Polymer 40 (1999) 5129–5135

polymer

Solvent effects on the miscibility of poly(methyl methacrylate)/poly(vinyl acetate) blends

I: Using differential scanning calorimetry and viscometry techniques

Edson Golembievski Crispim, Adley Forti Rubira, Edvani Curti Muniz*

Departamento de Química, Universidade Estadual de Maringá, CEP 87020-900, Maringá, Paraná, Brazil

Received 24 June 1998; accepted 22 August 1998

Abstract

The influence of solvent and temperature on the miscibility of poly(methyl methacrylate)/poly(vinyl acetate) (PMMA/PVAc) was investigated. Experiments using differential scanning calorimetry (DSC) and viscometry were performed. LCST curve was determined by measurements of transmitted light intensity against temperature, at several compositions of PMMA/PVAc, 15/85, 25/75, 50/50, 75/25 and 85/15. It was observed that the miscibility of the PMMA/PVAc blends depends on the solvent. The blends are miscible in chloroform at 30°C and 50°C, whereas in *N*,*N*-dimethyl formamide (DMF) at the same temperatures, the blends are immiscible. In toluene the miscibility depends on the temperature: the blends are miscible at 30°C and immiscible at 50°C. Results from viscometry match very well those of DSC. The film of PMMA/PVAc 50/50 cast from chloroform presents only one T_g. If cast from DMF, the blend presents two T_g values, close to those for pure polymers. The thermogram of the opalescent film, cast from DMF, is similar to the one obtained after a transparent film, cast from chloroform, was heated above the LCST curve.

Keywords: Solvent effects in the miscibility; Polymer blends; Viscometry

1. Introduction

To satisfy the growing needs of new materials with specific properties, such as engineering materials, new polymers have been synthesized [1–3] and chemical modifications in conventional polymers have also been proposed [4–6]. But the mixture of two or more polymers, forming a polymer blend, continues to be an economical method to obtain new polymeric material [7]. The final properties of a polymeric blend will commonly depend on the properties of its polymeric components, its composition and, mainly, on the miscibility of the polymers [8]. In some cases, by synergistic effects, the blend can present better properties than the pure components [7,8].

Several works on polymer–polymer miscibility have been developed in the last 20 years [9,10]. For such investigations, the techniques most commonly and widely used are electronic microscopy [11], spectroscopy [12], thermal analysis [13] and inverse gas chromatography [14]. Other techniques, using alternative properties [15] or less expensive techniques, for instance viscometry [16], have been also proposed.

However, the more sensitive a technique is, the smaller the domain it can detect. So, the level of homogeneity depends on the technique used in the investigation [8]. Thus, it is fundamental to use different techniques in studies of miscibilities of polymer blends.

A polymer blend may be obtained by several methods. Among them, melt mixing, co-precipitation and casting are considered the more common [7]. The blend miscibility is directly connected with the method of preparation. For example, the miscibility of the poly(methyl methacrylate) with poly(vinyl acetate), PMMA/PVAc, when obtained by casting, is known to depend on the solvent. Friese [17] observed that homogeneous solutions and transparent cast films were obtained when chloroform was used as solvent. However, opalescent films were always obtained by casting from homogeneous solutions of *N*,*N*-dimethyl formamide (DMF) or tetrahydrofuran (THF).

The presence of interactions between atoms, or groups of atoms, of unlike polymers is essential to obtain a miscible polymer blend [7,8]. For PMMA/PVAc blends, inverse gas chromatography studies showed that the polymer–polymer interaction parameter, *x*, have small positive values, so the

---

* Corresponding author.
E-mail address: ecmuniz@uem.br (E.C. Muniz)

PII: S0032-3861(98)00653-3

Table 1
Values of intrinsic viscosity [η] and *b* for pure polymers and their blends in chloroform at 30°C and 50°C. Units: [η] = mL/g; $b = (\mathrm{mL/g})^2$

Blend composition	30°C		50°C	
(W_{PMMA})	[η]	$b \times 10^{-3}$	[η]	$b \times 10^{-3}$
0	65.4	1.94	59.5	1.73
0.250	62.0	1.71	57.3	1.68
0.500	52.1	1.44	49.5	1.23
0.750	48.0	1.10	42.8	0.98
0.850	47.0	1.07	41.3	0.90
1.000	43.3	0.88	39.2	0.72

absence of specific interactions has been inferred [18]. Song et al. [19] suggested, based on their FTIR results, that conformation changes in PMMA/PVAc blends, in solution, from hydrogen interactions, are involved in miscible blends.

Dilute solution viscometry has been utilised to evaluate the presence of interactions in polymer A–solvent–polymer B system [20–22]. As published by Sun [23], the α parameter, calculated using the equation: $\alpha = K_{\mathrm{BLEND}} - K_1$, can be utilised to evaluate the presence of interactions. If $\alpha \geq 0$, attractive forces occur between polymers, showing miscibility. If $\alpha < 0$, repulsive forces prevail and immiscibility is expected. K_{BLEND} is the Huggins constant of the blend and K_1 is calculated from viscometric parameters of solutions of each polymeric component.

In this paper some results about the miscibility of PMMA/PVAc blends under two different conditions are reported: (i) in dilute solutions, using viscometry determination and (ii) in cast films, using DSC. The purpose of the present study is to correlate the miscibility of PMMA/PVAc blends in different solvents, studied by viscometry, using the Sun et al. [23] approach, and the results of DSC. Despite the great amount of experimental data on the PMMA/PVAc system, few studies have focused on the influence of solvent on PMMA/PVAc blends using DSC and viscometry techniques.

2. Experimental

Films of PMMA/PVAc blends (100/0, 85/15, 75/25,

Table 2
Values of intrinsic viscosity [η] and *b* for pure polymers and their blends in DMF at 30°C and 50°C. Units: [η] = mL/g; $b = (\mathrm{mL/g})^2$

Blend composition	30°C		50°C	
(W_{PMMA})	[η]	$b \times 10^{-3}$	[η]	$b \times 10^{-3}$
0	52.8	1.10	49.2	0.99
0.250	48.8	0.84	44.7	0.77
0.500	42.5	0.63	39.7	0.61
0.750	34.8	0.80	34.7	0.44
0.850	30.7	0.45	33.3	0.37
1.000	26.7	0.41	27.4	0.38

Table 3
Values of intrinsic viscosity [η] and *b* of pure polymers and their blends in toluene at 30°C and 50°C. Units: [η] = mL/g; $b = (\mathrm{mL/g})^2$

Blend composition	30°C		50°C	
W_{PMMA}	[η]	$b \times 10^{-3}$	[η]	$b \times 10^{-3}$
0	39.9	0.98	31.6	0.56
0.150	36.7	0.90	31.2	0.54
0.250	29.4	0.53	31.2	0.50
0.500	27.8	0.50	29.9	0.44
0.750	26.6	0.46	28.1	0.46
0.850	26.2	0.44	27.2	0.44
1.000	27.1	0.41	26.8	0.43

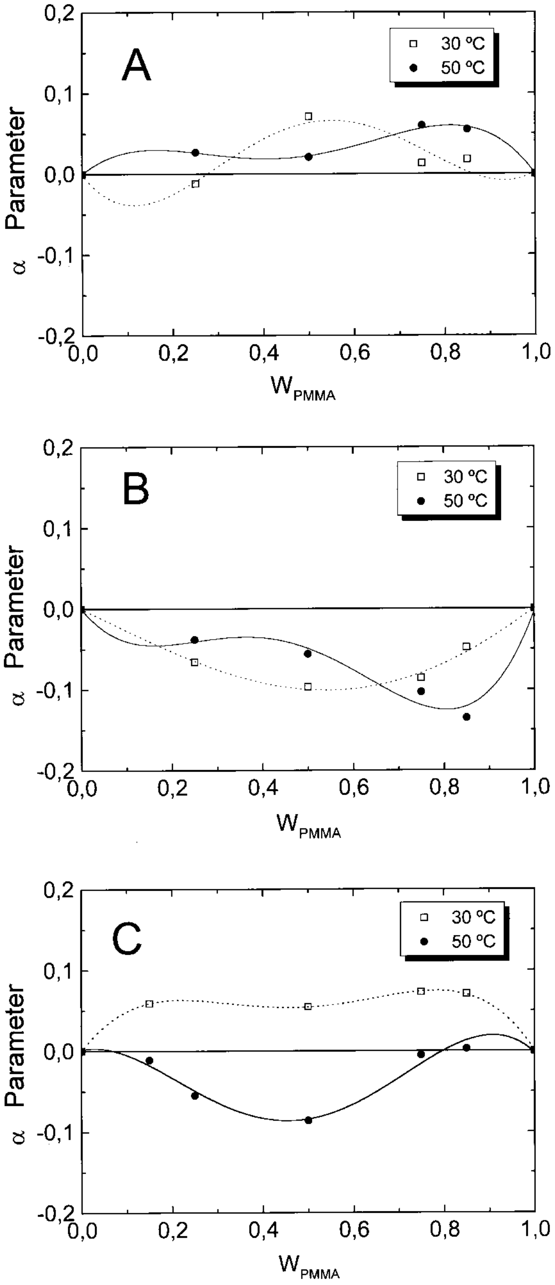

Fig. 1. The α parameter as a function of PMMA mass fraction for PMMA/PVAc blends at 30°C and 50°C in: (A) chloroform; (B) DMF; (C) toluene.

50/50, 25/75, 15/85 and 0/100) were obtained by casting from solutions (0.04 g/mL) of poly(methyl methacrylate), PMMA (Aldrich 18,224-9, $\bar{M}_V = 115.0$ kg/mol) and poly(vinyl acetate), PVAc (Aldrich, 18,949-9, $\bar{M}_W = 83.0$; $\bar{M}_V = 73.4$, both in kg/mol) in the following solvents: chloroform, toluene and DMF. All the solvents were used after previous distillation. The castings were carried out at temperatures of 30°C and 50°C in a Walita oven. The films were dried for 1 week under vacuum at controlled temperature.

The viscosity measurements of each blend composition were performed in a suspended-level Ubbelohde glass capillary viscometer, Cannon (50/F576), at temperatures of 30°C and 50°C. Flowtimes of each blend composition were determined by the serial dilution technique. Five dilutions, at least, were made for each blend composition. From the flowtime measurements, done for each blend composition, the specific, η_{sp}, and reduced, η_{red}, viscosities at different concentrations were calculated. Finally, the intrinsic viscosity, [η], was determined by plotting the η_{sp}/C against the solution concentration, C, for each blend composition, according to the equation [16]:

$$\eta_{sp} = [\eta]C + K_H[\eta]^2C^2 \tag{1}$$

where K_H is known as the Huggins constant.

DSC runs were carried out with a Shimadzu differential scanning calorimeter, model TA-50, at a heating rate of 10 or 20°C/min, in a nitrogen atmosphere flowing at 20 mL/min. Two thermograms were obtained after pre-heating to 110°C: in the first, the temperature changed from ambient to 130°C. The same procedure was adopted in the second thermogram; however, it was obtained after heating to 180°C and cooling to ambient, at a heating rate of 10°C/min. The onset of slope changes in the DSC plot was taken as T_g.

Cloud points were determined as described by Muniz et al. [24], using a method analogous to that of Schmidt et al. [25]. The temperature of an initially homogeneous blend, in film form, was increased at a rate of 5°C/min, using a Microquimica hot stage, Model MQSDCT-31, while the transmitted light intensity of a 1 mW He–Ne laser across the film was detected by a photodiode from EG&G Optoelectronics, Model HUV200B. The inflexion of the curve of relative transmitted light intensity, I/I_o, as a function of temperature, T, was considered as the cloud point.

3. Results and discussion

3.1. Viscometry measurements

Curves of η_{sp}/C vs. C were linear for all blend compositions in the different solvents studied. By linear regression of η_{sp}/C vs. C curves, the linear and angular coefficients of eqn (1) were calculated, giving, respectively, the intrinsic viscosity, [η], and b. In this case, $b = [d(\eta_{sp}/C)]/dC$ or more properly, $b = K_H[\eta]^2$. The values of [η] and b for pure polymers and their blends, obtained in chloroform, DMF and toluene, at 30°C and 50°C, are shown in Tables 1–3. As proposed by Sun et al. [23], the α parameter may be used to evaluate the miscibility of blends, from viscometric data. In this work, that evaluation was done using the equation [23]

$$\alpha = K_{BLEND} - K_1 \tag{2}$$

where K_{BLEND}, obtained experimentally, is the Huggins constant of the blend, K_1 is calculated using the equation [23]

$$K_1 = \frac{K_{PMMA}[\eta]^2_{PMMA}W^2_{PMMA} + K_{PVAc}[\eta]^2_{PVAc}W^2_{PVAc} + 2\sqrt{K_{PMMA}K_{PVAc}}W_{PMMA}[\eta]_{PVAc}W_{PVAc}[\eta]_{PVAc}}{(W_{PMMA}[\eta]_{PMMA} + W_{PVAc}[\eta]_{PVAc})^2} \tag{3}$$

where K_i is the Huggins constant and $[\eta]_i$ is the intrinsic viscosity of the ith pure polymeric component. As proposed by Sun [23], if $\alpha > 0$ attractive forces between polymers occur, showing miscibility. If $\alpha < 0$, repulsive forces prevail and immiscibility is expected. In Fig. 1 the curves of the α parameter against PMMA weight fraction, W_{PMMA}, are presented. Fig. 1A shows that PMMA/PVAc blends present positive α parameters in chloroform at 30°C as well as at 50°C. On the other hand, if DMF is used, such blends present negative α parameter values, as can be seen in Fig. 1B. This suggests that in chloroform there are attractive forces that induce miscible behaviour. From our viscometry data, in DMF such forces do not seem to exist. So, immiscibility behaviour for the blend is expected in DMF. These results are in agreement with those published by Song and Long [19], which observed that transparent cast films were always obtained from PMMA/PVAc solutions in chloroform whereas they are opaque when DMF is used. In this work we observed the same behaviour. But we also observed another interesting result: cast films of 50/50 PMMA/PVAc from toluene were transparent when the cast process was carried out at 30°C. When the casting temperature was maintained at 50°C opaque films were obtained for blends whose composition lies between 25 and 75 wt% in PMMA. According to the ultrasonic results of Singh et al. [26], blends of PMMA/PVAc are miscible at room temperature. In Fig. 2 a photograph showing the transparency or the opalescence of 50/50 PMMA/PVAc films when obtained by casting from toluene at 30°C or 50°C, is shown. These behaviours could be better understood by analysing Fig. 1C, where the curve of the α parameter for PMMA/PVAc at 30°C and 50°C in toluene as a function of W_{PMMA} is presented. In Fig. 1C it can be observed that at 30°C the blends present positive values of the α parameter. When the temperature is maintained at 50°C, the α parameter changes to negative values, as also shown in Fig. 1C.

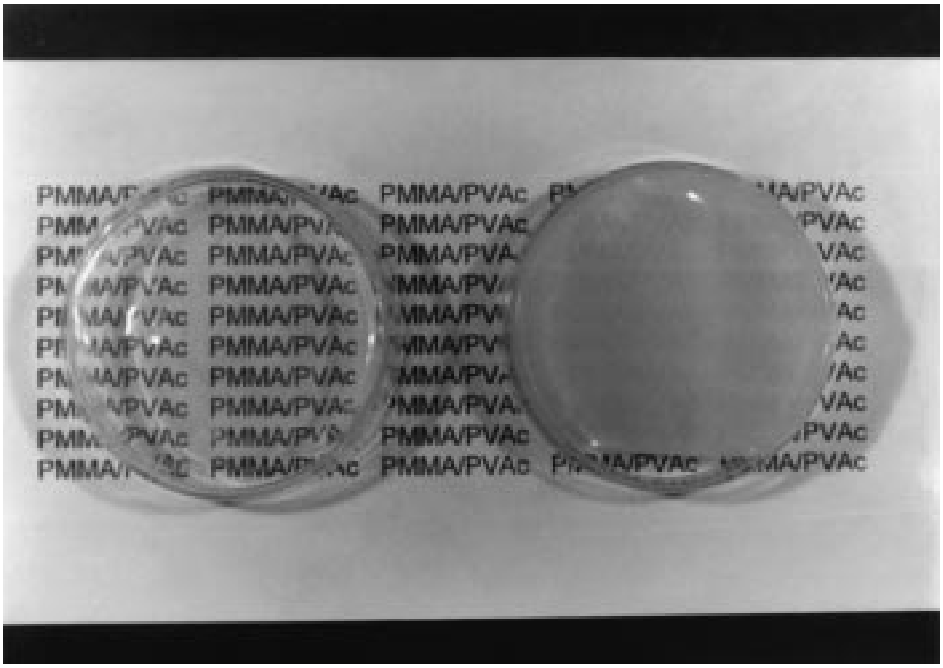

Fig. 2. Photograph showing the transparency or the opacity of the 50/50 PMMA/PVAc films cast from toluene at: (A) 30°C; (B) 50°C.

As will be discussed later, phase segregation beginning with macromolecules of PVAc, at temperatures higher than the glass transition of PVAc, ca. 40°C, slowly diffusing to rich PVAc phases, could be responsible for this behaviour.

3.2. LCST curve

In Fig. 3 the dependence of relative transmitted light intensity on temperature for three different blends is presented. By the determination of the cloud point for each composition, at the inflexion of the curve, the LCST curve presented in the Fig. 4 was obtained. The low critical solution temperature for this system is about 125°C and the minimum in the curve seems to be near 60% PMMA content. Song et al. [19] presented an LCST curve for PMMA/PVAc for which the low critical solution temperature is ca. 160°C. However, they used polymers with higher weight molar mass (in kg/mol): PMMA, $\bar{M}_W = 200$; PVAc, $\bar{M}_W = 260$ and polydispersity ($\bar{M}_W/\bar{M}_N$), $\cong 3$.

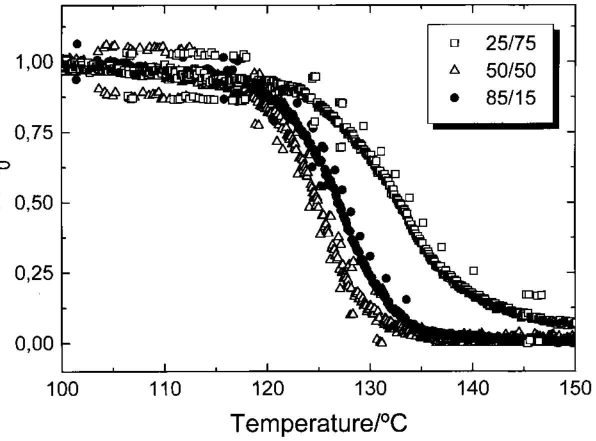

Fig. 3. Relative transmitted light intensity against temperature for PMMA/PVAc films having the following composition: (A) 25/75; (B) 50/50; (C) 75/25.

3.3. DSC analysis

In Fig. 5 the thermograms of the pure polymers are presented. The characteristic T_g for each polymer, as indicated, is 112°C and 40°C, for PMMA and PVAc, respectively. These values are close to those published in the literature [19,27]. In Fig. 6 the thermogram of the 50/50 PMMA/PVAc blend, obtained by casting from DMF, is presented. The thermogram was carried out after pre-heating from ambient temperature to 110°C. In the thermogram, inflexions referring to two T_gs with values close to those

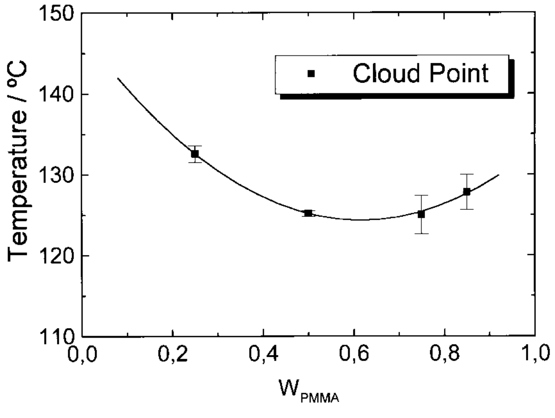

Fig. 4. Cloud point curve for the PMMA/PVAc system.

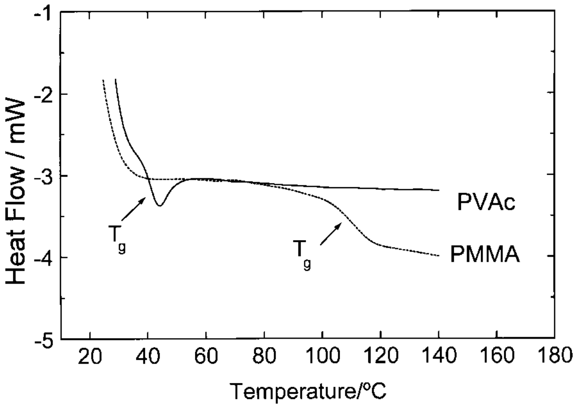

Fig. 5. DSC curves obtained for films of PMMA and PVAc, cast from chloroform at 30°C and obtained after pre-heating to 110°C.

characteristic of the pure polymers, can be observed. So, the blend may be characterized as immiscible. This result matches very well those obtained by viscometry, as shown in Fig. 1B and discussed in the last section. In Fig. 7 two thermograms obtained for the 50/50 PMMA/PVAc blend, casting from chloroform, are presented. The thermogram presented as 7A was obtained after pre-heating from ambient temperature to 110°C. In this thermogram the T_gs of the pure polymers could not be clearly observed, but only one slight change in the slope of the DSC curve is seen, at intermediate temperature. The thermogram presented as 7B was obtained after pre-heating the sample from ambient temperature to ca. 180°C. It can be observed that the thermogram of 7B is analogous to that presented in Fig. 6. After heating to 180°C, the transparent films became opaque, confirming the phase separation by overcoming the LCST curve. Thus, it can be pointed out that phase separation occurs in the 50/50 PMMA/PVAc blend that may occur due to the casting from DMF at ambient temperature or by heating a homogeneous film to ca. 180°C. The appearance of the film obtained at the end of both processes is almost the same and their thermograms are comparable. An analogous behaviour was also observed when transparent film of 50/50 PMMA/PVAc blend, cast from toluene at 30°C, is submitted to heating to 180°C.

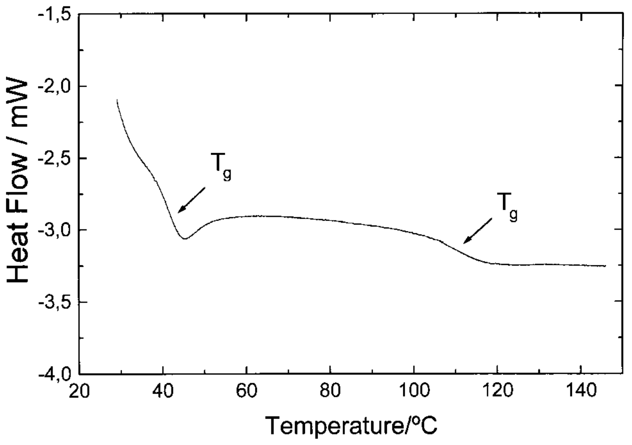

Fig. 6. DSC curve obtained for 50/50 PMMA/PVAc film, cast from DMF at 30°C and obtained after pre-heating to 110°C.

In Fig. 8 thermograms of 50/50 PMMA/PVAc blend cast from toluene at 30°C and 50°C are presented. Both thermograms were obtained after pre-heating to 110°C. It can be observed that the thermogram for the film cast at 50°C is analogous to the one obtained after heating over the LCST curve, as presented in Fig. 7B.

The PMMA/PVAc system was studied by Schenk et al. [28] by solid state NMR using, as sample, blends in film form, cast from benzene or toluene. They pointed out that, although films cast from benzene are inhomogeneous materials, intermolecular interactions were observed. They suggested that the interactions could originate from intermolecular contacts in the interphase regions. The authors also observed that, in contrast to blends prepared from benzene solutions, the films cast from toluene solutions, at ambient temperatures, seemed to be more compatible.

Based on their experimental data, Schenck et al. [28] pointed out that apparently in toluene solutions other specific interactions make smaller domains sizes possible, inducing a higher compatibility level. In this work these intermolecular contacts may be detected by viscometry, as discussed previously in Section 3.1. In toluene at 30°C these intermolecular contacts would be more favourable.

From their studies, Schenk et al. [28] suggested that at temperatures higher than the glass transition of PVAc (ca. 40°C) phase segregation in films, cast from toluene, begins slowly by diffusion of the PVAc macromolecules away from the interphases and directed to rich PVAc domains. This fact could be used to explain the behaviour discussed in Sections 3.1 and 3.2, presented in Fig. 1C, and in Figs 2 and 8.

In a very recent paper Pingping et al. [29] published their viscosity results concerning the miscible polymer blend, poly-ϵ-caprolactame and poly(vinyl chloride) or PCL/PVC, in various solvents. They concluded that the nature of the solvent may affect the polymer–polymer interaction of a determined blend and as a result, the miscibility of the blend. By analysis of the intrinsic viscosity values presented in Tables 1–3, chloroform is shown to be a better solvent than DMF and toluene, for PMMA and PVAc pure polymers. Although the solutions of the pure polymers and their blends are homogeneous, the coils would expand differently in each solvent. Also, it can be observed that the influence of the temperature on the intrinsic viscosity is more intense in chloroform and toluene than DMF. Viscosimetric results of PMMA/PVAc blends, that were obtained in THF, but not presented here [30], show a negative α parameter in agreement with the results observed by Song et al. [19]

The influence of solvent on the miscibility of the PMMA/PVAc blends was studied by Song et al. [19], from FTIR experiments. Their discussion was based upon the conformation energy. According to the Song et al. [19] arguments,

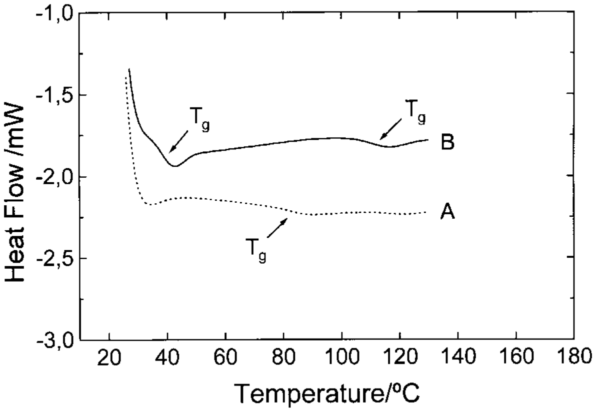

Fig. 7. DSC curves for 50/50 PMMA/PVAc films cast from chloroform at 30°C and obtained after pre-heating to (A) 110°C and (B) 180°C.

when solvent is evaporated, chain movement could be frozen and the high energy conformational structure would remain. The force of the hydrogen bonding in chloroform solution, originated from interactions of the solvent and polymeric species, could provide sufficient energy to overcome such energy. The authors suggested that in DMF solution there is no specific interaction between the polymers and the solvent. The PMMA/PVAc system was also studied by Ha et al. [31]. They suggested that the opalescence in the films of PMMA/PVAc, obtained by casting, will be driven by contribution of hydrogen bonding to the solubility parameter, δ_h. According to the Ha et al. [31] arguments, if δ_h of the solvent is higher than 6.5 $J^{1/2}$ $cm^{-3/2}$, the cast blends of PMMA/PVAc will be immiscible. In solvent having $\delta_h > 6.5$ $J^{1/2}$ $cm^{-3/2}$, it is probable that each component would exist in their own coils. Evidence of this behaviour is provided by the fact that the thermogram of the film cast from DMF ($\delta_h = 11.3$ $J^{1/2}$ $cm^{-3/2}$) is analogous to the thermogram obtained after the homogeneous film, cast from chloroform ($\delta_h = 5.7$ $J^{1/2}$ $cm^{-3/2}$), was heated above the LCST curve. However, it can also be pointed out that Ha's conclusions are not entirely valid if films of PMMA/PVAc, obtained in this work by casting from toluene ($\delta_h \approx 2.0$ $J^{1/2}$ $cm^{-3/2}$, at 50°C), are opalescent or homogeneous when cast from THF [30] ($\delta_h \approx 8.0$ $J^{1/2}$ $cm^{-3/2}$).

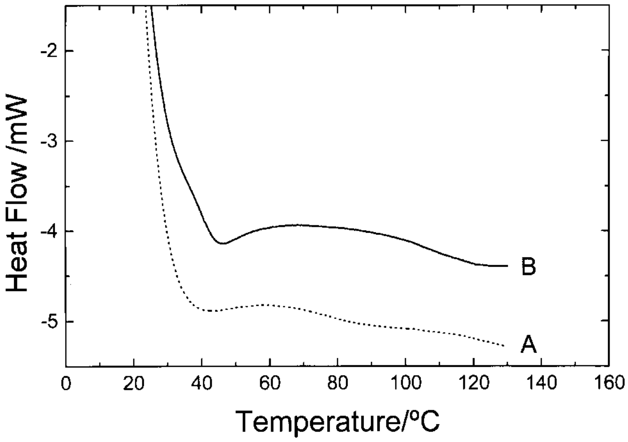

Fig. 8. DSC curves for 50/50 PMMA/PVAc films cast from toluene at (A) 30°C and (B) 50°C. Both curves were obtained after pre-heating to 110°C.

If the negative values of the α parameter are realistic, the coils of unlike polymers would repulse each other in DMF at 30°C and 50°C. In toluene the interactions seem to exist at 30°C. At 50°C, probably by thermodynamic effects, entropy and/or enthalpy, the attractive forces between the coils cease to exist.

These results confirm that viscometry, a non-expensive technique, can be applied to evaluate the existence of the repulsive or attractive interactions in polymer A–solvent–polymer B systems and show that viscometry results may be extrapolated to the solid state, in order to study polymer–polymer compatibility, as pointed out by Lizymol et al. [32].

The experimental observations done in this work support the theory that the dilute solution viscometry method can be used to evaluate the miscibility of polymer pairs [20,23,33], commonly studied by more sophisticated techniques.

4. Conclusions

We have performed DSC and viscosimetric experiments to investigate the influence of solvent on the miscibility of PMMA/PVAc blend. These techniques showed that the miscibility of these blends depends on the solvent. The blends are miscible in chloroform at 30°C and 50°C, whereas in DMF, at the same temperatures, the blends are immiscible. In toluene the miscibility depends on the temperature, the blends being miscible at 30°C and immiscible at 50°C. Results from viscometry match very well those of DSC. In DMF, the coils of unlike polymers would repulse each other, originating the phase separated structure, or opalescent film. The film of 50/50 PMMA/PVAc blend cast from chloroform presents only one T_g. If cast from DMF, the blend presents two T_g values close to the values of the pure polymers. The thermogram of the film, cast from DMF, is analogous to the thermogram obtained after the film cast from chloroform is heated above the LCST curve.

Acknowledgements

The authors are grateful for support from CNPq, Proc. no. 531533/96-1. and to Prof. Roy Edward Bruns (IQ-UNICAMP, Campinas, Brazil) for grammatical revision of the manuscript. E.G.C. is grateful to CAPES for a fellowship.

References

[1] Lipscomb GG, Banerjee T, Chhajer M. Polym Adv Tech 1993;5:708.
[2] Pinnau I. Polym Adv Tech 1993;5:733.

[3] Stadler R, Auschra C, Bekmann J, Krape U, Voigt-Martin I, Leibler L. Macromolecules 1995;28:3080.

[4] Gagnon KD, Lenz RW, Farris RJ. Polymer 1994;35:4368.

[5] Ikada Y. Biomaterials 1994;15:725.

[6] Ohya Y, Okawa K, Murata J, Ouchi T. Angew Makromol Chem 1996;240:263.

[7] Utracki LA. Polymer alloys and blends. Munich: Hanser Publishers, 1989.

[8] Olabisi O, Robeson LM, Shaw MT. Polymer–polymer miscibility. New York: Academic Press, 1979.

[9] Paul DR, Barlow JW, Keskula H. Polymer blends. New York: Academic Press, 1973.

[10] Cowie JMG. Miscibility. In Mark HF, editor. Encyclopaedia of polymer science and engineering. Supplement. New York: Wiley, 1985, p. 455.

[11] Inoue T, Ougizawa T. J Macromol Sci-Chem 1989;A26:147.

[12] Colemann MM, Painter PC. Appl Spectrosc Rev 1984;23:255.

[13] Hourston DJ, Zhang HX, Song M, Pollock M, Hammiche A. Thermochim Acta 1997;294:23.

[14] Mandal BM, Bhattacharya C, Bhattacharyya NS. J Macromol Sci Chem 1989;A26:175.

[15] Muniz EC, Vasquez PAM, Bruns RE, Nunes SP, Wolf BA. Makromol Chem Rapid Commun 1992;13:45.

[16] Chee KK. Eur Polym J 1990;26:423.

[17] Friese K. Plast Kaut 1968;15:646.

[18] O’Reilly JM, Mosher RA. Macromolecules 1981;14:602.

[19] Song M, Long F. Eur Polym J 1991;27:983.

[20] Corradini E, Rubira AF, Muniz EC. Eur Polym J 1997;33:1651.

[21] Yilmaz E, Yilmaz O, Caner H. Eur Polym J 1996;32:927.

[22] Zhou H, Xiang ML, Chen WJ, Jiang M. Macromol Chem Phys 1997;198:809.

[23] Sun Z, Wang W, Feng Z. Eur Polym J 1992;28:1259.

[24] Muniz EC, Pellegrini MC, Nunes SP. Acta Polym 1994;45:110.

[25] Schmidt JR, Wolf BA. Coll Polym Sci 1979;257:1188.

[26] Singh YP, Singh RP. Eur Polym J 1983;19:535.

[27] Bandrup J, Immergut EH, editors. Polymer handbook, 3rd ed. New York: Wiley, 1988, V-77, V-71.

[28] Schenk W, Reichert D, Schneider H. Polymer 1990;31:329.

[29] Pingping Z, Haiyang Y, Shiqiang W. Eur Polym J 1998;34:91.

[30] Corradini E, Rubira AF, Muniz EC. 19th Annual Meeting of the Brazilian Chemical Society, Poços de Caldas-MG, Brazil, 1996, Abstracts, p. QM-68.

[31] Ha CS, Lee WK, Cho WJ. Macromol Symp 1994;84:279.

[32] Lizymol PP, Thomas S. Eur Polym J 1994;34:1135.

[33] Danait A, Deshpande DD. Eur Polym J 1995;31:1221.