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Study of the Compatibility of Polymer-Polymer Mixtures in Solution by Dilute-Solution Viscometry Method

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The viscosity behavior of mixtures of poly(methyl methacrylate) (PMMA) with other polymers such as ploy(vinyl chloride) (PVC), polystyrene (PS) and poly(isobutyl methacrylate) (PiBMA) in dilute tetrahydrofurane (THF) was studied at 29°C. The ternary systems assayed, and denoted solvent (1)/polymer (2) / polymer (3), poly(methyl methacrylate) PMMA as polymer 2, and poly(vinyl chloride) PVC, poly(styrene) PS and poly(isobutyl methacrylate) PiBMA as polymer 3. The intrinsic viscosity and viscosity interaction parameter were experimentally measured for the binary (solvent/polymer) as well as for the ternary systems and have served for the estimation of the compatibility of the different mixtures by means of the signs of Δb_m and $\Delta[\eta]_m$.

Key Words: Intrinsic viscosity, Polymer compatibility, Polymer-solvent interaction, Dilute solution viscometer method.

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[1–8] Dilute-solution viscometer (DSV) is the best technique for polymer-polymer compatibility study among the other techniques, which are time-consuming and experimentally demanding[9]. 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[10–14]. Mean while the intrinsic viscosity of the 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 not.

In the present study the technique of dilute solution viscometry (DSV) was used, we have performed a study on the viscosity behavior of mixtures of poly(methyl methacrylate) (PMMA) with other polymers such as poly(vinyl chloride) (PVC), polystyrene (PS) and poly(isobutyl methacrylate) (PiBMA) in THF as a solvent. The compatibility of the mixtures of polymers is discussed in two different ways: First through Δb_m values where, $\Delta b_m > 0$ for compatible mixtures and $\Delta b_m < 0$ for incompatible[11]. Second in the present work, using a new idea based on the intrinsic viscosity results will be applied. However, the new idea does not contain any mathematical operations, where the intrinsic viscosity is handled as an excess property of the solution.

Theoretical

The theoretical consideration starts from the derivation by Krigbaum and Wall[15]and Cragg-Bigelow[16]. The specifc viscosity $\eta_{sp,m}$ 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[12], when component 2 is in the solution alone. (This also applies to b_{22}.)

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

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[13], 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[14] 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 parameter (b_m^{exp}) 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[15]. 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[19]. The second compatibility criteria based on the difference between the experimental and theoretical values of $[\eta]_m$. Therefore, another 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[14],

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

EXPERIMENTAL

Four different polymers were used in this work. poly(methyl methacrylate) (PMMA), poly(vinyl chloride) PVC, polystyrene PS, poly(isobutyl methacrylate) PiBMA were purchased from Aldrich (USA). The molar masses of the polymers were listed in Table 1. Tetrahydrofuran (THF) was used as received from laboratory chemicals Haifa 26110, Israel.

TABLE-1
VISCOSITY DATA FOR THE POLYMERS IN THF SOLVENT AT 29°C.

Polymer	M_w	Solvent THF $[\eta]_i$ (dL/g)	b_{ii} $(dL/g)^2$
PMMA	120.000	1.4057	−1.0577
PVC	43.000	1.6523	−1.1238
PS	29.300	1.1464	−1.0498
PiBMA	300.000	1.8450	−1.0225

Viscometric measurement: All measurements were performed at (29 ± 0.1°C) by a Cannon—Fenske-type capillary viscometer equipped with a model OSK 2876. The stock solution of each binary or ternary system was made by dissolving the polymer samples in filtered solvent up to concentration of 1.0 g/dL. Dilutions to prepare, at least, five lower concentrations were made by adding the appropriate aliquots of solvent. 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 minutes. 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

Figure 1 shows the variation of reduced viscosity of the binary systems, THF/PiBMA, THF/PVC, THF/PMMA and THF/PS respectively versus the concentration of the polymer solvent mixture. The intrinsic viscosities as well as the viscometric interaction parameters for the different binary systems at 29°C are compiled in Table-1. One can see that the intrinsic viscosity for PiBMA is the highest which is accordance with its molecular weight. The values of viscometric interaction parameter, bii, for PiBMA is the highest also ,denoting that the solvent thermodynamic quality of THF is better for PiBMA.

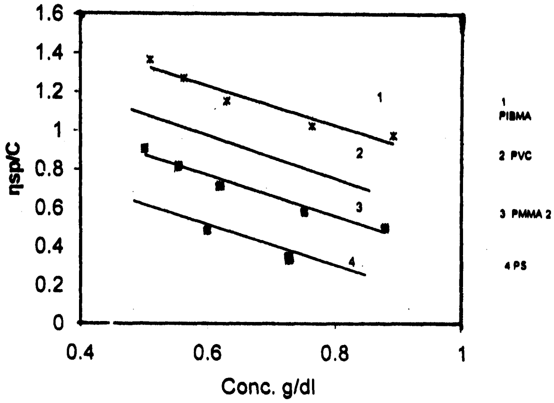
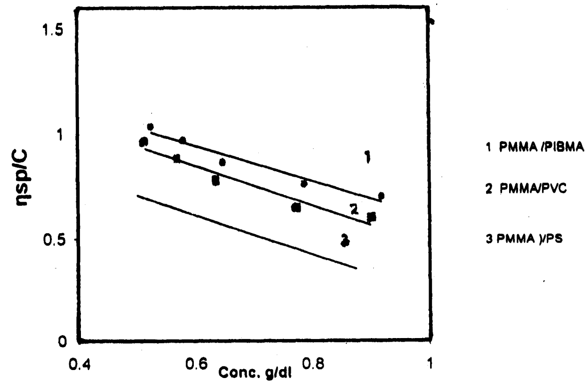


Fig. 1. Reduced Viscosity Dependence on Different Binary Systems concentration and Huggins Linearization through eq. (10) For The Different Polymers in THF as Solvent.

Figure 2 shows plots for the ternary systems THF/PMMA/PVC, THF/PMMA/PS and THF/PMMA/PiBMA when $w_2 = 0.50$ as example, the reduced viscosities as well as the concentrations for each polymer mixture in THF at weight fraction of PMMA = 0.50 are given in Table-2. From Figure 2, the sign of the slopes is negative and the negativity increased when PiBMA is predominate in the mixture making it less compatible, as it will be discussed later with the two compatibility criteria.



Fig, 2. Reduced Viscosity on Polymer Mixture Concentration and Huggins Linearization Through Eq.(2) When $w_2 = 0.50$ For the Polymer pairs in THF as Solvent.

It is not fruitful to pay attention to the sign of b_m values but only to the sign of Δb_m, so the compatibility of the polymer mixtures was investigated by considering the compatibility criteria based on the difference between the experimental and theoretical values of $[\eta]_m$ and b_m values which are reported in Table-3 and calculated using equations from 1–8 which are given in the theoretical part.

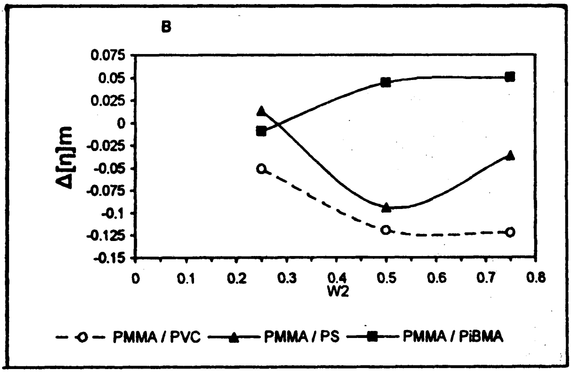
TABLE-2
EXPERIMENTAL VALUES OF THE REDUCED VISCOSITIES $(\eta_{sp}/C)_m$ AND CONCENTRATIONS FOR THE TERNARY POLYMER MIXTURES IN THF AT 29°C AT WEIGHT FRACTION 0.50 g.

Polymer mixture	V (ml)	C_m (g/dl)	$(\eta_{sp}/C)_m$ (dl/g)
PMMA/PVC	12	0.900	0.603
	14	0.772	0.652
	17	0.635	0.777
	19	0.568	0.886
	21	0.514	0.960
PMMA/PS	12	0.875	0.384
	14	0.750	0.434
	17	0.617	0.576
	19	0.552	0.662
	21	0.500	0.732
PMMA/PiBMA	12	0.919	0.706
	14	0.787	0.763
	17	0.648	0.866
	19	0.580	0969.
	21	0.525	1.034

TABLE-3
EXPERIMENTAL AND THEORETICAL VISCOMETRIC DATA FOR THE TERNARY POLYMER MIXTURES IN THF AS SOLVENT 29°C

Polymer mixtures	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)
PMMA/PVC	0.25	1.540	−1.003	1.591	−1.107	0.104	−0.050
	0.50	1.409	−0.934	1.529	−1.090	0.156	−0.119
	0.75	1.345	−0.996	1.467	−1.074	0.078	−0.122
PMMA/PS	0.25	1.225	−1.072	1.211	−1.052	−0.020	0.014
	0.50	1.182	−0.947	1.276	−1.053	0.106	−0.094
	0.75	1.305	−1.049	1.340	−1.055	0.006	−0.035
PMMA/PiBMA	0.25	1.726	−1.094	1.735	−1.031	−0.063	−0.009
	0.50	1.670	−1.175	1.625	−1.040	−0.135	0.044
	0.75	1.566	−1.052	1.515	−1.048	−0.003	0.050

The comparison of the experimental and theoretical values of b_m could give accurate information on interactions between polymer pairs. On the other hand the negative b_m values indicate that the polymer chains prefer to interact with themselves, so the sign of Δb_m will give the degree of polymer-polymer compatibility. In this way, $\Delta b_m > 0$ refers to attractive interaction between polymer segments and compatibility, whereas $\Delta b_m < 0$ is found for solution of systems containing incompatible polymers. The compatibility data in Fig. 3 shows the dramatic evolution of Δb_m and $\Delta[\eta]_m$ for different weight fractions of PMMA



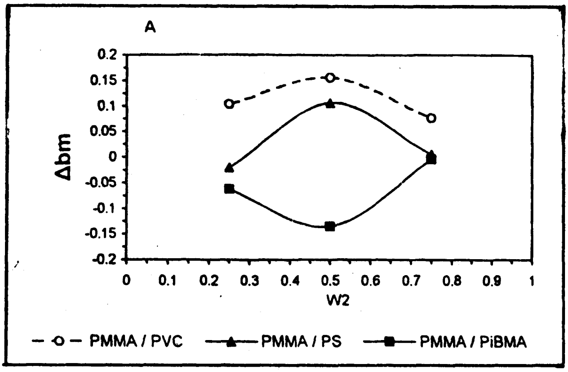


Fig. 3. Plots of different compatibility magnitudes as a function of mixture composition for the polymer pairs at different weight fractions of PMMA in THF as solvent.

with other three different polymer mixtures. It is seen that the compatibility order for the mixtures of polymers is as follow PMMA/PVC > PMMA/PS > PMMA/PiBMA. It can be seen that PMMA is compatible with PVC in all composition ranges due to the specific interaction between the carbonyl group of PMMA and the α-hydrogen of PVC. This positive deviation reflects an increase of the effective hydrodynamic specific volume, which suggests expansion of the coil due to favorable PMMA/PVC interactions. PMMA with PS is, high compatible at 0.50, that means when the polymer mixture is at 50 : 50. The strong repulsion interaction of macromolecules is shown in PMMA/PiBMA where all values of Δb_m are negative and $(\Delta[\eta]_m)$ values are positive, that means they are incompatible in all composition ranges, since the two polymers have carbonyl group so there is no interaction between them[2, 3].

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