

Solution and Solid-State Blend Compatibility of Poly(vinyl alcohol) and Poly(methyl methacrylate)

S. G. Adoor,¹ L. S. Manjeshwar,¹ K. S. V. Krishna Rao,² B. V. K. Naidu,¹ T. M. Aminabhavi¹

¹Membrane Separations Division, Center of Excellence in Polymer Science, Karnatak University, Dharwad, 580003, India

²Department of Chemistry, Sri Krishanadevaraya University, Anantapur, 515 003, India

Received 8 February 2005; accepted 26 July 2005

DOI 10.1002/app.23337

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

ABSTRACT: The blend miscibility of poly(vinyl alcohol) and poly(methyl methacrylate) in *N,N'*-dimethylformamide solution was investigated by viscosity, density, ultrasonic velocity, refractive index, and UV and fluorescence spectra studies. Differential scanning calorimetry and scanning electron microscopy were used to confirm the blend miscibility

in the solid state. Blends were compatible when the concentration of poly(vinyl alcohol) was greater than 60 wt %. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2415–2421, 2006

Key words: blends; fluorescence; miscibility

INTRODUCTION

Polymer–polymer miscibility has been widely studied in the polymer literature.¹ Such studies have great significance for engineering applications of polymers. Polymer blends can be incompatible due to unfavorable entropies of mixing,^{2,3} but for blends to be compatible, covalent, H-bond, or charge-transfer interactions are important.^{4,5} Polymer blend compatibility has been studied widely with a large number of techniques.^{6–13} Poly(vinyl alcohol) (PVA) and poly(methyl methacrylate) (PMMA) are widely used polymers in many engineering areas.^{14–17} A literature search suggested that no previous studies have been made on the blend compatibility of PVA and PMMA. This prompted us to investigate the compatibility of PVA and PMMA in *N,N'*-dimethylformamide (DMF) solution by the measurement of viscosity, density (ρ), ultrasonic velocity (u), refractive index (n_D), and UV and fluorescence spectra. Blend compatibility in the solid state was confirmed by differential scanning calorim-

etry (DSC) and scanning electron microscopy (SEM) techniques.

EXPERIMENTAL

Materials

PVA (molecular weight \approx 125,000; S. D. Fine Chemicals, Mumbai, India) and PMMA (molecular weight \approx 15,000; Himedia Laboratories Pvt., Ltd., Mumbai, India) were used as received. 1,4-Bis-[2-(5-phenyloxazoloyl)] benzene (POPOP) dye was purchased from CDH Laboratory Reagents (New Delhi). Analytical grade DMF was purchased from S. D. Fine Chemicals.

Preparation of the blend solutions

Dilute solutions of 1% (w/v) PVA and PMMA in DMF were prepared separately in different stoppered conical flasks. Different blend compositions, namely, 20/80, 40/60, 50/50, 60/40, and 80/20, were prepared by mixture of the appropriate quantities of stock solutions of PVA and PMMA. From each composition of the blend, 0.2, 0.4, 0.5, 0.6, 0.8, and 1.0% (v/v) concentrations were prepared in DMF.

Preparation of the blend films

Blend solutions prepared in this way were cast on a clean glass plate. Films were dried initially at room temperature and were then kept in a vacuum oven at 40°C for 48 h to remove any residual DMF solvent. These films containing different amounts of PVA were designated as pure PVA, PVA-20, PVA-40, PVA-50, PVA-60, PVA-80, and PVA-90.

This article is Center for Excellence in Polymer Science Communication #50.

Correspondence to: T. M. Aminabhavi (aminabhavi@yahoo.com).

Contract grant sponsor: University Grants Commission, New Delhi; contract grant number: F1-41/2001/PPP-II (to establish the Center of Excellence in Polymer Science).

Contract grant sponsor: Council of Scientific and Industrial Research; contract grant number: 80(0042)/02/EMR-II (to B.V.K.N. and T.M.A.).

Journal of Applied Polymer Science, Vol. 100, 2415–2421 (2006)
© 2006 Wiley Periodicals, Inc.

Solution and solid state property measurements

Density

The densities of the individual polymers and their blend solutions prepared in DMF were measured with a high-precision, vibrating-tube, digital density meter (Anton Paar, DMA model 4500/5000, Graz, Austria) at 30, 40, and 50°C. The temperature of the measuring cell was automatically controlled within an uncertainty of $\pm 0.01^\circ\text{C}$ by an inbuilt integrated Pt 100 measuring sensor. The instrument was calibrated with air and double-distilled freshly degassed water at the temperature of measurement during every session. The densities of all of the mixtures belonging to a given system (including pure components) were measured during a single session. Experimental uncertainty (i.e., reproducibility in the measured densities) was up to five units in the second decimal place.

Before injecting the sample, we made adjustments if deviations between displayed values and reference values of density standards exceeded the specifications of the instrument. Air and double-distilled freshly degassed water were used for calibration. The ρ values of water and dry air at specific atmospheric pressure were stored in the memory of the instrument over the complete temperature range investigated. If the compared values agreed within $\pm 0.05 \text{ kg/m}^3$, measurements were started after the measuring cell was dried.

Viscosity

Dilute solution viscosities of PVA, PMMA, and their blends were measured at 30, 40, and 50°C with a Scott-Gerate viscometer (model AVS350, Hofheim, Germany). The viscometer automatically measured the flowthrough times in capillary tubes. Efflux times were determined on a digital display to an accuracy of $\pm 0.01 \text{ s}$. The temperature of the bath (Scott-Gerate, model CT 050/2) was kept constant within an accuracy of $\pm 0.01^\circ\text{C}$. The estimated error in viscosity was $\pm 0.001 \text{ mPa s}$. An approximate volume of 5 cm^3 was taken in the viscometer tube and was equilibrated to the desired temperature for about 10 min before the flow time measurements.

Refractive index

The n_D values for the sodium D-line were measured with a thermostatically controlled Abbe refractometer (Atago, model 3T, Tokyo). The uncertainty in n_D was ± 0.0001 units at 30, 40, and 50°C.

Ultrasonic velocity

Ultrasonic velocities were measured with a Mittal Enterprises ultrasonic interferometer operating at 3 MHz

within an accuracy of 0.2% at 30°C. We kept the temperature of the solution constant by circulating water from the thermostatic bath inside the double-walled jacket covering the interferometer cell.

At least three independent readings of all of the physical properties were taken for each mixture. The average of these values were used when we analyzed the data.

Spectroscopic measurements

UV absorbance measurements were made on a Secomam (model Anthelie UV spectrophotometer, France). Fluorescence measurements were carried out on a Hitachi (Tokyo) F-2000 fluorescence spectrophotometer. POPOP solution (1 mL of a $2 \times 10^{-3} \text{ M}$ solution prepared in DMF) was mixed with 2 mL of polymer solutions of different concentrations. The absorbance of POPOP at 360 nm with the corresponding polymer(s) and blend solutions was measured with the plain polymer-polymer blend solution considered as the blank. The same solutions were used for fluorescence measurements excited at 360 nm.

Differential scanning calorimetry (DSC)

DSC measurements were carried out on a DSC SP model instrument (Rheometric Scientific, Ashtead, UK) on the fabricated films of PVA, PMMA, and their blends. Measurements were performed over a temperature range of 25–600°C at a heating rate of $10^\circ\text{C}/\text{min}$ under the nitrogen atmosphere.

Scanning electron microscopy

Scanning electron micrographs of the PVA/PMMA blends were obtained with a Leica Stereoscan-440 scanning electron microscope (Cambridge, UK). These data were obtained at the National Chemical Laboratory, Pune (courtesy of S. B. Halligudi, Catalysis Division).

RESULTS AND DISCUSSION

Solution property studies

Density, viscosity, and refractive index of the blend solutions were measured at 30, 40, and 50°C, whereas ultrasonic velocity was measured at 30°C for six concentrations, namely, 0.2, 0.4, 0.5, 0.6, 0.8, and 1.0% (v/v), of the blends. The results of absolute viscosity versus wt % of PVA in the PVA/PMMA blend displayed in Figure 1 exhibited curvature (nonlinear) trends up to 50% PVA in the blend. However, at 60, 80, and 90 mass % PVA in the PVA/PMMA blends, linear trends were observed, indicating blend compatibility at these compositions. The nonlinear (curvature)

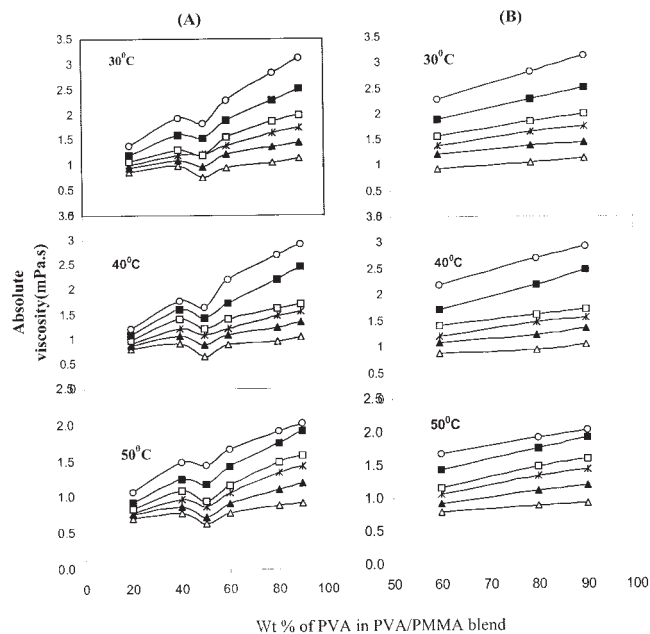


Figure 1 Absolute viscosity versus composition of PVA/PMMA blends at 30, 40, and 50°C for different blend concentrations: (Δ) 0.2, (\blacktriangle) 0.4, (*) 0.5, (\square) 0.6, (\blacksquare) 0.8, and (\circ) 1%.

trends indicated the incompatibility of PVA and PMMA. Similar trends were observed for ρ , u , and n_D results, as displayed in Figures 2–4, respectively.

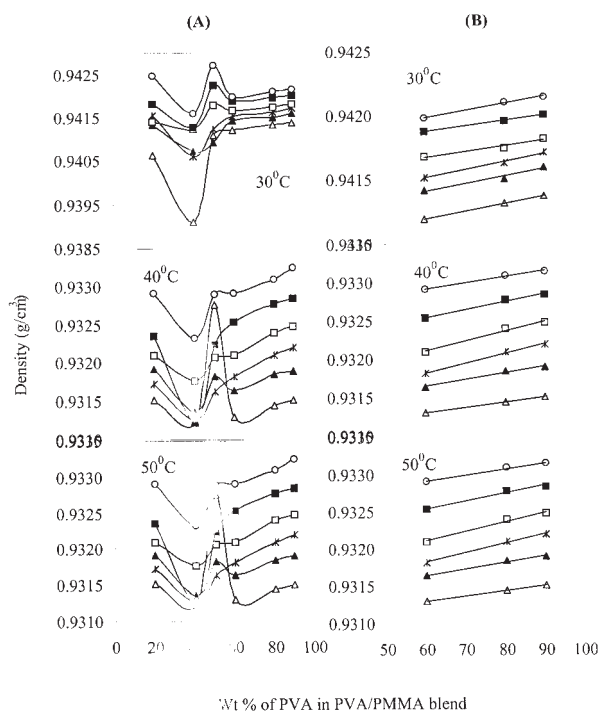


Figure 2 ρ versus composition of the PVA/PMMA blends at 30, 40, and 50°C for different blend concentrations: (Δ) 0.2, (\blacktriangle) 0.4, (*) 0.5, (\square) 0.6, (\blacksquare) 0.8, and (\circ) 1%.

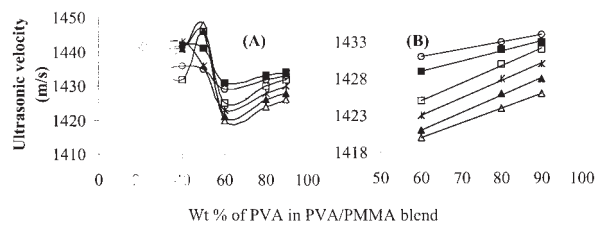


Figure 3 u versus composition of the PVA/PMMA blends at 30°C for different blend concentrations: (Δ) 0.2, (\blacktriangle) 0.4, (*) 0.5, (\square) 0.6, (\blacksquare) 0.8, and (\circ) 1%.

In earlier studies,¹⁸ u was used in predicting the miscibility of cellulose acetate–PMMA blends, wherein nonlinear dependence was attributed to the incompatible nature of the blend. The linear variation in case of a PMMA/poly(vinyl acetate) blend was the result of their miscibility.^{19,20} From the viscosity data, blend miscibility in the solution was studied²¹ with the following relationship:

$$b_m = x_1^2 b_{11} + 2x_1 x_2 b_{12} + x_2^2 b_{22} \quad (1)$$

where x_1 and x_2 are the mass fractions of polymer 1 and 2, b_{11} and b_{22} are the respective interaction parameters, b_{12} is the interaction parameter of the blend system, and b_m represents the global interaction parameter between the individual polymers. The interaction parameters b_{11} , b_{22} , and b_m were calculated from the slopes of the plot of reduced viscosity versus con-

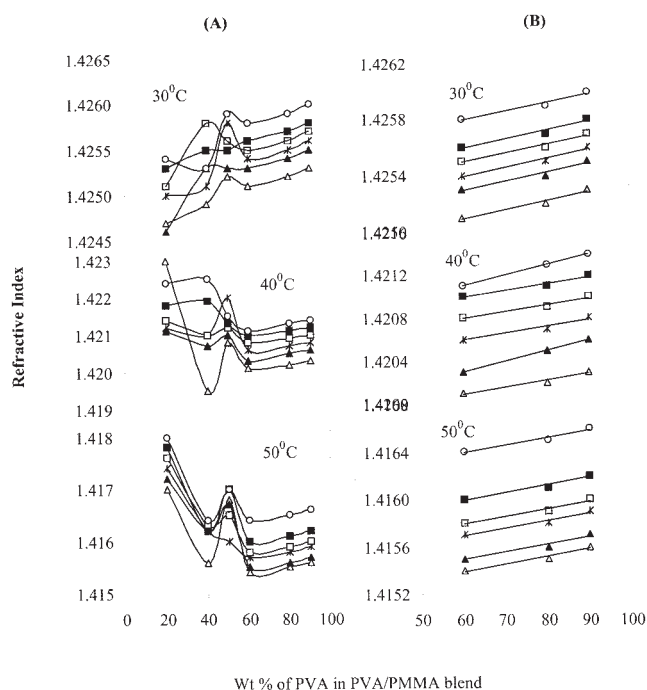


Figure 4 n_D versus composition of the PVA/PMMA blends at 30, 40, and 50°C for different blend concentrations: (Δ) 0.2, (\blacktriangle) 0.4, (*) 0.5, (\square) 0.6, (\blacksquare) 0.8, and (\circ) 1%.

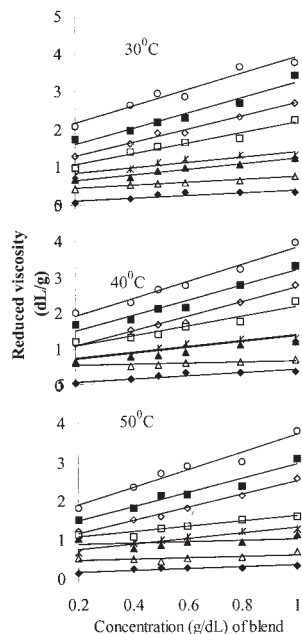


Figure 5 Reduced viscosity versus concentration of the PVA/PMMA blends at 30, 40, and 50°C for different blend compositions: (Δ) 20, (\blacktriangle) 40, ($*$) 50, (\square) 60, (\blacksquare) 80, and (\circ) 90% PVA; (\blacklozenge) pure PMMA; and (\diamond) pure PVA.

centration (see Fig. 5). The interaction parameter b_{12}^* was then calculated theoretically with

$$b_{12}^* = (b_{11}b_{22})^{1/2} \quad (2)$$

The values of b_{11} and b_{22} were the slopes of the plots of reduced viscosity versus concentration of individual polymers as calculated from the Huggins equation:²²

$$\eta_{sp}/c = [\eta] + bc \quad (3)$$

where η_{sp} is the specific viscosity, c is the concentration $[\eta]$ is the intrinsic viscosity, and b is the Huggins constant.

The difference (Δb) calculated from the theoretical b_{12}^* from eq. (2) and the experimental b_{12} with eq. (1) is given as

$$\Delta b = (b_{12} - b_{12}^*) \quad (4)$$

If $\Delta b > 0$, blends are compatible; if $\Delta b < 0$, phase separation occurs. The calculated values of Δb for all of the blends at different temperatures are given in Table I. Positive Δb values at 60, 80, and 90% PVA in the blend at all the temperatures indicated the compatible nature of the blends, whereas the negative Δb values at other compositions (i.e., 20–50% PVA) indicated blend immiscibility.

TABLE I
 Δb Values for the PVA/PMMA Blends at Different Temperatures

PVA/PMMA (w/w)	30°C	40°C	50°C
20/80	-0.416	-0.771	-0.406
40/60	-0.075	-0.186	-0.406
50/50	-0.074	-0.122	0.134
60/40	0.633	0.435	0.091
80/20	1.258	1.156	1.263
90/10	1.372	1.445	1.686

Isentropic compressibility (K_s) was also used to study the miscibility of blends.²³ It was calculated from ρ and u of the solutions with

$$K_s = \left(\frac{1}{u^2\rho} \right) \quad (5)$$

Plots of K_s versus composition of the blend are displayed in Figure 6 at 30°C. Linear variation of K_s with 60–90 wt % PVA suggested their miscibility, whereas the nonlinear trends in the composition range 20–50% PVA indicated their incompatible nature. These results are in conjunction with those of the ρ , viscosity, and n_D data discussed previously.

The heat of mixing (ΔH_m) was also used as a measure to study the blend compatibility.^{24–26} According to Schneier,²⁶ ΔH_m of the polymer blends is given by

$$\Delta H_m = \{w_1M_1\rho_1(\delta_1 - \delta_2)^2[w_2/(1 - w_2)M_2\rho_2 + (1 - w_1)M_1\rho_1]^2\}^{1/2} \quad (6)$$

where w , M , and ρ are the weight fraction of the polymer, the monomer molecular weight, and the polymer density, respectively, and δ represents the solubility parameter of the polymer. The δ values of PVA [$12.6 \text{ (cal/cm}^3)^{1/2}$] and PMMA [$9.1 \text{ (cal/cm}^3)^{1/2}$] were taken from the literature,²⁷ and these values were used to calculate ΔH_m with eq. (6). Figure 7 shows the variation of ΔH_m versus blend composition. Here also, linear trends are observed over the range of

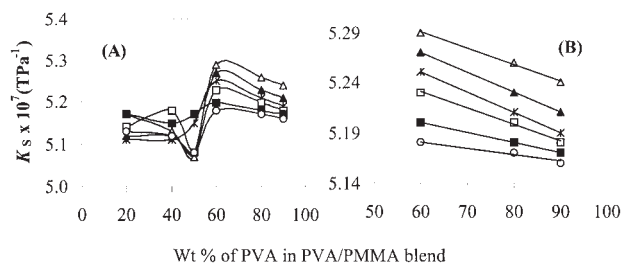


Figure 6 K_s versus composition of the PVA/PMMA blends at 30°C for different blend concentrations: (Δ) 0.2, (\blacktriangle) 0.4, ($*$) 0.5, (\square) 0.6, (\blacksquare) 0.8, and (\circ) 1%.

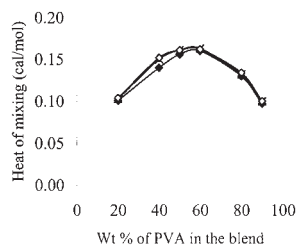


Figure 7 ΔH_m versus composition of the PVA/PMMA blends at (◆) 30, (×) 40, and (◇) 50°C.

60–90 mass % of PVA in the blend, thus confirming the blend compatibility in the studied region.

Interaction parameter

The polymer–solvent interaction parameter (χ) was computed from Flory–Huggins theory²⁵ with

$$\chi_i = \left(\frac{V_i}{RT} \right) (\delta_2 - \delta_1)^2 \quad (7)$$

where δ_1 and δ_2 are the solubility parameters of solvent and polymer, respectively, and V_i , R , and T are the molar volume of the solvent, universal gas constant, and temperature (K), respectively. Equation (7) was also used by others^{28,29} to calculate χ of the blends. The blend δ was calculated from the additivity relationship

$$\delta = x_1\delta_1 + x_2\delta_2 \quad (8)$$

where x_1 and x_2 are the mass fractions and δ_1 and δ_2 are the solubility parameters of the component polymers in the blend system. The interaction parameters of the polymer–polymer blend systems are presented in Table II, whereas the blend–solvent interaction parameters are given in Table III. From these data, we observed that polymer–polymer interactions were quite higher than those observed for blend–solvent interactions for blend compositions containing 80–90% PVA at all of the temperatures. Such a large difference between polymer–polymer interactions and

TABLE II
Polymer–Polymer Interaction Parameters of the PVA and PMMA in the Blend

Temperature (°C)	Polymer	χ_i calculated from eq. (7)
30	PVA	0.72
	PMMA	1.75
40	PVA	0.73
	PMMA	1.75
50	PVA	0.72
	PMMA	1.74

TABLE III
Blend–Solvent Interaction Parameters at Different Temperatures

Temperature (°C)	PVA/PMMA (w/w)	δ calculated from eq. (8)	χ_i calculated from eq. (7)
30	20/80	9.8	0.698
	40/60	10.5	0.340
	50/50	10.9	0.209
	60/40	11.2	0.200
	80/20	11.9	0.006
	90/10	12.3	0.002
40	20/80	9.8	0.683
	40/60	10.5	0.333
	50/50	10.9	0.205
	60/40	11.2	0.107
	80/20	11.9	0.006
	90/10	12.3	0.002
50	20/80	9.8	0.668
	40/60	10.5	0.326
	50/50	10.9	0.200
	60/40	11.2	0.105
	80/20	11.9	0.006
	90/10	12.3	0.002

blend–solvent interactions suggested the compatible nature of the blends in the range 80–90% PVA.

Spectroscopic studies

UV and fluorescence studies have been made to analyze the compatibility of blends.^{8,13} Because both PVA and PMMA were not suitable for studying the energy-transfer processes, they do not emit radiation in the UV region. Therefore, we added a small quantity of POPOP dye, which had a wavelength maximum, λ_{\max} value at 360 nm. Absorbance of POPOP in each blend solution was measured at 360 nm, whereas POPOP fluorescence data were collected at 420 nm. Figures 8 and 9 display, respectively, the variation of dye absorbance and fluorescence versus blend composition. Linear trends observed in the range 60–90% PVA were a further proof of blend compatibility.

DSC studies

One of the most commonly used methods for estimating the polymer–polymer compatibility is to deter-

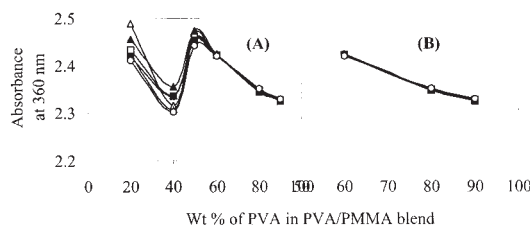


Figure 8 Dye absorbance at 360 nm versus composition of the PVA/PMMA blends for different blend concentrations: (△) 0.2, (▲) 0.4, (*) 0.5, (□) 0.6, (■) 0.8, and (○) 1%.

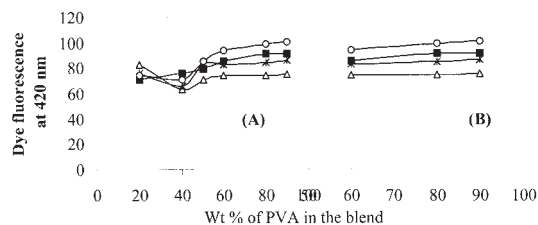


Figure 9 Dye fluorescence at 420 nm versus composition of the PVA/PMMA blends for different blend concentrations: (Δ) 0.2, ($*$) 0.5, (\blacksquare) 0.8, and (\circ) 1%.

mine the glass-transition temperature of the blend and compare it with the glass-transition temperature of the component polymers. If one of the component polymers is crystalline in nature, the depression in the melting temperature (T_m) can be used to study the blend compatibility.^{30–32} In this study, DSC was used to estimate T_m to investigate the compatibility of PVA and PMMA blends. Figure 10 displays the DSC thermograms of PVA in the PVA/PMMA blends. The T_m of PVA is observed at 190.55°C. In this study, variations in T_m of PVA in the blend were considered a measure of blend compatibility. T_m did not show any systematic trend between 20 and 50% PVA in the blend, but a systematic depression in T_m for PVA in the blend was observed for 60–90% PVA in the blend. Such a systematic depression in T_m between 60 and 90% of PVA in the blend indicated blend compatibility in the aforementioned range.

SEM studies

In the earlier literature,³³ SEM was used to study blend compatibility. In preparing the blend films of PVA and PMMA, phase separation occurred at less than 50% PVA, indicating its immiscibility. However, good films were obtained at 60, 80, and 90% PVA in the blend. A typical SEM photograph of the 80/20 PVA/PMMA blend, shown in Figure 11, confirmed the blend compatibility as seen by a single phase.

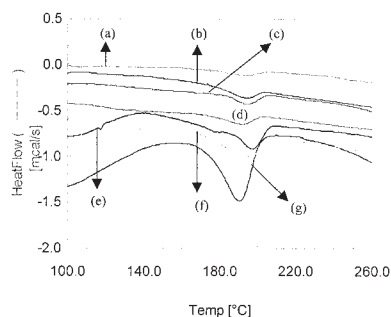


Figure 10 DSC thermograms of the PVA/PMMA blends: (a) PVA-50, (b) PVA-40, (c) PVA-60, (d) PVA-20, (e) PVA-90, (f) PVA-80, and (g) pure PVA.

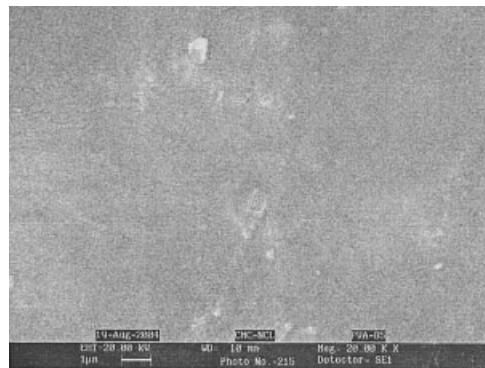


Figure 11 SEM photograph of the 80/20 PVA/PMMA blend.

These results were in accordance with those confirmed by the ρ , viscosity, u , n_D , and spectroscopic studies.

CONCLUSIONS

Binary blend solutions and solid films of PVA and PMMA were prepared in DMF and studied for their physical, spectroscopic, and thermal properties. Judging from the experimental observations, we concluded that PVA and PMMA could form thermodynamically miscible phases at higher contents of PVA (>60%) in the blend.

References

1. Polymer Blends; Paul, D. R.; Newman, S. Eds.; Academic: New York, 1978; Vols. 1 and 2.
2. Olabisi, O.; Robeson, L. M.; Shaw, M. T. Polymer-Polymer Miscibility; Academic: New York, 1979.
3. Coleman, M. M.; Graf, J. F.; Painter, P. C. Specific Interactions and the Miscibility of Polymer Blends; Technomic: Lancaster, PA, 1991.
4. Varnell, D. F.; Runt, J. P.; Coleman, M. M. *Polymer* 1983, 24, 37.
5. Woo, E. M.; Barlow, J. W.; Paul, D. R. *J Appl Polym Sci* 1986, 32, 3889.
6. Liu, Y.; Messmer, M. C. *J Phys Chem B* 2003, 107, 9774.
7. Zhang, X.; Kale, D. M.; Jenekhe, S. A. *Macromolecules* 2002, 35, 382.
8. Radhakrishnan, J.; Tanigaki, N.; Kaito, A. *Polymer* 1999, 40, 1381.
9. Chee, K. K. *Eur Polym J* 1990, 26, 423.
10. Paladhi, R.; Singh, R. P. *Eur Polym J* 1994, 30, 251.
11. Chowdoji Rao, K.; Varadarajulu, A.; Venkata Naidu, S. *Acta Polym* 1989, 40, 743.
12. Toti, U. S.; Aminabhavi, T. M. *J Membr Sci* 2004, 228, 199.
13. Vijaya Kumar Naidu, B.; Mallikarjuna, N. N.; Aminabhavi, T. M. *J Appl Polym Sci* 2004, 94, 2548.
14. Masuda, K.; Kaji, H.; Horii, F. *J Polym Sci Part B: Polym Phys* 2000, 38, 1.
15. Plexiglass Design and Fabrication Data; PL-53i; Rohm and Haas: Philadelphia, 1993.
16. Ravi Prakash, S. D.; Ramakrishna, H. V.; Rai, S. K.; Varada Rajulu, A. *J Appl Polym Sci* 2003, 90, 33.
17. Rajendran, S.; Sivakumar, M.; Subadevi, R. *Mater Lett* 2004, 58, 641.

18. Varada Rajulu, A.; Lakshminarayana Reddy, R.; Ranga Reddy, R. N. V. *Acoustica* 1997, 83, 1.
19. Singh, Y. P.; Singh, R. P. *Eur Polym J* 1983, 19, 535.
20. Singh, Y. P.; Das, S.; Maiti, S.; Singh, R. P. *J Pure Appl Ultrason* 1981, 3,1.
21. Kurkuri, M. D.; Kulkarni, A. R.; Aminabhavi, T. M. *Polym Plast Technol Eng* 2002, 41, 469.
22. Huggins, M. L. *J Am Chem Soc* 1942, 64, 2716.
23. Subha, M. C. S.; Nagamani, C.; Surendra Babu, N.; Chowdoji Rao, K.; Sadasiva Rao, A.; Vijaya Kumar Naidu, B. *J Acoust Soc India* 1999, 27, 367.
24. Krause, S. *J Macromol Sci Polym Rev* 1972, 7, 251.
25. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
26. Schneier, B. O. *J Appl Polym Sci* 1973, 17, 3175.
27. Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*; Wiley-Interscience: New York, 1999.
28. Kern, R. J. *J Polym Sci* 1956, 21, 19.
29. Hildebrand, J. H.; Scott, R. L. *The Solubility of Non-Electrolytes*, 3rd ed.; Van Nostrand Reinhold: Princeton, NJ, 1950.
30. Nishi, T.; Wang, T. T. *Macromolecules* 1975, 8, 909.
31. Imken, R. L.; Paul, D. R.; Barlow, J. W. *Polym Eng Sci* 1976, 16, 593.
32. Miura, K.; Kimura, N.; Suzuki, H.; Miyashita, Y.; Nishio, Y. *Carbohydr Polym* 1999, 39, 139.
33. Kressler, J.; Higashida, N.; Inoue, T.; Heckman, W.; Seitz, F. *Macromolecules* 1993, 26, 2090.