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Effect of Variations of Temperatures on the Compatibility of Poly(Methyl Methacrylate)/Polyvinyl Chloride in THF Ternary System

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The intermolecular interaction between poly (methyl methacrylate) (PMMA) and polyvinyl chloride (PVC) in THF has been studied at different temperatures using dilute-solution viscometry method. The intrinsic viscosity and viscometric interaction parameter were experimentally measured for the binary (solvent/polymer) and ternary (solvent (1)/polymer (2)/polymer (3) systems. These results have served for the estimation of the compatibility of the polymer mixture at different temperatures by means of the sign of Δb_m and $\Delta[\eta]_m$. The results show that the polymer mixture is compatible in THF as the temperature increases, while the incompatibility observed at 34°C may be due to the enhancement in the interactions between THF and the polymers at this temperature.

Key Words: Temperature, Variations effect, Compatibility, Poly(methyl methacrylate), Polyvinyl chloride.

INTRODUCTION

The study of the compatibility between pairs of polymers in a common solvent is a very interesting and actual field of research, which is generally considered as the result of interactions between polymer segments[1–18]. Due to its interest, polymer-polymer compatibility has been extensively studied by several techniques[19]. Mot of them are experimentally demanding and time-consuming techniques. Dilute-solution viscometer (DSV) is the best technique to study polymer-polymer compatibility[12, 13, 20–26]. It is an inexpensive technique and has also been used in polymer science to determine the molecular weight and its distribution or branching degree[24, 27, 28]. The viscometric interaction parameter, b_m, characterizes the overall interaction (hydrodynamic as well as thermodynamic) between like chains of both polymers and can be used to determine polymer-polymer compatibility[13, 14, 29, 31]. Meanwhile the intrinsic viscosity of the ternary mixture, $[\eta]_m$, denotes the coil dimensions which can be altered by a contraction or expansion of the coil whether the interactions between unlike **i–j** polymer segments are attractive or repulsive.

The compatibility of poly (methyl methacrylate) (PMMA) with poly (vinyl chloride) (PVC) in tetrahydrofuran (THF) has been studied by DSV method at

28°C[13, 32]. It was found that PMMA and PVC are compatible over the whole range of compositions.

In this paper, the effect of variations of temperature on the compatibility of the ternary system THF(1)/PMMA(2)/PVC(3) has been studied. The compatibility of the polymer mixture is discussed in two different criteria, through the signs of Δb_m and $\Delta[\eta]_m$.

Theoretical

The theoretical consideration starts from the derivation by Krigbaum and Wall[18] and Cragg-Bigelow[17]. The specific viscosity $\eta_{sm,\,m}$ of a mixed polymer solution can be expressed as follows:

$$\eta_{sp,\,m} = [\eta_2]C_2 + [\eta_3]C_3 + b_{22}C_2^2 + b_{33}C_3^2 + 2b_{23}C_2C_3 \tag{1}$$

where $[\eta_2]$ is the intrinsic viscosity of component 2 alone in the solution with common solvent, C_2 is the concentration of component 2 in mixed polymer solution and b_{23} is the interaction coefficient for the mixture of components 2 and 3. The coefficient b_{22} is related to the constant, K, in the Huggins equation, when component 2 is in the solution alone. (This also applies to b_{22}).

$$\frac{(\eta_{sp})_m}{C_m} = [\eta]_m + K[\eta]^2C_m \tag{2}$$

The relationship between b_{22} and K is written as:

$$b_{22} = K_2[\eta_2]^2 \tag{3}$$

The interaction coefficient between the two polymers (b_{23}) according to Williamson and Wright[15] can be expressed as

$$b_{23} = (b_{22} + b_{33})/2 \tag{4}$$

Eq. (2) can be expressed in a weight- average form since after some mathematical procedure[4], the general form for b_m is:

$$b_m = b_{22}w_2^2 + b_{33}w_3^2 + 2b_{22}^{1/2}b_{33}^{1/2}w_2w_3 \tag{5}$$

This equation is used to define the theoretical value of the global viscometric interaction parameter between chains of different polymers.

$$b_{23}^{theor} = b_{22}^{1/2}b_{33}^{1/2} \tag{6}$$

On the other hand, the experimental value of this b_m^{exp} parameter, is given by parallelism as:

$$b_m^{exp} = b_{22}w_2^2 + b_{33}w_3^2 + 2b_{23}^{exp}w_2w_3 \tag{7}$$

where b_m^{exp} is obtained from the slope of Eq. (2), and b_{22} and b_{33} are easily determined from the binary systems formed by polymers 2 or 3 in the solvent respectively through Eq. (1). Then, the criteria for compatibility in the polymer mixture is based on the comparison between experimental and theoretical b_{23} values[18]. The values of $b_{23}^{exp} > b_{23}^{theor}$ represent compatibility between polymers, or would attractive molecular interactions, whereas values of $b_{23}^{exp} < b_{23}^{theor}$ would provide incompatibility or repulsive molecular interactions. In the hypothetical case where $b_{23}^{exp} = b_{23}^{theor}$ it would signify that chains do not interact neither favorably nor unfavorably. The second compatibility criteria based on the difference between the experimental and theoretical values of $[\eta]_m$. Therefore, this criteria will be used to explain the compatibility between two polymers, where, it would be compatible if $\Delta[\eta]_m = ([\eta]_m^{exp} - [\eta]_m^{theor}) < 0$ incompatible if $\Delta[\eta]_m = ([\eta]_m^{exp} - [\eta]_m^{theor}) > 0$ where $[\eta]_m^{exp}$ is determined from the intercept of plots of Eq. (2) and $[\eta]_m^{theor}$ can be calculated by using the mathematical derivation[4],

$$[\eta]_m = \sum_i [\eta]_i w_i = [\eta]_2 w_2 + [\eta]_3 w_3 \tag{8}$$

EXPERIMENTAL

PMMA with average molecular weight 350,000 g/mol and PVC with average molecular weight of 43,000 g/mol were purchased from Aldrich (USA). Tetrahydrourance (THF) was used as recived from laboratory chemicals Haifa 26110 (Israel).

The viscosity measurements were made with a conventional cannon-Fenske-type capillary viscometer equipped with a model OSK 2876, which was immersed in a water bath. The temperatures were measured close to the capillary by a thermometer with an accuracy of 0.01°C. The stock solution of each ternary or binary system was made by dissolving the polymer samples in filtered THF solvent. The total polymer mixture in the solution was 1.0 g/dL.

Dilutions to prepare, at least, five lower concentrations. For each solution 12 mL of the sample was loaded to minimize drainage errors into the viscometer and placed in the thermostatic bath. Measurements started until an equilibration time of 5–10 min. The elution time of each solution is then determined as the average of several readings. The dilution finished after the solution volume becomes 21 mL. Kinetic energy corrections were taken into account for the evaluation of the intrinsic viscosity $[\eta]$ which was determined by extrapolation to infinite dilution (zero solute concentration) of Huggins plots, *i.e.*, η_{sp}/C *vs.* C.

RESULTS AND DISCUSSION

Fig. 1 shows the plot of the reduced vicosity (η_{sp}/C) *vs.* concentrations of PMMA and PVC in THF at different temperatures. It can be seen that all plots are linear in the whole ranges of concentration. It can be seen that, the measured intrinsic viscosities at higher temperatures, for both PMMA and PVC are larger than those measured at lower temperatures. This indicates that at higher temperatures, the polymer-solvent interaction increases and the polymer coils will expand. The experimental results for reduced viscosities in the ternary system, THF(1)/PMMA(2)/PVC(3) at constant polymer concentrations ranging from 0.50–0.80 g/dl at PMMA weight fraction of 0.25 as an example, at different temperatures as shown in Fig. 2. It can be seen that the intrinsic viscosities of PMMA/PVC in THF at $w_2 = 0.25$ blend are larger than the intrinsic viscosities of PMMA and PVC in THF at the different temperatures studied. The reasonable interpretation is that the attractive interaction between PMMA and PVC in THF decreases the intermolecular excluded volume, so the PMMA coils expand which lead to increase the hydrodynamic volumes of polymer blend.

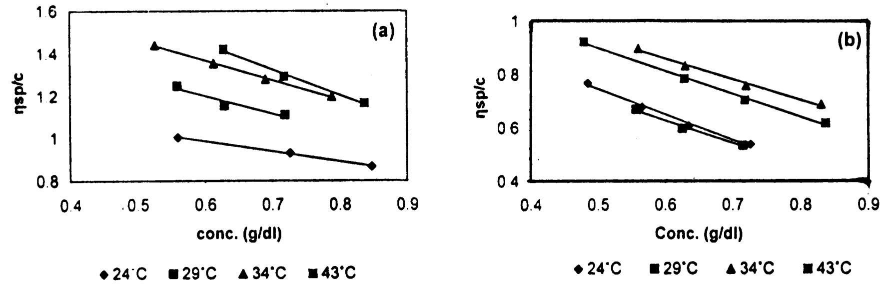

Fig. 1. Plots of reduced viscosity *vs*. concentrations for the binary polymers PMMA (a) and PVC (b) in THF at different temperatures

At finite polymer concentrations the polymer-polymer interaction is of importance, and this effect can be illustrated by the interaction parameter, b, defined by the Huggins' equation (Eq. 2). The most prominent feature in Figs. 1 and 2 are the increase in [η] accompanied by the decrease in b as the temperature increases from 24–43°C. This increase in [η] can be attributed to the specific interactions between the carbonyl group of PMMA and the α-hydrogen of PVC, which suggestes expansion of the coil due to favorable PMMA/PVC interaction as the temperature increases. The significant increase in [η] is, at 34°C compared with other temperatures may be attributed to the interactions between THF and the polymers at this temperature.

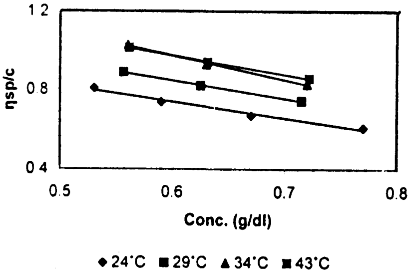

Fig. 2. The variation of reduced viscosity *vs*. concentrations for PMMA/PVC at weight fraction 0.25 in THF at different temperatures

The compatibility of the two polymers was investigated by considering the compatibility criterias based on the difference between the experimental and theoretical values of [η] and b. The compatibility criterias Δb_m and $\Delta[\eta]_m$ at different temperatures, are reported in Table-1. The comparison of the experimental and theoretical values of b_m could give an information about the interactions between polymer chains. On the other hand the negative values of b_m indicate that the polymer chains prefer to interact with themselves, so the signs of Δb_m and $\Delta[\eta]_m$ will give the degree of polymer-polymer compatibility. The compatibility occurs when $\Delta b_m > 0$ and $\Delta[\eta]_m < 0$. On the contrary, the two polymers would be incompatible if $\Delta b_m < 0$ and $\Delta[\eta]_m > 0$. Taking into account the above comments, the effect of temperatures on the compatibility may be discussed in terms of such parameters (Δb_m and $\Delta[\eta]_m$).

TABLE-1
EXPERIMENTAL AND THEORETICAL VISCOMETRIC DATA FOR THE TERNARY MIXTURE PMMA/PVC IN TETRAHYDROFURAN AS SOLVENT AT DIFFERENT TEMPERATURES

Temp. (°C)	w_2	$[\eta]_m^{exp}$ (dL/g)	b_m^{exp} $(dL/g)^2$	$[\eta]_m^{id}$ (dL/g)	b_m^{id} $(dL/g)^2$	Δb_m $(dL/g)^2$	$\Delta[\eta]_m$ (dL/g)
24	0.25	1.2349	−0.8241	1.2360	−0.8334	0.0090	−0.0011
	0.50	1.2518	−0.8489	1.2483	−0.7155	−0.1334	0.0035
	0.75	1.1344	−0.5533	1.2608	−0.5964	0.0431	−0.1268
29	0.25	1.3945	−0.9113	1.3005	−0.8765	−0.0348	0.0940
	0.50	1.5466	−0.9774	1.4381	−0.8682	−0.1092	0.1085
	0.75	1.5283	−0.7283	1.5756	−0.8596	0.1313	−0.0473
34	0.25	1.7217	−1.2435	1.4713	−0.8679	−0.3756	0.2504
	0.50	2.1572	−1.9502	1.6342	−0.9073	−1.0429	0.5230
	0.75	2.0153	−1.2641	1.7972	−0.9466	−0.3175	0.2181
43	0.25	1.5608	−0.9745	1.5366	−0.8813	−0.0932	0.0242
	0.50	1.8411	−1.1948	1.7485	−0.9901	−0.2047	0.0926
	0.75	1.8657	−0.9522	1.9604	−1.0988	0.1466	−0.0947

The compatibility data in Fig. 3 and 4 show the dramatic evolution of Δb_m and $\Delta[\eta]_m$ for constant PMMA weight fractions at different temperatures. It can be seen that the polymer mixtures of PMMA(2)/PVC(3) is compatible at 24, 29 and 43°C. It is also clear from Figs. 3 and 4, that as the temperature increases, the compatibility of polymer blend at different weight fractions increases. The decrease in the compatibility of PMMA/PVC at 34°C may be attributed to increase the solubility of PMMA and PVC in THF at 34°C and also the increase in polymer-solvent interaction will lead to decrease in polymer-polymer interaction at that temperature. On the other hand the usual interaction between the carbonyl group of PMMA and α-hydrogen of PVC becomes weak at 34°C. If so we would expect the polymer blend is incompatible at 34°C as indeed observed in Figs. 3 and 4.

Conclusion

From the present study, it can be concluded that the compatibility of PMMA/PVC in THF is affected by the temperature. As the temperature increases, the compatibility will increase and the incompatibility of the polymer mixture enhanced at 34°C.

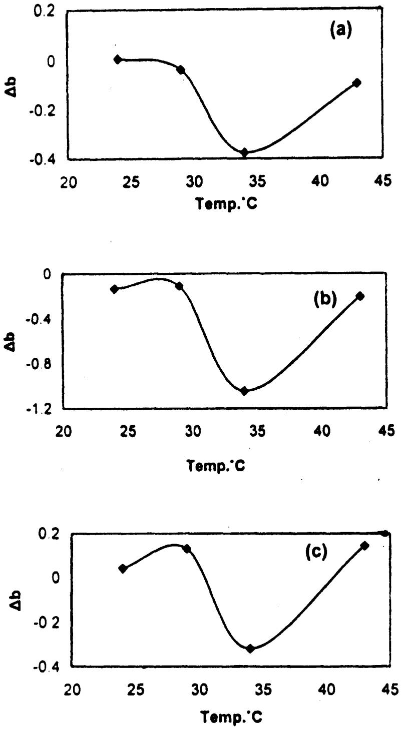

Fig. 3. Plots of compatibility magnitude (Δb) as a function of different temperatures for the polymer mixture PMMA/PVC at (a) w_2 =.0.25, (b) w_2 = 0.50 and (c) w_2 = 0.75 in THF

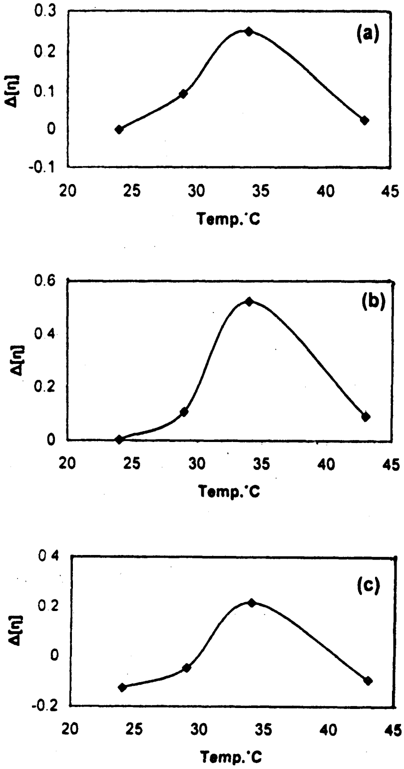

Fig. 4. Plots of compatibility magnitude Δ[η] as a function of different temperatures for the polymer mixture PMMA/PVC at (a) w_2 = 0.25, (b) w_2 = 0.50 and (c) w_2 = 0.75 in THF

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