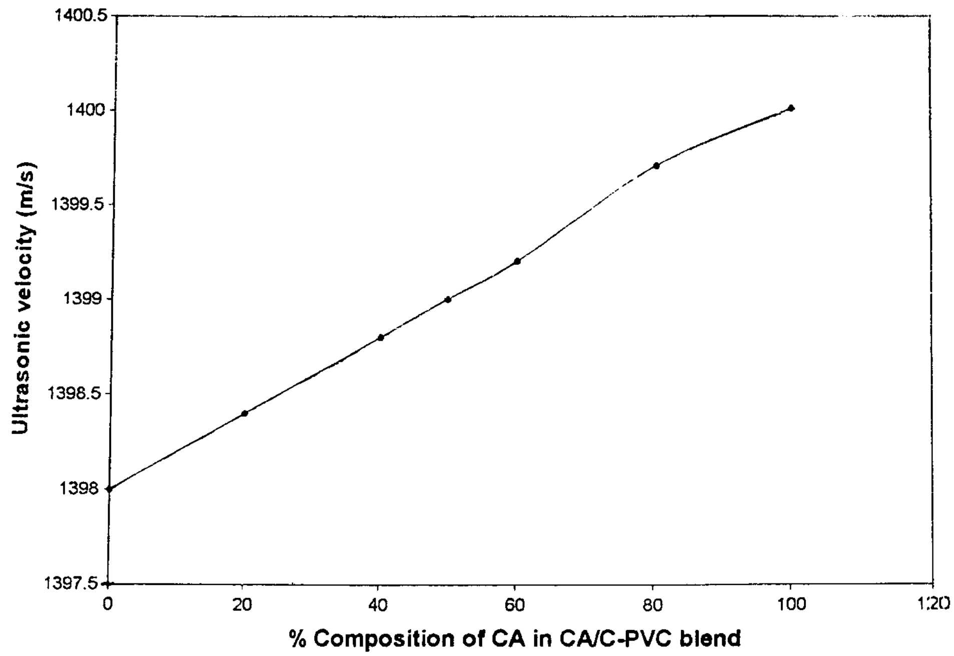


Figure 2 Variation of ultrasonic velocity with composition in CA/C-PVC blend in cyclohexanone at 30°C.

ponents and b is related to the Huggins coefficient K_H as

$$b = K_H[\eta]^2 \tag{2}$$

For a ternary system, it is also given by

$$b = W_1^2 b_{11} + W_2^2 b_{22} + 2W_1W_2b_{12} \tag{3}$$

where b_{12} is the slope of the viscosity curve for the blend solution.

Using these values, Chee[3] defined a more effective parameter:

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

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component solutions. The blend is miscible if $\mu \geq 0$ and immiscible when $\mu < 0$.[3] In the present study, the value of μ for CA/C-PVC was computed to be 1.275, indicating that the blend is miscible. But in the case of the CA/PVC system, μ was reported[10] to be -0.075, indicating that the CA/PVC blend is immiscible. But, recently, Sun et al.[4] suggested a new formula for the determination of the miscibility of polymers:

$$\alpha = K_m - \frac{K_1[\eta]_1^2W_1^2 + K_2[\eta]_2^2W_2^2 + 2\sqrt{K_1K_2}\,[\eta]_1[\eta]_2W_1W_2}{\{[\eta]_1W_1 + [\eta]_2W_2\}^2} \tag{5}$$

where K_1, K_2, and K_m are the Huggins constants for individual pure components 1 and 2 and the blend, respectively. While deriving this equation, long-range hydrodynamic interactions are taken into account. Sun et al.[4] suggested that a blend will be miscible if $\alpha \geq 0$ and immiscible when $\alpha < 0$. In the present study, the α value was found to be 146, indicating that it is miscible. In the case of the CA/PVC blend,[10] the α value was reported to be -0.0209, indicating the immiscible nature. The presence of common $COOCH_3$ groups both in CA and C-PVC may be responsible for the miscibility of the CA/C-PVC blend.

To employ simple techniques to investigate the miscibility of the polymer blends under study, the variation of the ultrasonic velocity, density, and refractive index of the polymer blend solutions with composition are depicted in Figures 2–4, respectively. From these figures, it is clearly evident that the variation is linear, indicating a single phase for CA/C-PVC. In the case of the CA/PVC blend system,[10] this variation was reported to be nonlinear, which was attributed to its im-

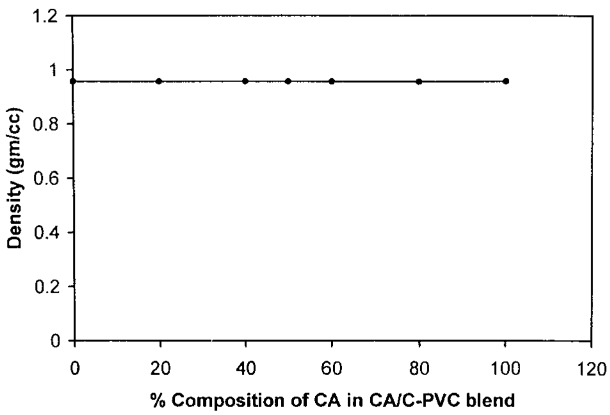


Figure 3 Variation of density with composition in Ca/C-PVC blend in cyclohexanone at 30°C.

miscible nature. Varada Rajulu et al.[9] used these techniques for a miscibility study of a cellulose acetate/poly(methyl methacrylate) blend, where the nonlinear variation of the ultrasonic velocity and refractive index with the blend composition was attributed to the immiscible behavior of the blend. Similarly, the linear variation of the ultrasonic velocity with the blend composition in the case of poly(methyl methacrylate)/poly(vinyl acetate)[6] was attributed to the miscible nature of the blend. Further, it is observed that the ultrasonic velocity, density, and refractive index of CA/C-PVC did not vary much more than did those of the pure components. But in the case of CA/PVC, the variation was found to be more.[10] These observations indicate that greater interaction exists between CA and C-PVC due to the presence of common groups in them. The optical polarizing micrograph of the CA/C-PVC blend of a 50:50

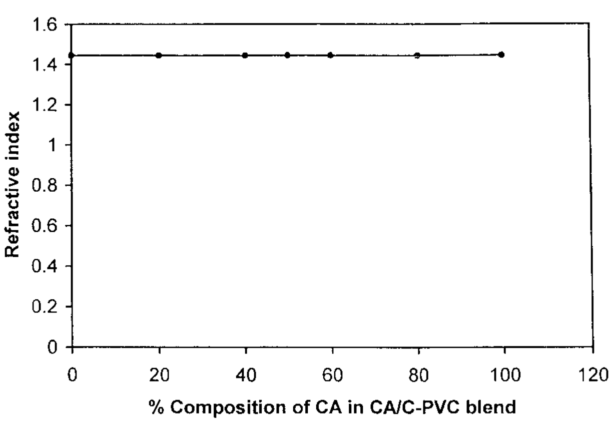
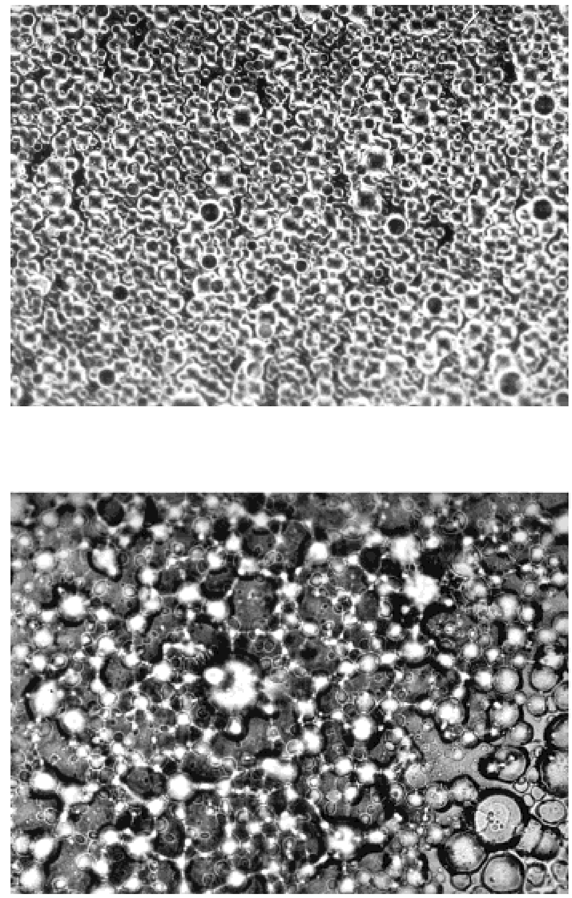


Figure 4 Variation of refractive index with composition in CA/C-PVC blend in cyclohexanone at 30°C.



a

b

Figure 5 Polarized optical micrograph of CA/C-PVC blend of 50:50 composition. Magnification: (a) ×25; (b) ×200.

composition is presented in Figure 5. From this figure, it is clearly evident that a uniform dispersion of the components is present in the blend, as the phase agglomeration is minimum. Chatopadhyay and Banerjee[13] also used the polarizing microscopic technique to confirm the miscibility or immiscibility of the blends in film form.

CONCLUSIONS

Using viscosity, ultrasonic velocity, refractive index, density, and polarizing microscopic methods, the polymer blend of CA/C-PVC was found to be miscible.

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