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Viscometric study of poly(vinyl chloride)/poly(vinyl acetate) blends in various solvents

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Abstract

The intermolecular interactions between poly(vinyl chloride) (PVC) and poly(vinyl acetate) (PVAc) in tetrahydrofuran (THF), methyl ethyl ketone (MEK) and *N*,*N*′-dimethylformamide (DMF) were thoroughly investigated by the viscosity measurement. It has been found that the solvent selected has a great influence upon the polymer–polymer interactions in solution. If using PVAc and THF, or PVAc and DMF to form polymer solvent, the intrinsic viscosity of PVC in polymer solvent of (PVAc + THF) or (PVAc + DMF) is less than in corresponding pure solvent of THF or DMF. On the contrary, if using PVAc and MEK to form polymer solvent, the intrinsic viscosity of PVC in polymer solvent of (PVAc + MEK) is larger than in pure solvent of MEK. The influence of solvent upon the polymer–polymer interactions also comes from the interaction parameter term Δb, developed from modified Krigbaum and Wall theory. If PVC/PVAc blends with the weight ratio of 1/1 was dissolved in THF or DMF, $\Delta b < 0$. On the contrary, if PVC/PVAc blends with the same weight ratio was dissolved in MEK, $\Delta b > 0$. These experimental results show that the compatibility of PVC/PVAc blends is greatly associated with the solvent from which polymer mixtures were cast. The agreement of these results with differential scanning calorimetry measurements of PVC/PVAc blends casting from different solvents is good. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Viscosity measurement; Intermolecular interactions; Poly(vinyl chloride)/poly(vinyl acetate) blends; Miscibility

1. Introduction

The viscosity study on ternary systems of two different polymers and a solvent has been a subject of continuing interest, mainly due to its simplicity and effectiveness in the characterization of the intermolecular interactions between the two different polymers in solution [1–15]. The effectiveness of using dilute solution viscosity (DSV) measurement to study polymer–polymer compatibility rely on the assumption that the repulsive or attractive intermolecular interaction between two different polymers in solution should make a different contribution to the viscosity of the polymer solution. As a result, the value of the viscosity of ternary system (polymer A–polymer B–solvent) may be either lower or higher than the value calculated from viscosities of both pure blend components on the assumption of the additivity law [16–22]. Though the intermolecular interactions between the two different polymers in solution are believed to play a key role in determining the viscosity of polymer solution, it can be changed by the solvent from which the two different polymers were dissolved [6,8]. As it is well known, the intermolecular interactions in polymer solution of binary system (polymer A–solvent) can be either repulsive or attractive, depending on the solvent selected. For example, if a given polymer was dissolved in a solvent at temperature above θ, the segments of a given polymer would repel one another and the repulsive intermolecular interactions should be expected. On the contrary, if the polymer was

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dissolved in a solvent at temperature below θ, the segments of the polymer would attract one another and the attractive intermolecular interactions should be expected [23]. The similar phenomenon also exists in polymer solutions of ternary systems, to which little attention has been devoted [1,6,8]. Therefore, to perform DSV measurement, the influence of the solvent upon the intermolecular interactions between the two different polymers in solution should also be taken into account.

The compatibility of poly(vinyl chloride) (PVC) with ethylene–vinyl acetate copolymers (EVA) has been thoroughly investigated [24–35]. It has been concluded that a wide compositional range of EVA containing from about 45% to 87% VAc are compatible with PVC [24]. In fact, PVC/EVA blends constitute one of the first reported examples in the literature in which copolymers form compatible blends with another polymer when the two homopolymers do not, i.e. PVC is not compatible with either polyethylene (PE) or poly(vinly acetate) (PVAc) but it is compatible with some of their copolymers. However, after a careful thermal analysis of PVC/PVAc blends prepared by casting from different solvents (tetrahydrofuran (THF) and methyl ethyl ketone (MEK)), Bhagwagar and co-workers [36] pointed out that the compatibility of PVC/PVAc blends depended greatly upon the solvent from which PVC/PVAc blends were cast. If PVC/PVAc blends were prepared by casting from THF, differential scanning calorimetry (DSC) thermograms exhibited two distinct T_g's, corresponding to the essentially pure PVC and PVAc. This suggests that the PVC/PVAc blends cast from THF were multiphased. On the other hand, if PVC/PVAc blends were prepared by casting from MEK, DSC thermograms displayed only one, relatively broad, intermediate T_g, good evidence that a compatible system has been formed. A similar phenomenon also existed in PMMA/PVAc blends [1,6,37]. The reasonable interpretation is that, in different solvents, the intermolecular interactions between two different polymers are quite different. Fortunately, the DSV measurement has proved to be a useful technique to investigate polymer–polymer interactions in solution. In the present work, the experimental results on the viscosity measurement of PVC, PVAc and PVC/PVAc blends in different solvent (THF, MEK and *N*,*N*′-dimethylformamide (DMF)) are presented. The DSC measurement was also used to determine the compatibility of PVC/PVAc blends cast from MEK, which is in good agreement with the conclusions drawn from the viscosity measurement.

2. Experimental

2.1. Materials and preparation of blends

PVC was supplied by Hefei Chemical Plant (Hefei, China), with the viscosity-average molecular weight of 70,000. PVAc was kindly supplied by Professor Guo Qipeng of University of Science and Technology of China (Hefei, China), with a viscosity average of 83,000. All polymers were not further purified.

1.2% (w/v) solutions of PVC in pure and polymer solvent were prepared. To facilitate the dissolution of PVC, the solutions containing PVC were prepared by slight heating and continuous stirring. The polymer solvents containing a constant concentration of 0.5 g/dl PVAc in THF, MEK and DMF were prepared.

Viscometric measurements were carried out using a dilution Ubbelohde viscometer immersed in a constant temperature bath. Temperature was measured close to the capillary by a thermometer with an accuracy of 0.02°C.

PVC/PVAc blends (25:75 wt.%) were prepared by solution casting from DMF at 30°C. To remove the residual solvent, after casting, the blends were dried in a vacuum oven at 60°C for two weeks.

2.2. Differential scanning calorimetry

The calorimetry measurements were made on a Perkin-Elmer Pyris-1 DSC in a dry nitrogen atmosphere. A heating rate of $20°\mathrm{C\,min^{-1}}$ was used.

3. Results and discussion

As one of the effective technique to investigate polymer–polymer interactions by the DSV measurement, the method of polymer solvent has proved to be a subject of special interest [6,7,12–15]. According to this method, the intrinsic viscosity of polymer A (referred to as the probe polymer) in solution containing a constant concentration of polymer B (referred to as the matrix polymer), $[\eta_A]_B$, can be determined conveniently. It is generally believed that $[\eta_A]_B$ should indicate the change in polymer dimensions of polymer A brought about by the presence of polymer B or said more directly, by the intermolecular interactions between polymer A and B in solution. By comparing $[\eta_A]_B$ with the intrinsic viscosity of polymer A in pure solvent, $[\eta]_0$, a novel criterion for determination of polymer–polymer compatibility by viscosity measurement was presented by Danait and Deshapande [13]. The modification of this criterion was suggested by Yang et al. [7].

Fig. 1 shows the plots of reduced viscosity (η_{sp}/C) vs. concentration (C) for PVC in pure solvent of THF and in polymer solvent of (PVAc + THF) at 30°C. All the plots are linear in the whole range of concentration. On extrapolating to zero concentration, the intrinsic viscosity of PVC can be obtained, which is of 1.032 dl/g in THF and 0.941 dl/g in (PVAc + THF), i.e. the intrinsic viscosity of PVC in (PVAc + THF) is less than in THF.

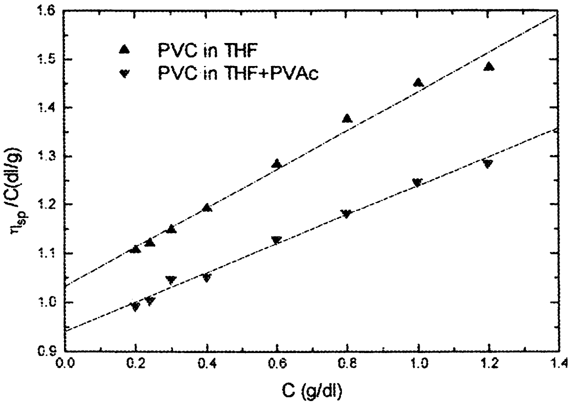

Fig. 1. Plots of the reduced viscosity (η_{sp}/C) vs. concentration (C) for PVC in THF and in (THF + PVAc) at 30°C.

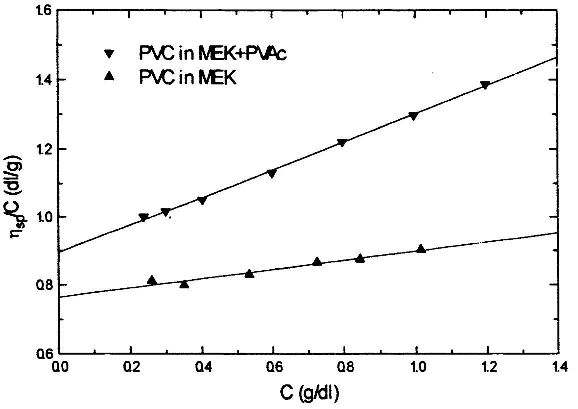

Fig. 2. Plots of the reduced viscosity (η_{sp}/C) vs. concentration (C) for PVC in MEK and in (MEK + PVAc) at 30°C.

The reasonable interpretation is that the repulsive interaction existed between PVC and PVAc in polymer solvent of (PVAc + THF). This repulsive interaction increased the intermolecular excluded volume effect, resulting in the contraction of PVC coils in solution and thus the decrease of the intrinsic viscosity of PVC in polymer solvent. If the repulsive interactions between PVC and PVAc exist in solution, the coils overlap and interpenetration between PVC and PVAc at higher concentrations ($C > C^*$) might not occur. As a result, PVC/PVAc blends casting from THF were multiphased, exhibiting two distinct T_g's corresponding to the essentially pure PVC and PVAc components as pointed out by Bhagwagar et al. [36].

Fig. 2 shows the plots of reduced viscosity (η_{sp}/C) vs. concentration (C) for PVC in pure solvent of MEK and in polymer solvent of (PVAc + MEK) at 30°C. It is noted that the intrinsic viscosity of PVC in (PVAc + MEK) is larger than in MEK. The reasonable interpretation is that the attractive interactions between PVC and PVAc exist in polymer solvent of (PVAc + MEK). These attractive interactions decreased the intermolecular excluded volume effect. As a consequence, the PVC coils expands which causes an increase of the intrinsic viscosity of PVC in (PVAc + MEK) compared with in pure solvent of MEK.

If attractive interactions between PVC and PVAc indeed exist in MEK, then, in the process of preparing PVC/PVAc blends casting from MEK, with the evaporation of MEK, the coils overlap and interpenetration between PVC and PVAc might become possible in concentrated solutions ($C > C^*$). That could be the interpretation as to why PVC–PVAc blends casting from MEK are compatible, exhibiting only one, relatively broad, intermediate T_g.

Fig. 3 shows the plot of the reduced viscosity (η_{sp}/C) vs. concentration (C) for PVC in pure solvent of DMF and in polymer solvent of (PVAc + DMF) at 30°C. It can be seen that the intrinsic viscosity of PVC in (PVAc + DMF) is less than in DMF. This suggests that the repulsive intermolecular interactions between PVC and PVAc exist in DMF solution. According to the discussion before, if prepared by casting from DMF, the PVC/PVAc blends should be multiphased. The same conclusion also comes from the interaction parameter term Δb, developed from modified Krigbaum and Wall theory.

Krigbaum and Wall [22] presented the following equation for mixed polymer solution:

$$\eta_{sp,m} = [\eta]_1 C_1 + [\eta]_2 C_2 + b_{11} C_{11}^2 + 2b_{12} C_1 C_2 + b_{22} C_{22}^2 \tag{1}$$

where b_{12} represented the mutual intermolecular interactions between polymer 1 and 2. If no specific

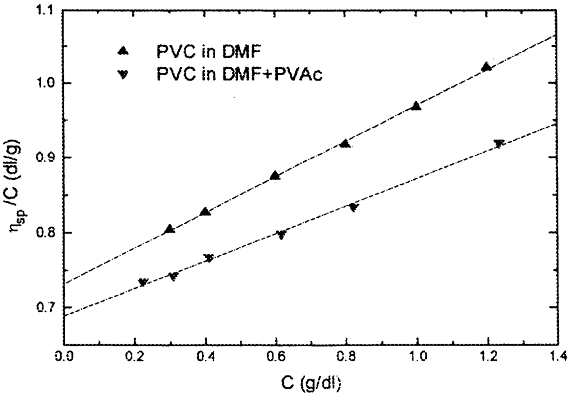

Fig. 3. Plots of the reduced viscosity (η_{sp}/C) vs. concentration (C) for PVC in DMF and in (DMF + PVAc) at 30°C.

intermolecular interaction between polymer 1 and 2 exists, b_{12} is related to b_{11} and b_{22} obtained in binary system by the equation

$$b_{12} = \sqrt{b_{11}b_{22}} \tag{2}$$

If specific intermolecular interactions between polymer 1 and 2 exist, however, Eq. (2) cannot be satisfied. Expressing parameter Δb as below

$$\Delta b = b_{12} - \sqrt{b_{11}b_{22}} \tag{3}$$

where b_{12} is experimentally determined by using Eq. (1). Obviously, Δb which directly indicated mutual intermolecular interactions between polymer 1 and 2 was suggested as a criterion to predict polymer–polymer compatibility. $\Delta b > 0$ signifies compatibility, whereas $\Delta b < 0$ indicates incompatibility [18].

Figs. 4–6 show the plots of the reduced viscosity (η_{sp}/C) vs. concentration (C) for PVC, PVAc and PVC/PVAc blends with the weight ratio of 1/1 in pure solvent of THF, MEK and DMF at 30°C. All the plots are linear in the whole range of concentration investigated. On extrapolating to zero concentrations, both the intrinsic viscosity and the slope of the plot can be obtained, which are shown in Table 1. According to Eqs. (1) and (3), both the mutual intermolecular interaction parameter b_{12} and Δb can be determined. The results are also shown in Table 1. It can be seen that, for PVC/PVAc blends in THF, $\Delta b < 0$, indicating that PVC and PVAc are incompatible blends if cast from THF; whereas in MEK, $\Delta b > 0$, indicating that PVC and PVAc are compatible blends if cast from MEK. This conclusion coincides with the DSC measurement of PVC/PVAc blends cast from THF and MEK presented by Bhagwagar et al. [36]. From Table 1 it can also be seen that, for PVC/PVAc blends in DMF, $\Delta b < 0$. It is of interest to know whether PVC and PVAc are incompatible blends or not if cast from DMF. Fig. 7 shows DSC thermograms of PVC/PVAc blends (25:75 wt.%, the same weight ratio as reported by Bhagwagar et al. [36]) cast from DMF. The two distinct T_g's indicate that the PVC/PVAc blends casting from DMF are indeed multiphased.

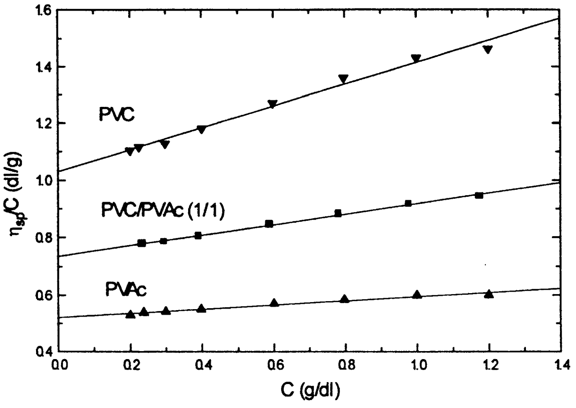

Fig. 4. Plots of the reduced viscosity (η_{sp}/C) vs. concentration (C) for PVC, PVAc and PVC/PVAc blends with the weight ratio of 1/1 in THF at 30°C.

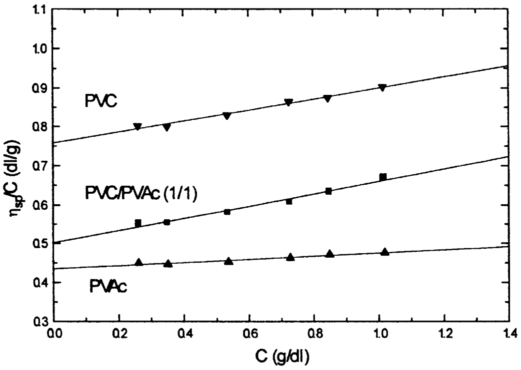

Fig. 5. Plots of the reduced viscosity (η_{sp}/C) vs. concentration (C) for PVC, PVAc and PVC/PVAc blends with the weight ratio of 1/1 in MEK at 30°C.

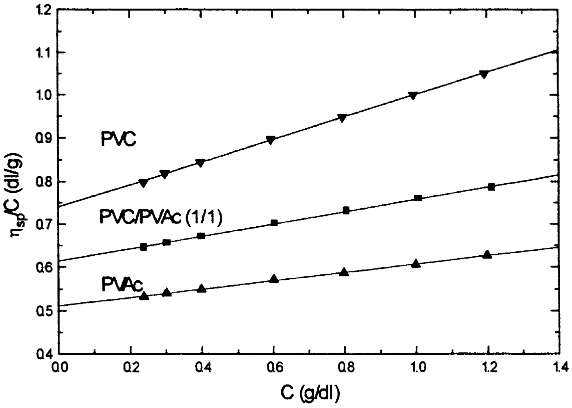

Fig. 6. Plots of the reduced viscosity (η_{sp}/C) vs. concentration (C) for PVC, PVAc and PVC/PVAc blends with the weight ratio of 1/1 in DMF at 30°C.

Table 1
Viscosity data for PVC, PVAc and PVC/PVAc blends in different solvents at 30°C

Solvent	$[\eta]_{PVC}$	b_{PVC}	$[\eta]_{PVAc}$	b_{PVAc}	Δb
THF	1.014	0.401	0.501	0.078	−0.028
MEK	0.752	0.108	0.434	0.040	0.176
DMF	0.738	0.262	0.511	0.091	−0.041

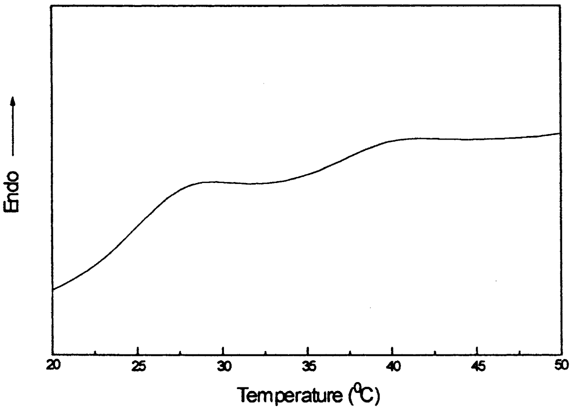

Fig. 7. DSC thermograms of PVC–PVAc blends (25:75 wt.%) casted from DMF.

4. Conclusion

The intermolecular interactions between PVC and PVAc in solution are greatly associated with the solvent from which PVC/PVAc blends were dissolved. In MEK, the attractive intermolecular interactions between PVC and PVAc existed. On the contrary, in either THF or DMF, the repulsive intermolecular interactions between PVC and PVAc existed. These different intermolecular interactions can be used to interpret the phase behavior of PVC/PVAc blends cast from different solvents. The conclusions developed from viscosity studied are in good agreement with the DSC measurement of PVC/PVAc blends cast from various solvents.

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