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Influence of molecular weight of poly (methyl methacrylate) on its miscibility with poly (vinyl chloride) in the solution

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Summary

In this work, the molecular weight effect on miscibility between poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) in cyclohexanone(CH) solutions at 30°C was examined by the viscometric method. Three samples of PMMA were prepared by emulsion polymerization, which molecular weights were changed by tert-dodecyl-mercaptan (TDDM) content. The parameter Δb is used to predict polymer-polymer miscibility of PVC/PMMA/cyclohexanone blend. Δb values indicated that the highest molecular weight of PMMA is immiscible with PVC resin. The molecular weight of PMMA decrease with the increase of the contention of TDDM, and the contribution of miscibility PVC/PMMA blend in CH is better.

Keywords

Miscibility; PVC/PMMA blends; viscosity

Introduction

The polymer blends often exhibit properties that are superior to each individual component polymer [1-2]. Hence, blending or alloying of polymers is a method of producing desirable materials without the effort of devising new syntheses. However, the superior properties of polymer blends are determined by the miscibility of homopolymers on molecular scale [3]. There have been various techniques to widely study the miscibility of PVC/PMMA blend over the last few decades. The first study on PVC/PMMA blends was done by J. W. Schurer et al., from their results it appeared that isotactic PMMA and PVC form an almost completely incompatible system, but syndiotactic PMMA and PVC form a compatible system up to 60 wt% syndiotactic PMMA [4]. The PMMA and PVC blend is a well known system in hydrogen-bonding type of specific interaction between the α-hydrogen of PVC and the carbonyl groups of PMMA [5]. But, Weisheng Li [6] and co-workers found that the intermolecular force is fairly weak by FTIR, separate Tg and two-phase structures were observed in their DSC and microscopy measurements. Therefore, they considered that

PVC/PMMA blends are not miscible at the molecular level over the whole composition range.

In the recent works many authors have chosen to study solution-cast films of poly (methyl methacrylate) and poly (vinyl chloride). Disagreement exists as to the bulk miscibility as measured by thermal analysis of PVC/PMMA blends. There are two typical results from the literature. Razinskaya et al. [7] were unable to produce compatible blends of PVC/PMMA from tetrahydrofuran (THF). Walsch and McKeown [8] have reportedly produced compatible blends using methyl ethyl ketone (MEK) as a mutual solvent, and they were unable to produce compatible blends from THF. Jager et al. [5] and Tremblay and Prud'homme [9] have also produced compatible blends from MEK. Hence, Po-Da Hong et al. [10] have studied of the solvent effect on miscibility blends of PVC/PMMA in the solution state by viscometric measurement. From their results it appeared that the PVC/PMMA/THF solutions exhibit miscibility up to 60% PMMA, on the contrary, due to similar affinity of DMF to PVC and PMMA, the PVC/PMMA/DMF solutions exhibit a slighter immiscibility at $W_{PMMA} \leq 0.3$ and $W_{PMMA} \geq 0.7$. There have been various techniques of studying the miscibility of the PVC/PMMA blends. And we found that viscosity measurements are simple, low cost and rapid techniques. Recently, A. Varada Rajulu et al. [11] have reported that PVC/PMMA blend solutions in cyclohexanone are miscible system by viscosity, ultrasonic velocity and refractive index.

PVC is a typical example of brittle thermoplastic and for years [12], many efforts have been made to improve its toughness. All the commercialized modifiers for toughening PVC, the traditional grafted rubber-thermoplastic type, such as methacrylate-butadiene-styrene (MBS) and all-acrylics impact modifier, which are all core-shell structure and PMMA is outer glassy polymer layer. The PMMA shells are grafted onto rubbery core by chemical bonds, which act as a compatibilizer on PVC. Thereby, in the present study, a series of poly (methyl methacrylate) (PMMA) were prepared via emulsion polymerization. The authors have chosen PVC and the different molecular weight of PMMA blends in cyclohexanone solutions at 30°C were examined by the viscometric method. Detailed studies on their miscibility may contribute to prepare blend with emulsion.

Experimental

Materials

PVC and three samples of PMMA were the products supplied by Table 1, methyl methacrylate (MMA) was the industrial product supplied by Jilin Chemical CO. LTD., China.

Synthesis of PMMA

The PMMA were prepared by emulsion polymerization using a 50-liter stainless steel reactor in a nitrogen atmosphere. The half of MMA monomer and initiator were fed into the reactor. The other half of MMA monomer and molecular weight regulator (TDDM) were mixed, and then they were charged to the reactor. The stirring speed of the impeller was 180rpm, and the polymerization temperature was 75°C. The polymerization time was about 3h. The molecular weights of PMMAs are shown in Table 1.

Sample preparation and testing

In this experiment, we have synthesized various molecular weight of PMMA via incorporating molecular weight regulator (TDDM) by emulsion polymerization. The blends of PVC/PMMA of different compositions have been prepared by mixing solutions of the polymers in CH. The molecular weights and their distributions of the different polymers were determined by gel permeation chromatography (GPC, Waters-410) relative to polystyrene standards. These measurements were performed in THF at 35°C, flow rate was 1ml/min. The molecular weights of poly (methyl methacrylates) and poly (vinyl chloride) used in this study are listed in table 1. The polymer solutions were prepared in a wind-mouthed bottle with heating blew the boiling point of the solvent for 24h until they were dissolved to give a homogeneous solution. The total weight of the two components in solution is always maintained in 8g/L. The stock solutions were diluted with solvent to obtain the desired concentrations. The viscosity of the polymer solutions was determined by using an Ubbelohde viscometer immersed in a thermostatic water bath, the temperature is maintained at 30±0.05°C. Efflux times of each blend composition were measured by the serial dilution technique. Through the classical Huggins equation [13],

$$\begin{aligned}\frac{(t-t_0)}{t_0}*\frac{1}{c}=\frac{\eta_{sp}}{c}&\\ =[\eta]+bc&\\ =[\eta]+k[\eta]^2c&\end{aligned}\qquad(\mathbf{1})$$

the intrinsic viscosity [η] and the Huggins constant k could be obtained, where t is the flowing time of the solution, t_0 the flowing time of the pure solvent, c the concentration of polymer and from the efflux time measurements, the specific viscosity, $[\eta]_{sp}$, was calculated at different concentration. The parameter b is the Huggins slope coefficient related to the polymer-polymer interaction and the parameter k is the Huggins constant. In the polymer A/polymer B/solvent ternary solution, the Huggins equation could be expanded as [10]:

$$\begin{aligned}\frac{\eta_{spm}}{c_m}&=[\eta]_m+b_m c_m\\ &=[\eta]_m+k[\eta]_m^2 c_m\end{aligned}\qquad(\mathbf{2})$$

Where $c_m = c_A + c_B$ is the total polymer concentration. The parameters$[\eta]_m$, b_m and k_m are the intrinsic viscosity, the Huggins slope coefficient and the Huggins constant, respectively.

Table 1. Molecular weights of the polymer

Polymer	Type	Producer	TDDM cotent (%)	Mn (kg/mol)	Mw (kg/mol)	Mw/Mn
PVC	SG-5	Jilin Chemical CO. LTD., China	-	102172	209254	2.048
PMMA 1	-	laboratory	0	215828	689146	3.193
PMMA 2	-	laboratory	0.5	33102	51091	1.543
PMMA 3	-	laboratory	1.0	26370	40185	1.524

Results and discussion

Figure 1 shows the plots of the reduced viscosity η_{sp}/c versus polymer concentration c for PVC and different kinds of PMMA blends in CH solutions at different weight fraction of PMMA W_{PMMA}, and presents a linear relationship between the η_{sp}/c and c values. The linear and angular coefficient of η_{sp}/c vs. c curves were calculated by the linear regression procedure, giving, respectively, the intrinsic viscosity, $[\eta]$, and $b=k[\eta]^2$, or more properly, the slope of η_{sp}/c vs. c curves. The plots are linear and no cross-over is observed to show that the blends are miscible. A sharp cross-over in plots of reduced, η_{sp}/c vs. c is shown by immiscible blends[14,24]. So that, we can obtain PVC/PMMA1 blends are incompatible blends from figure 1(A).

The interaction between the polar polymer and the polar solvent has been discussed in many literatures [15-22]. The donor-acceptor electron property and the charge-density rearrangement directly cause the highly attractive interaction between polar polymer and polar solvent. The α-hydrogen of PVC could easily be attacked by electron donors such as the electronegative oxygen atom in carbonyl group in CH. In addition, the same functional group (C=O) in both PMMA and CH, this factor is useful to increase the PMMA/CH interaction. This fact must significantly affect the miscibility of the PVC/PMMA mixtures in the solvent.

In the ternary polymer solution, dilute solution viscosity method by Krigbaum and Wall [23] have defined a theoretical polymer A /polymer B interaction parameter $b_{AB,t}$, many authors[24-31] have discussed it in details. We characterized the compatibility of the polymer blends by parameter $b_{AB,t}$ in this work. According to these authors, the $[\eta]_m$ is the intrinsic viscosity of the mixture and b_m is the Huggins slope coefficient characterizing the interactions of all polymer species, given by

$$b_m = b_A w_A^2 + b_B w_B + 2b_{AB} w_A w_B \tag{3}$$

$$b_{AB} = \frac{b_m - \left(b_A w_A^2 + b_B w_B^2\right)}{2w_A w_B} \tag{4}$$

here, W_A and W_B are the weight fractions of the polymers; b_A, b_B and b_{AB} are the interaction terms of like (AA,BB) and unlike (AB) polymer molecules, given by:

$$b_{AB} = k_{AB}[\eta]_A[\eta]_B \tag{5}$$

b_{AB} is a complex parameter including the thermodynamic and hydrodynamic interactions in the system. Supposing only hydrodynamic interaction, the theoretical values of b_{AB} are calculated as the geometric means of b_A and b_B [29]:

$$b_{AB,t} = \left(b_A b_B\right)^{0.5} \tag{6}$$

The different between the experimental and the theoretical values Δb_{AB} exhibit the degree of the polymer A/polymer B interaction, as given in

$$\Delta b_{AB} = b_{AB} - b_{AB,t} \tag{7}$$

positive Δb_{AB} values refer to the attractive interactions and miscibility between unlike polymers, whereas negative Δb_{AB} values refer to the repulsive interactions and immiscible polymer A/polymer B mixtures.

The Δb_{AB} values are calculated and the Δb_{AB} as function of W_{PMMA} in the PVC blends in CH solutions are plotted in Figure 2. We can observe different miscibility with the various molecular weight of PMMA.

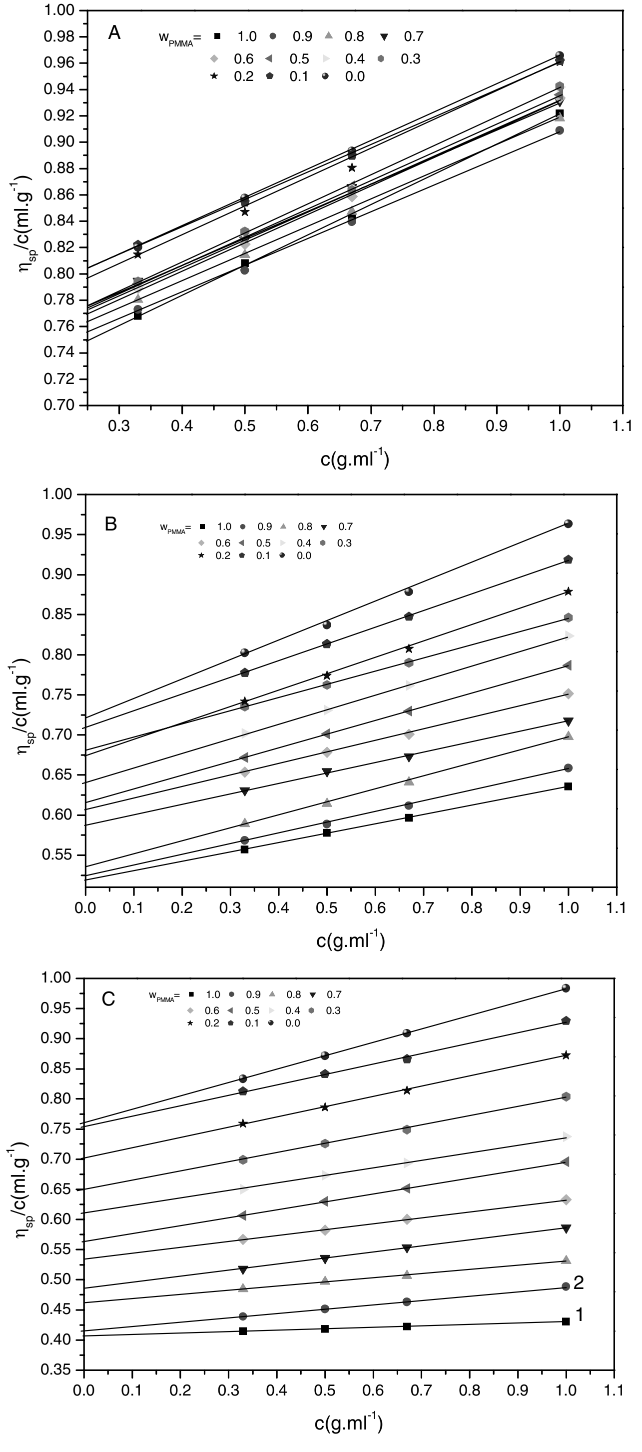

Figure 1. Reduced viscosity η_{sp}/c' as a function of polymer concentration c in PVC/PMMA/CH solutions: A PVC/PMMA1/CH blends; B PVC/PMMA2/CH blends; C PVC/PMMA3/CH blends.

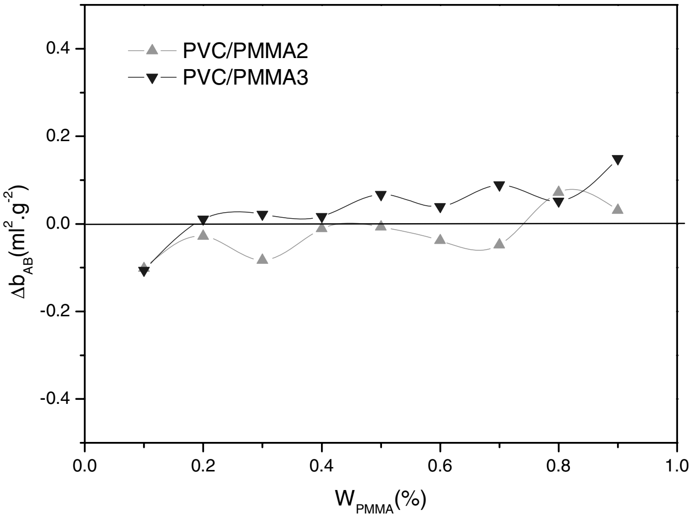

Figure 2. Plot of the thermodynamic interaction parameters Δb_{AB} versus W_{PMMA} in PVC/PMMA/CH solution.

In the PVC/PMMA2/CH solutions of Figure 2, we can find out positive Δb_{AB} values at $W_{PMMA} \geq 75\%$, indicating only high miscibility at higher content of PMMA2. In the PVC/PMMA3/CH solutions, then change to positive Δb_{AB} values at $W_{PMMA} \geq 20\%$, indicating high miscibility could be obtained in PVC/PMMA3/CH solutions, the miscibility windows become wide.

In order to explain the observed dependence of miscibility on the PMMA molecular weight, one should take into account factors contributing to the free energy of mixing. With increasing Mw, the contribution of combinatorial entropy is diminished, and the formation of polymer blends compatible on a molecular level must result from a reduction in enthalpy upon mixing. This reduction may be due to strong favorable interactions between molecules of the two polymer species. The molecular chain of PMMA decreased and the viscosity of the blend increased with the increase of the quantity of TDDM. This means that the miscibility of PVC with lower Mw PMMA3 in solutions most likely results from the favorable contribution of the combinatorial entropy of mixing (which is expected to be higher for the lower Mw system) , because the enthalpy of PVC/PMMA interaction ceases to favor mixing with increasing PMMA chain length. In a binary polymer system, for the molecular weight dependence of the critical Flory-Huggins interaction parameter χ_c we can write [32]

$$\chi_c = \frac{1}{2}\left(\frac{1}{X_A^{1/2}} + \frac{1}{X_B^{1/2}}\right)^2 \qquad \textbf{(8)}$$

where X_A and X_B are the numbers of repeating units of components A and B, respectively. We can obtain χ_c will decrease with the increase of the PMMA molecular weight from equation (8). The two polymers can prepare the miscibility of homopolymers on the condition of Flory-Huggins interaction parameter $\chi_1<\chi_c$. But, at $\chi_1>\chi_c$, the two polymers can yield heterogeneous polymer. Therefore, from our results it appeared that PVC and lower molecular weight of PMMA form an almost completely miscible system, but, PVC and the higher molecular weight of PMMA form an immiscible system.

Conclusions

The treatments of the viscometric method results could be used to discuss the molecular weight effect on the miscibility between PVC and PMMA in a ternary polymer solution. The analyses show that the miscibility of PVC/PMMA blends solutions is different with various molecular weight of PMMA. High molecular weight (M_W>689146) of PMMA are immiscible with PVC, lower molecular weight (M_W<689146) of PMMAs are partial miscibility with PVC.

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