

NOTE

Blend Compatibility Studies of Polystyrene/Poly(methyl methacrylate) and Polystyrene/Styrene–Acrylonitrile by Densitometry, Viscometry, Refractometry, Ultraviolet Absorbance, and Fluorescence Techniques at 30°C

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Received 17 April 2004; accepted 3 May 2004

DOI 10.1002/app.20973

Published online in Wiley InterScience (www.interscience.wiley.com).

INTRODUCTION

Polymer blends have been reported extensively in the literature.¹ A small fraction of polymer mixtures is fully miscible at the molecular level, but most polymer blends are not.² In the literature, the compatibility of polymer blends has been studied with a variety of techniques, such as optical microscopy,³ differential scanning calorimetry,⁴ dynamic mechanical analysis,⁵ infrared spectroscopy,⁶ nuclear magnetic resonance,⁷ and inverse gas chromatography.⁸ Most of these methods are quite complicated and time-consuming. Hence, it is desirable to use simple yet accurate methods such as viscosity, ultrasonic velocity, and refractive-index measurements^{9–11} to study the miscibility or immiscibility of polymer blends. Recently, Radhakrishnan et al.¹² used fluorescence and ultraviolet (UV) absorbance techniques to study the blend compatibility of polysilanes.

In this note, we present experimental data on blend solutions of polystyrene (PS) with poly(methyl methacrylate) (PMMA) and of PS with styrene–acrylonitrile (SAN). The data were obtained with viscosity, density, refractive-index, UV absorbance, and fluorescence techniques. The polymers chosen in this study could neither absorb nor emit radiation, and so for the absorption and fluorescence measurements, a scintillating dye, 1,4-bis-[2-(5-phenyloxazolyl)]benzene (POPOP), was added in a small quantity

so that the absorbance and emission of POPOP at 360 nm in blend solutions prepared in 1,4-dioxane at 30°C could be measured. With these data, the compatibility of the blends was predicted.

EXPERIMENTAL

Materials and blend preparation

Gift samples of PS and SAN were received from CIPET (Mysore, India). PMMA was purchased from Himedia Chemicals (Mumbai, India). The POPOP dye was purchased from CDH Laboratory Reagents (New Delhi, India). Analytical-reagent-grade 1,4-dioxane was purchased from S.D. Fine Chemicals (Mumbai, India). The 1% stock solutions of all the polymers were prepared in 1,4-dioxane. The blend solutions of PS/PMMA and PS/SAN were prepared in ratios of 20/80, 40/60, 50/50, 60/40, and 80/20. To these solutions, a $1 \times 10^{-4}M$ solution of POPOP dye prepared in 1,4-dioxane was added for absorbance and emission measurements.

Methods

Viscosity measurements

The dilute solution viscosities of 1,4-dioxane, polymer solutions, and blend solutions of the polymers were measured at 30°C with a Scott–Gerate (Hofheim, Germany) model AVS 350 viscometer. The viscometer automatically measured the flow-through times in capillary tubes. The efflux times were determined on a digital display to an uncertainty of ± 0.01 s. The temperature of the bath (model CT 050/2, Scott–Gerate) was kept constant at 30°C within an uncertainty of $\pm 0.01^\circ\text{C}$. The estimated error in the viscosity was ± 0.001 mPa s. Approximately 5 cm³ of the polymer or blend solution was placed the viscometer tube. The liquid was allowed to equilibrate

This article is CEPS Communication #45.

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Contract grant sponsor: University Grants Commission (New Delhi, India); contract grant number: F1-41/2001/CPP-II.

Contract grant sponsor: Council of Scientific and Industrial Research (New Delhi, India); contract grant number: 80(0042)/02/EMR-II.

TABLE I
Reduced Viscosity, Density, Refractive Index, Absorbance, and Fluorescence
of PS/PMMA and PS/SAN Blend Solutions at 30°C

Blend composition	Reduced viscosity (dL/g)	Density (g/cm ³)	Refractive index	Absorbance at 360 nm	Fluorescence at 406 nm
PS/PMMA blend					
0/100	40.81	1.02372	1.4185	2.205	64.23
20/80	57.66	1.02364	1.4188	2.473	73.52
40/60	51.31	1.02362	1.4187	2.349	68.00
50/50	64.13	1.02325	1.4194	2.439	64.04
60/40	68.44	1.02275	1.4189	2.632	69.73
80/20	75.26	1.02283	1.4182	2.596	69.16
100/0	106.59	1.02260	1.419	2.618	68.14
PS/SAN blend					
0/100	79.63	1.02297	1.4190	2.318	73.86
20/80	83.09	1.02289	1.4190	2.301	72.66
40/60	87.97	1.02282	1.4190	2.280	71.83
50/50	90.24	1.02277	1.4190	2.265	71.26
60/40	93.42	1.02272	1.4190	2.242	70.64
80/20	99.32	1.02263	1.4190	2.214	69.29
100/0	106.59	1.02254	1.4190	2.205	68.14

ibrate to the desired temperature for about 10 min, and the flow times were measured.

Density measurements

The densities of 1,4-dioxane, solutions of the polymers, and blend polymer solutions were measured with a high-precision vibrating tube digital density meter (DMA 4500/5000, Anton Paar, Graz, Austria). The temperature of the measuring cell was automatically controlled within an uncertainty of $\pm 0.01^\circ\text{C}$ by an inbuilt and integrated Pt 100 measuring sensor. The instrument was calibrated with air and double-distilled and freshly degassed water at 30°C during every session. The densities were measured within the experimental uncertainty of $\pm 0.00005 \text{ g cm}^{-3}$.

Refractive-index measurements

The refractive indices for the sodium D-line were measured at 30°C with an Atago model 3T (Tokyo, Japan) thermostatically controlled Abbe refractometer. The uncertainty in the refractive index was ± 0.0001 units.

UV and fluorescence spectroscopy

The absorbance measurements were made on a Secomam (Domont, France) Anthelie UV spectrophotometer. The fluorescence measurements were carried out on a Hitachi (Tokyo, Japan) F-2000 fluorescence spectrophotometer. One milliliter of $1 \times 10^{-4} \text{ M}$ POPOP in 1,4-dioxane was mixed with a 2-mL polymer solution with a 1% concentration. The absorbance of POPOP at 360 nm with the corresponding polymer as well as the blend solution was measured as a blank. The same solutions were used for fluorescence measurements excited at 406 nm.

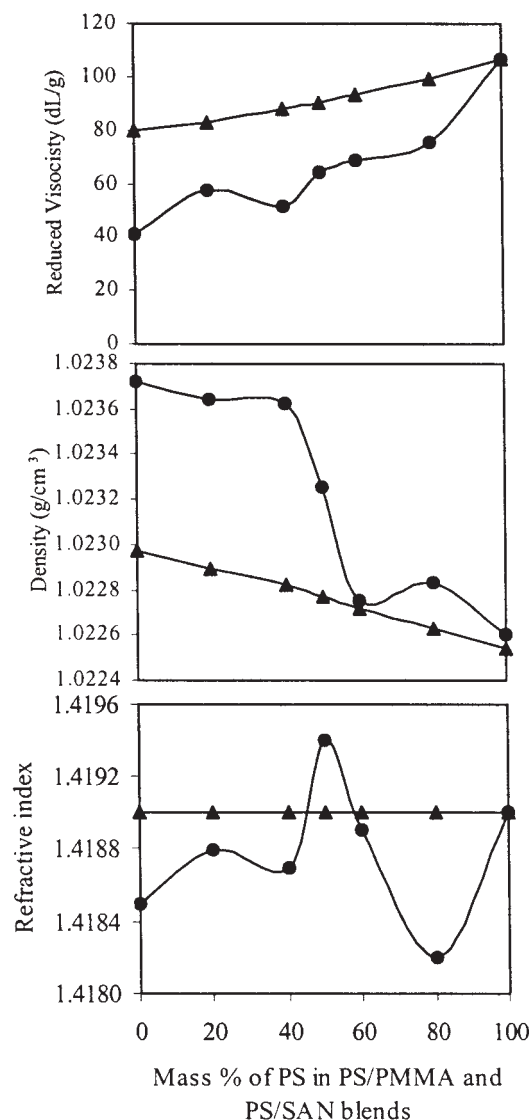


Figure 1 Plots of the reduced viscosity, density, and refractive index versus the mass percentage of PS in (●) PS/PMMA blends and (▲) PS/SAN blends at 30°C .

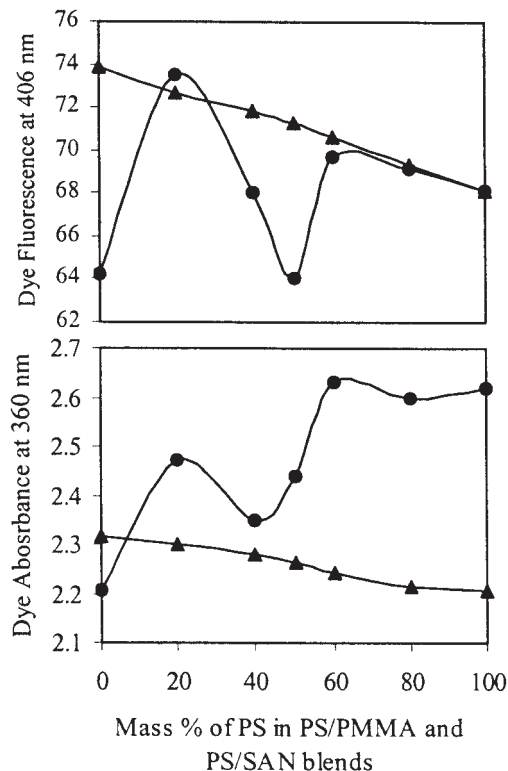


Figure 2 Plots of the absorbance and fluorescence of blend solutions versus the mass percentage of PS in (●) PS/PMMA blends and (▲) PS/SAN blends at 30°C

RESULTS AND DISCUSSION

The experimental results are presented in Table I, whereas the plots of the reduced viscosity, density, and refractive index versus the blend compositions are displayed in Figure 1. For the PS/PMMA blends, nonlinear trends can be observed, suggesting their incompatibility. A similar observation was made earlier for these blends.^{13–15} On the other hand, the linear trends observed for the PS/SAN blends suggest their compatibility.

The polymers used in this study are not suitable for studying energy-transfer processes, and so the absorbance and emission measurements were performed in solutions containing a small quantity of POPOP dye. The compatibility of the PS/SAN blends and the incompatibility of the PS/PMMA blends displayed in Figure 2 confirm the results shown in Figure 1.

CONCLUSIONS

The blending of two or more polymers is well known to manipulate their physical properties without the need for the synthesis of new polymers. However, blends of conjugated polymers are known to exhibit absorption and emission properties. To study the blend compatibility of nonradiative polymers such as PS, PMMA, and SAN, we added a small quantity of a scintillating dye (POPOP). The compatibility or incompatibility results of the absorbance and emission spectra were in good agreement with those determined from physical properties such as the density, viscosity, and refractive index. It can be concluded that PS/PMMA blends are incompatible, whereas PS/SAN blends are compatible.

T. M. Aminabhavi thanks the University Grants Commission (New Delhi, India) for its support in establishing the Center of Excellence in Polymer Science. B. V. K. Naidu thanks the Council of Scientific and Industrial Research (New Delhi, India) for a research associateship.

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