

Full Length Research Paper

Miscibility studies of PVC/PMMA and PS/PMMA blends by dilute solution viscometry and FTIR

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The effect of polymer-polymer interactions on the miscibility of PVC/PMMA and PS/PMMA blends were studied in a broad composition range using viscosity and FTIR techniques. From the viscometric data, the presence of attractive forces among different polymers was evaluated according to Sun et al. (1990), by the determination of α parameter. Based on sign convention involved in the criterion, PS/PMMA system was found as immiscible while miscibility was observed in PVC/PMMA blend. FTIR analysis also supports the viscometric data.

Key words: Viscosity, polymer blends, poly (methyl methacrylate), poly (vinyl chloride), polystyrene, fourier transform infrared spectroscopy.

INTRODUCTION

Polymer blending provides a powerful route to engineering new properties in materials using available polymers. From Polymer blending it is possible to produce a range of materials with properties that are superior to that of each individual component polymers (Rhoo et al., 1997; Oh and Kim, 1999; Pielichowski, 1999; Stephen et al., 2000; Tang and Liao, 2000; Pielichowski and Amerton, 2000). The main advantages of the blended systems are simplicity of preparation and ease of control of physical properties by compositional changes, (Acosta and Morales, 1996; Rocco et al., 2001) and also it usually requires little or no extra expenditure compared to new polymer synthesis. However, the miscibility between the constituents of polymer mixture on molecular scale is responsible for material with superior properties (Rajulu et al., 1999).

Miscibility may arise from specific interactions, such as dipole-dipole forces (Aubin et al., 1983) and charge transfer complexes (Ohno and Kumantani, 1979) for homopolymer mixtures or segment-segment repulsion inside the blends. However, due to very small entropy gain in the mixing of long chain polymers and because of the

usually encountered positive heat of mixing, most polymer blends form two phases. The majority of known polymeric mixtures are immiscible; however, several miscible polymer blends have been found in the last three decades.

There have been numerous techniques of studying the miscibility of the polymeric blend. The most useful techniques are viscometry measurements (Sun et al., 1992), thermal analysis (Song and Long, 1991), ultrasonic velocity (Singh and Paladhi, 1994), refractive index (Rajulu et al., 1999), NMR method (Crispim et al., 2000) and optical spectroscopy (Wu et al., 1999). Dilute solution viscometry (DSV) method provides information about both polymer-polymer interactions and polymer solvent interactions in a solution. The effectiveness of DSV method is based on the assumption that the mutual interactions of macromolecules in the solution have a great influence on the viscosity in the ternary systems. It is assumed that polymer-polymer interaction usually dominates over polymer-solvent ones (Pingping et al., 1999). Attraction between the two component polymers may cause swelling of macromolecular coils resulting in an increase in viscosity and repulsion may cause shrinkage of the macromolecular coils, giving a decrease in viscosity.

Various blends have been studied by several authors, Paul and Newman (1978), Schurer et al. (1975), Shen

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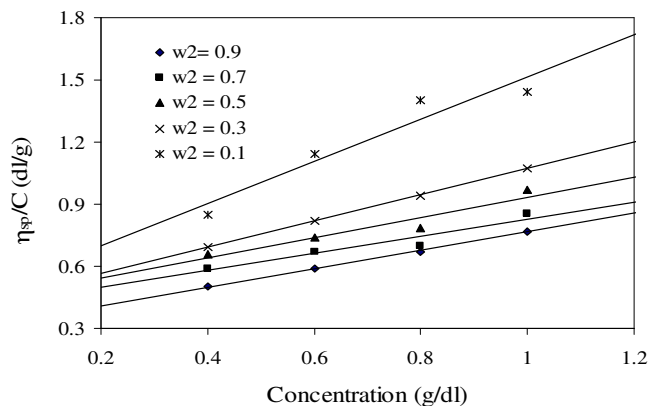


Figure 1. Plot of η_{sp}/C vs. concentration for PVC/PMMA/THF ternary systems.

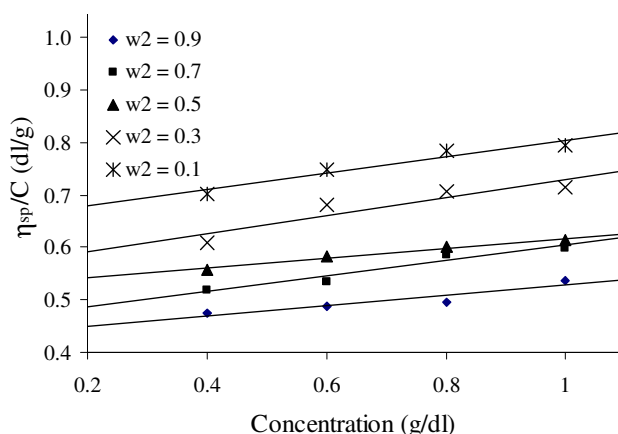


Figure 2. Plot of η_{sp}/C vs. concentration for PMMA/PS/THF ternary systems.

and Torkkelson (1992), Karlou and Schneider (2000) Sato et al., (1991), Ramesh et al. (2002), Bensemra et al. (2002), Zhou and Prud'homme (1991) and Honeycutt (1994). The goal of the present study was to correlate the miscibility of commercially important polymers PVC/PMMA and PS/PMMA in dilute solutions and in solid state by using DSV and FTIR methods. A systematic study on this at wide range of composition is not available so it is desirable to work on such system and correlate the two different techniques.

MATERIALS

Chemicals

AR grade Tetrahydrofuran (THF) supplied by Aldrich Co. was used as solvent. It was further purified by distillation, and kept in desiccators to minimize moisture uptake. Poly (methyl methacrylate) (PMMA), Poly (vinyl chloride) (PVC) and Polystyrene (PS) polymers with molecular weight 100,000 were obtained from BDH chemicals, England.

Table 1. Intrinsic viscosities $[\eta]$ of different polymers at 30°C.

Polymer	$[\eta]$ (dl/g)
PMMA	0.3009
PS	0.5274
PVC	0.6527

METHODS

Preparation of polymeric blends

Ternary solutions for the present system were prepared by mixing the calculated quantity of polymer solutions in different weight ratios up to the concentration of 1.0% (w/v). Dilutions to yield four lower concentrations were made by adding the appropriate aliquots of solvent.

Viscometry

The viscometric behavior of the polymers and polymer blends solutions were determined at 30°C by using Cannon-Fenske routine type viscometer. The flow times were measured with the accuracy of ± 0.01 s. From the efflux time measurements, the specific viscosity (η_{sp}) was calculated at different concentration. The intrinsic viscosity $[\eta]$ was determined by plotting reduced viscosity (η_{sp}/C) against the solution concentrations (C) according to the well known Huggin's equation.

FTIR analysis

FTIR spectra were recorded on Shimadzu-8001 Spectrophotometer using thin films. The films were prepared by casting the ternary solutions on glass plates. The number of scans per samples was 200 and resolution of the measurements was 4 cm^{-1} .

RESULTS AND DISCUSSION

Viscometric analysis

Viscometry is a simple and effective technique for monitoring the interactions in polymer blend's solutions. From viscometric measurements, relative and reduced viscosities of pure polymers and their blends are obtained. Figures 1 and 2 shows the Huggins plots for the PVC/PMMA and PS/PMMA blends at 30°C for different weight fractions of polymer 1 and polymer 2 ($w_1:w_2$), respectively.

The values of $[\eta]$ were determined by extrapolation to infinite dilution of the Huggin's plots and the values of 'b' are the slopes of the plots. The values of $[\eta]$ for pure polymers and their blends are shown in the Tables 1 and 2. In order to evaluate the miscibility of polymer blends, a thermodynamic parameter α , proposed by Sun et al. (1990), has been used. The α was calculated by using the following equation:

$$\alpha = K_{\text{blend}} - K_1 \quad (2)$$

Table 2. Viscometric data i.e. $[\eta]$, b and α , of PVC/PMMA and PS/PMMA blends.

System	W_{PMMA}	$[\eta]$ (dl/g)	b (dl/g) ²	α
PS/PMMA/ THF	0.1	0.6201	0.1281	-0.0983
	0.3	0.5069	0.1727	-0.1699
	0.5	0.4744	0.0925	-0.3697
	0.7	0.4067	0.1473	-0.1566
	0.9	0.38	0.0981	-0.1448
	0.1	0.4941	1.0205	0.2225
PVC/PMMA/ THF	0.3	0.4394	0.6322	0.4118
	0.5	0.4462	0.4885	0.2911
	0.7	0.4149	0.4115	0.3050
	0.9	0.3203	0.4462	0.0235

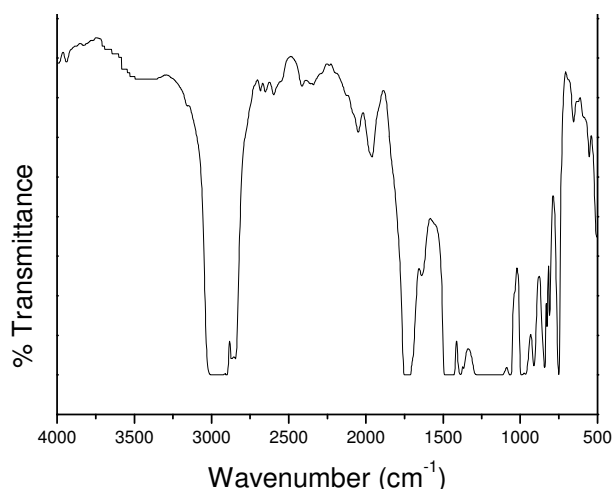


Figure 3. FTIR spectrum of pure PMMA.

Where K_{blend} is the Huggins constant that was obtained experimentally for the blends and K_1 was calculated using the following equation:

$$k_1 = \frac{k_A[\eta]_A^2 W_A^2 + k_B[\eta]_B^2 W_B^2 + 2(k_A k_B)^{1/2} [\eta]_A [\eta]_B W_A W_B}{(W_A [\eta]_A + W_B [\eta]_B)^2}$$

According to Sun et al. (1990), if $\alpha > 0$, attractive forces between polymers occur, showing miscibility. If $\alpha < 0$, repulsive forces exist and hence immiscibility is expected. The α parameter values for the polymer blends are presented in Table 2.

The α parameter for PS/PMMA blend reveals negative values and for PVC/PMMA it presents positive values. This suggests that over the whole composition range, PVC/PMMA blend is miscible while PS/PMMA blend sys-

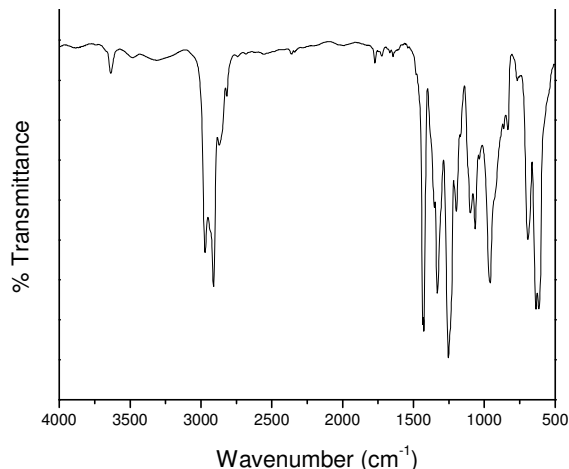


Figure 4. FTIR spectrum of pure PVC.

tem is immiscible.

FTIR analysis

The FTIR spectrum of PMMA in the frequency range 4000-400 cm^{-1} is shown in Figure 3, in transmittance mode.

This spectrum is comparable to that of earlier reports of Saikia and Kumar (2005). Two distinct bands appeared at 2978.4 and 2877.8 cm^{-1} , the first band arises from the asymmetrical (as) stretching mode in which two C-H bonds of the methyl group are extending, while the third one is contracting ($\nu_{as}CH_3$) and the second band arises from symmetrical (s) stretching ($\nu_s CH_3$) in which all three of the C-H bonds extend and contract in phase. The bands at 1387.2 and 1456.2 cm^{-1} correspond to symmetrical bending vibration ($\nu_s CH_3$) and asymmetrical bending vibration ($\nu_{as} CH_3$) of methyl group, respectively. At approximate 1025 cm^{-1} ether lone pair peak is also present. Strong peak appearing in the region 1730.14 cm^{-1} corresponds to C=O stretching vibrations. Broader and stronger bands in the region 1300-1000 cm^{-1} correspond to C-O stretching vibrations, which usually consists of two asymmetric coupled vibrations. I.e. C-C (=O)-O and O-C-C. Peak at 749 cm^{-1} corresponds to out of plane C-H bending. The FTIR spectrum of PVC is shown in Figure 4.

This spectrum is comparable to that of earlier report, Subban and Arof (2004). Vibrational bands of PVC are obtained at 2974 cm^{-1} (ν C-H of CHCl), 2912.9 cm^{-1} (ν_{as} , C-H of CH₂), 1435.9 cm^{-1} (w, CH₂), 1334.1 cm^{-1} (δ , C-H of CHCl), 1257.6 cm^{-1} (δ , C-H of CHCl), 1068 cm^{-1} (ν (C-C)), 966 cm^{-1} (r, CH₂), 698 cm^{-1} (ν , C-Cl), 638 cm^{-1} (ν (C-Cl)) and 616 cm^{-1} (ν , C-Cl)).

The FTIR spectrum recorded on PS/PMMA blend did not indicate the existence of any interaction between the components. There is no change in the position of either peak of aromatic ring of PMMA or the ether lone pair

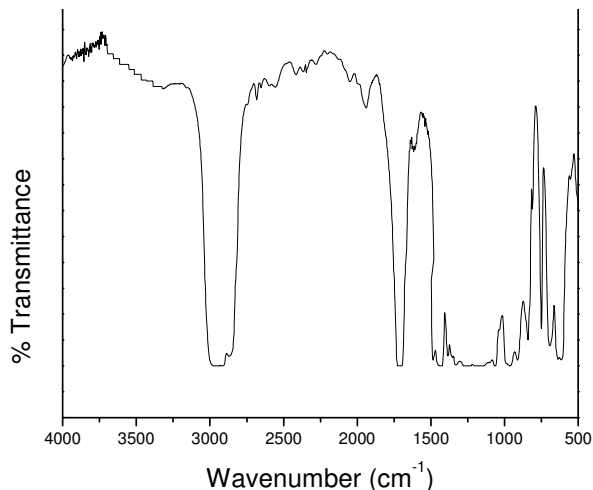


Figure 5. FTIR spectrum of 30/70-wt% PMMA/PVC blend.

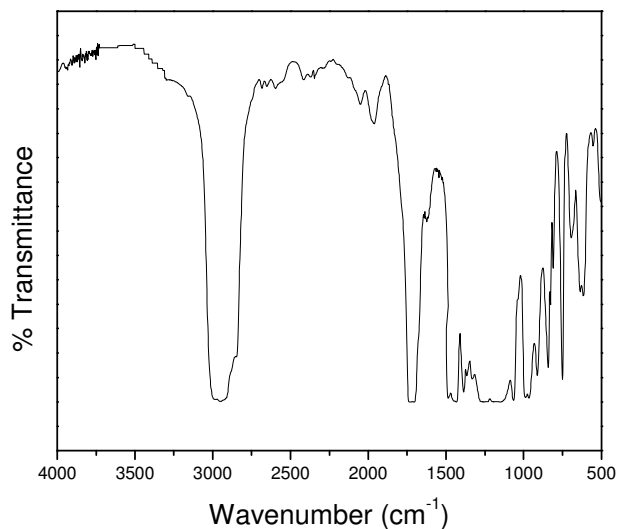


Figure 7. FTIR spectrum of 70/30 wt% PMMA/PVC blend.

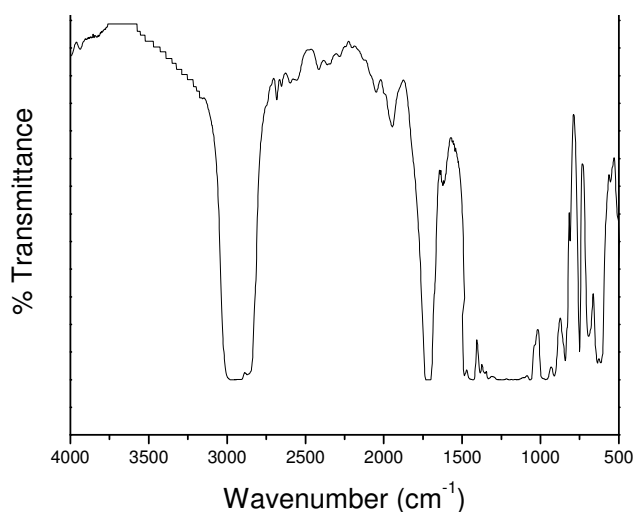


Figure 6. FTIR spectrum of 50/50 wt% PMMA/PVC blend.

peak of PS, which means that neither ether linkage is interacting nor the aromatic ring is affected by blending these two polymers. On the other hand, in the PVC/PMMA blends specific interaction seems to exist between the carbonyl groups of PMMA and the hydrogen atom of CHCl group of PVC in the entire composition range.

Figures 5- 7 show the FTIR spectra of PMMA/PVC blend with 30, 50 and 70% contents of PMMA, respectively.

The peak position for the C=O stretching (i.e. 1730.14 cm^{-1}) in pure PMMA shows slight shifting (1722.28 cm^{-1} , 1724.35 cm^{-1} , 1722.42 cm^{-1}) for the blend ratio (3:7), (1:1) and (7:3), respectively.

It is to be pointed here that the Sun's formula seems

to be well applicable in describing the miscibility of PS/MMA and PMMA/PVC blend system. Further the behavior explained on the basis of Sun's formula has been supplemented by FTIR studies which means its applicability.

Conclusion

Viscometric and FTIR techniques have been successfully employed to study the miscibility of PS/PMMA and PVC/PMMA blends. Both techniques pointed out the existence of interaction between PVC and PMMA in both, solution and solid state. The values calculated from the viscometric data for η parameter suggests immiscibility for PS/PMMA and miscibility for PVC/PMMA. FTIR spectroscopy also revealed specific interaction between PMMA and PVC. However, in the case of PS/PMMA blend no interaction was shown, even it failed to identify any perturbation of the ether lone-pair electron of PMMA and the benzene ring vibration of PS as a result of blending the PS and PMMA. This means that both the polymers are immiscible

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REFERENCES

- Acosta JL, Morales E (1996). Structural, morphological and electrical characterization of polymer electrolytes based on PEO/PPO blends. *Solid State Ionics*. 85:85-90
- Aubin M, Bedard Y, Morrisette MF, Prud HRE (1983). Miscible blends prepared from two crystalline polymers. *J Polym Sci: Polym Phys Ed*.

- 21(2): 233-240.
- Bensemra NB, Belaabed B, Bedda A (2002). Study of miscibility and the thermal degradation of PVC/PMMA blends. *Macromol Symp.* 180(1): 203-216.
- Crispim EG, Schuquel ITA, Rubira AF, Muniz EC (2000). Solvent effects on the miscibility of PMMA/PVAc blends: II. Using two-dimensional NMR method, NOESY. *Polymer* 41(3): 933-945.
- Honeycutt JD (1994). A Theoretical study of tacticity effects on poly(vinylchloride) poly(methyl methacrylate) miscibility. *Macromolecules* 27 (19): 5377-5381.
- Karlou K, Schneider HA (2000). DSC and PVT study of PVC/PMMA blends. *J. Therm. Anal. Calorim.* 59(1-2): 59.
- Oh B, Kim YR (1999). Evaluation and characteristics of a blend polymer for a solid polymer electrolyte. *Solid state Ionics.* 124(1-2): 83-89.
- Ohno N, Kumanotani J (1979). Synthesis and Physical Properties of Blends of Donor Polymers from 2-(*p*-Dimethylaminobenzyl)-1,3-propanediol and Acceptor Polymers from 2-(3,5-Dinitrobenzyl)-1,3-propanediol: A New Phase Composed of Donor and Acceptor Polymers. *Polym J.*, 11(12) : 947-954.
- Singh RP, Paladhi R (1994). Miscibility and interaction studies on some aqueous polymer blend solutions by ultrasonic and rheological techniques. *J. Appl. Polym. Sci.*, 51(9): 1559-1565.
- Paul DR, Newman S (1978). *Polymer blends vol. 1*, Academic Press, New York
- Pingping Z, Haiyang Y, Yiming Z (1999). Viscosity behavior of incompatible poly(vinyl chloride) (PVC)/polystyrene (PS) blends in various solvents. *Eur Polym J* 35(5): 915-921
- Pielichowski K (1999). Thermal energy storage systems based on poly(vinyl chloride) blends. *Eur. Polym. J.*, 35(1): 27-34.
- Pielichowski K, Hamerton I (2000). Compatible poly(vinyl chloride)/chlorinated polyurethane blends: thermal characteristics. *Eur Polym J* 36(1): 171-181.
- Rajulu AV, Reddy RL, Raghavendra SM, Ahmed SA (1999). Miscibility of PVC/PMMA blend by the ultrasonic and refractive index method. *Eur Polym J* 35(6): 1183-1186.
- Ramesh S, Yahaya AH, Arof AK (2002). Miscibility study of PVC blends (PVC/PMMA and PVC/PEO) based polymer electrolytes. *Solid State Ionics.* 148(3-4): 483-486.
- Rhoo HJ, Kim HT, Park JK, Hwang TS (1997). Ionic conduction in plasticized PVC/PMMA blend polymer electrolytes. *Electrochim. Acta* 42(10): 1571-1579.
- Rocco A M, Pereira R P, Felisberti M I (2001). Miscibility, crystallinity and morphological behavior of binary blends of poly(ethylene oxide) and poly(methyl vinyl ether-maleic acid). *Polymer* 42(12): 5199-5205.
- Saikia D, Kumar A (2005). Ionic transport in P(VDF-HFP)-PMMA-LiCF₃SO₃-(PC + DEC)-SiO₂ composite gel polymer electrolyte. *Eur Polym J.* 41(3): 563-568.
- Sato T, Tsujita Y, Takizawa A, Kinoshita T (1991). Miscibility and volume changes of mixing in the poly(vinyl chloride) poly(methyl methacrylate) blends system. *Macromolecules* 24(1): 158-160.
- Schurer JW, de Boer A, Challa G (1975). Influence of tacticity of poly(methylmethacrylate) on the compatibility with poly(vinyl chloride). *Polymer* 16(3):201-204.
- Shen S, Torkelson JM (1992). Miscibility and phase separation in poly(methyl methacrylate)/poly(vinyl chloride) blends: study of thermodynamics by thermal analysis. *Macromolecules* 25(2): 721-728.
- Song M, Long F (1991). Miscibility in blends of poly(vinyl acetate) with poly(methyl methacrylate) studied by FTIR and DSC. *Eur. Polym. J.*, 27(9): 983-986
- Stephen AM, Kumar TP, Renganathan NG, Pitchumani S, Thirunakaran R, Muniyandi N (2000). Ionic conductivity and FT-IR studies on plasticized PVC/PMMA blend polymer electrolytes. *J. Power Sources* 89(1): 80-87.
- Subban RHY, Arof AK (2004). Plasticizer interactions with polymer and salt in PVC-LiCF₃SO₃-DMF electrolytes. *Eur. Polym. J.*, 40(8): 1841-1847.
- Sun Z, Wang W, Feng Z (1992). Criterion of polymer-polymer miscibility determined by viscometry. *Eur Polym J* 28(10): 1259-1261.
- Tang M, Liao WR (2000). Solvent effect on the miscibility of poly(4-hydroxystyrene)-poly(ethylene oxide) blends. *Eur. Polym. J.* 36(12),2597-2603.
- Wu W, Luo X, Ma D (1999). Miscibility of the segmented polyurethane blends with chlorinated poly(vinyl chloride). *Eur. Polym. J.*, 35(6): 985-990.
- Zhao Y, Prud'homme RE (1991). A nonradiative energy transfer fluorescence spectroscopy study of poly (vinylchloride)/poly (methyl methacrylate) blends. *Polym Bull* 26(1): 101.