

## Viscometric Study on Polystyrene/polydimethylsiloxane Blends in Various Solvents

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The viscometric measurements were carried out for polystyrene (PS), polydimethyl siloxane (PDMS) and PS/PDMS in three different solvents at 25°C. The results showed that the choice of solvent is believed to play a key role in characterizing the viscosity behaviour of the polymer solution. The intrinsic viscosity and the viscometric interaction parameters have been experimentally measured for the binary (solvent/polymer) as well as for the ternary systems and also theoretically evaluated for the latter. The estimation of the compatibility degree in the different solvents have been done by means of the signs of  $\Delta b'_m$  and  $\Delta[\eta]_m$ . The results show that the compatibility of PS/PDMS blend in toluene while incompatibility in THF and benzene, respectively.

**Key Words:** PS/PDMS blend, Polymer compatibility, Different solvents, Dilute solution viscometry.

### INTRODUCTION

The study of viscosity on a ternary system which is composed of two different polymers and a solvent is a very interesting subject, mainly due to its simplicity and importance in the characterization of the intermolecular interaction between the two different polymers in solution<sup>1-18</sup>. Dilute-solution viscometer (DSV) is the best technique for polymer-polymer compatibility study among the other techniques, which are time-consuming and experimentally demanding<sup>19</sup>. The effectiveness of this method relies on the assumption that the attractive or repulsive intermolecular interaction between two polymers in solution (polymer (1)-polymer (2) interaction) have a great influence on the viscosity of the polymer solution. The two polymers are dissolved in a common solvent, so that their hydrodynamic volumes are affected by the solvent selected. The intermolecular interaction between the two different polymers in solution may also play a key role in characterizing the viscosity behaviour of ternary system to which little attention has been devoted<sup>20-22</sup>. As it is well known that the intermolecular interaction in polymer solution of binary system (polymer (1)-solvent) can be either repulsive or attractive depending on the solvent selected<sup>23</sup>, for example, if a given polymer was

dissolved in a solvent at a temperature above  $\theta$ , the segments of a given polymer would repel one another and the repulsive intermolecular interaction should be expected. On the other hand, if the polymer was dissolved in a solvent at temperature below  $\theta$ , the segments of the polymer would attract one another and the attractive intermolecular interaction should be expected. Therefore, in order to perform dilute solution viscometry measurements, the influence of solvent on the intermolecular interaction between the two different polymers in solution should be also taken into account.

In this work, the viscosity measurement of PS, PDMS and PS/PDMS blends in different solvent (benzene, toluene and THF) are presented. The compatibility of the polymer mixture is evaluated through the signs of  $\Delta b'_m$  and  $\Delta[\eta]_m$ .

### EXPERIMENTAL

Polystyrene (PS) with average molecular weight 350,000 g/mol and polydimethyl siloxane (PDMS) with average molecular weight of 95,000 g/mol were purchased from Aldrich (USA). Benzene, Toluene and THF were purchased from laboratory chemicals Riedel-de Haen (Germany) and used as received.

**Viscometric measurements:** All measurements were performed at  $25 \pm 0.1^\circ\text{C}$  using a canon-Fenske type capillary viscometer. The stock solutions of each ternary or binary system were made by dissolving the polymer samples in filtered solvents (benzene, toluene and THF) up to concentration of 1.0 g/dL. Five sample solutions of lower concentrations were prepared by adding appropriate aliquots of solvent to the stock solution. For each solution, 12 mL of the solution was loaded to minimize drainage errors to the viscometer and placed in the thermostat. The elution time of each solution was then determined as the average of several readings. The dilution finished after the solution volume reached 21 mL. Kinetic energy corrections were taken into account for the evaluation of the intrinsic viscosity  $[\eta]$  and viscometric interaction parameter ( $b$ ), which were determined by extrapolation to infinite dilution (zero solute concentration) and from the slope of the linear plots, respectively, Huggins plots, *i.e.*  $\eta_{sp}/c$  vs.  $c$ .

### RESULTS AND DISCUSSION

The reduced viscosity of the binary or ternary polymers in solution follows the linear relationship given by Huggins equation:

$$\frac{(\eta_{sp})_i}{c_i} = [\eta]_i + b_{ii}c_i \quad (1)$$

Krigbaum and Wall developed the following equation for mixed polymer solution<sup>18</sup>.

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

where  $\eta_{sp,m}$  is the specific viscosity of polymer solution,  $[\eta_2]$  and  $[\eta_3]$  are the intrinsic viscosity of polymer components 2 and 3, respectively and  $b_{22}$  and  $b_{33}$  are the specific interaction parameters of components 2 and 3 in binary system (polymer-solvent).  $b_{23}$  is the specific interaction parameter of components 2 and 3 in solution (ternary system) which can be expressed according to Williamson and Wright<sup>15</sup>,

$$b_{23} = (b_{22} \times b_{33})^{1/2} \quad (3)$$

has been used when the viscometric parameters of the two homo polymers are positive and :

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

When one or both of them take a negative value. Eq. (3) can be expressed in a weight-average form since after some mathematical procedure<sup>24</sup> the general form  $b_m$  is:

$$b_m^{id} = b_{22}w_2^2 + b_{33} + 2b_{22}^{1/2}b_{33}^{1/2}w_2w_3 \quad (5)$$

Generally, eq. (4) is used to define the ideal value of the viscometric interaction parameter, between chains of both polymers in the mixture. To avoid the erroneous from the values of  $b_{23}$  in eq. (4) depending on the signs of the viscometric interaction parameter, a new viscometric interaction parameter,  $b'_m$ , which can be defined as:

$$b'_m = b_{22}w_2^2 + b_{33}w_3^2 \quad (6)$$

Which compared with eq. (4) eliminates the uncertainty of defining the  $b_{23}$  parameter. On the other hand, the experimental value of  $b_m^{exp}$  is given by parallelism as:

$$b_m^{exp} = b_{22}w_2^2 + b_{33}w_3^2 + 2b_m^{exp}w_2w_3 \quad (7)$$

where  $b_{22}$ ,  $b_{33}$  and  $b_{23}$  are obtained from the slope of eq. (1) for binary and ternary systems, respectively. Therefore the first compatibility criterion, proposed in this paper, is as follows: Compatibility if  $\Delta b'_m = (b_m^{exp} - b_m^{(id)}) > 0$  or,  $b_m^{exp} > b_m^{(id)}$  and incompatibility if  $\Delta b'_m = (b_m^{exp} - b_m^{(id)}) < 0$  or  $b_m^{exp} < b_m^{(id)}$ . The second compatibility criteria based on the difference between the experimental and the ideal values of  $[\eta]_m$ , therefore, it would be compatible if  $\Delta[\eta]_m = ([\eta]_m^{exp} - [\eta]_m^{id}) < 0$  and incompatible if  $\Delta[\eta]_m = ([\eta]_m^{exp} - [\eta]_m^{id}) > 0$ , where  $[\eta]_m^{exp}$  is determined from the intercept of the plots of eq. (1) and  $[\eta]_m^{id}$  can be calculated by using the mathematical derivations<sup>24</sup> which can be seen in the following equation:

$$[\eta]_m = [\eta]_2 w_2 + [\eta]_3 w_3 \quad (8)$$

The intrinsic viscosities as well as the viscometric interaction parameters for the different binary systems at 25°C are compiled in Table-1. From this table, it is observed that the PS or PDMS in different solvents have a negative value of  $b$  which makes it impossible to calculate the  $b_{23}$  according to eq. 3, so we can neglect this parameter if we use  $b_m^{(id)}$  criteria. The values of the intrinsic viscosity for PS or PDMS in THF is a better solvent for PS and PDMS, therefore, the polymer-solvent interaction THF is larger than in toluene or benzene, which lead to swelling of the polymer chains in solution and thus increases the intrinsic viscosity of the polymer solution. Fig. 1 shows the plots of the reduced viscosity  $h_{sp}/c$  vs.  $c$  for PS/PDMS blends with weight fractions of 0.0, 0.25, 0.50, 0.75 and 1.0 in benzene, toluene and THF, respectively at 25°C. All the plots are linear. On extrapolating  $h_{sp}/c$  vs. zero concentration, both  $[\eta]$  and the viscometric interaction parameter ( $b$ ), can be obtained for the ternary polymer system, which are tabulated in Table-2. The  $[\eta]$  values of PS in binary polymer solution are larger than  $[\eta]$  values of PS/PDMS ternary polymer solution at different weight fractions and in different solvent as shown in Table-2. A reasonable explanation is that the repulsive interactions between PS and PDMS in different solvents would increase the intermolecular excluded volume and the contraction of PS/PDMS coils in solvent and thus decrease the  $[\eta]$ .

TABLE-1  
VISCOSITY DATA FOR POLYSTYRENE AND POLYDIMETHYL  
SILOXANE IN DIFFERENT SOLVENTS AT 25°C

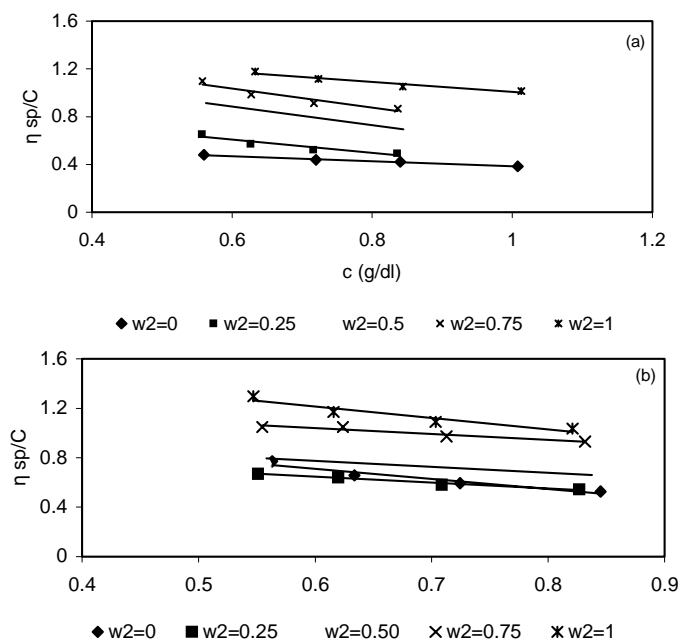
Solvent	$[\eta]$ (dL/g)	$b$ (dL/g) <sup>2</sup>	$[\eta]$ (dL/g)	$b$ (dL/g) <sup>2</sup>
	PS	PS	PDMS	PDMS
Benzene	1.43	-0.424	0.592	-0.206
Toluene	1.76	-0.918	1.200	-0.817
THF	1.84	-0.860	1.340	-0.781

The next step has considered of evaluating the magnitudes that make it possible to establish the degree of compatibility in the polymer mixture. The first criteria is  $\Delta b_m^{(id)}$  determined with values of  $b_m^{(id)}$  and  $b_m^{exp}$  which are tabulated in Table-2. Using eqs. 1-5, the second criteria is  $\Delta[\eta]_m$  evaluated through the difference between  $[\eta]_m^{exp}$  and  $[\eta]_m^{id}$  which are tabulated in Table-2. Fig. 2 shows the variation of a)  $\Delta b_m^{(id)}$  and b)  $\Delta[\eta]_m$  with different weight fractions of PS and PDMS mixtures in benzene, toluene and THF, respectively. The information about thermodynamic intermolecular interactions between polymer (2) and (3) should be obtained from comparison between experimental  $b_m^{exp}$  from eq. 1 and  $b_m^{(id)}$  values from eq. 5 by mean of a parameter  $\Delta b_m^{(id)}$ . Negative values of  $\Delta b_m^{(id)}$  are found for solutions of systems containing incompatible polymers, while positive ones indicate attractive interaction and compatibility. In the hypothetical case that

$\Delta b'_m = 0$ , it would signify that chains interact neither favourably nor unfavourably<sup>14,25-27</sup>. It can be seen from Fig. 2 that the same behaviour is obtained with the two criteria, within a certain degree, PS is completely compatible with PDMS in toluene in all composition ranges which PS incompatible with PDMS in THF and benzene in all composition ranges. The incompatibility between PS and PDMS in THF and benzene could be attributed to the strong repulsive intermolecular interactions between the polymer chains in THF and benzene, where all values of  $\Delta b'_m$  are negative and  $\Delta[\eta]_m$  are positive.

TABLE-2  
EXPERIMENTAL AND THEORETICAL VISCOMETRIC DATA  
FOR THE TERNARY MIXTURE PS/PDMS IN  
DIFFERENT SOLVENTS AT 25°C

Solvent	$W_2$	$[\eta]_m^{\text{exp}}$	$b_m^{\text{exp}}$	$[\eta]_m^{\text{id}}$	$b_m^{(\text{id})}$
Benzene	0.25	0.9466	-0.5651	0.8015	-0.1424
	0.50	1.3580	-0.7872	1.0110	-0.1575
	0.75	1.5130	-0.7984	1.2210	-0.2514
Toluene	0.25	0.9282	-0.4729	1.3400	-0.5170
	0.50	0.9902	-0.3605	1.4800	-0.4340
	0.75	1.3260	-0.4775	1.6200	-0.5670
THF	0.25	1.4550	-0.8180	1.4650	-0.4931
	0.50	1.6470	-0.8660	1.5900	-0.4103
	0.75	1.7800	-0.9680	1.7200	-0.5326



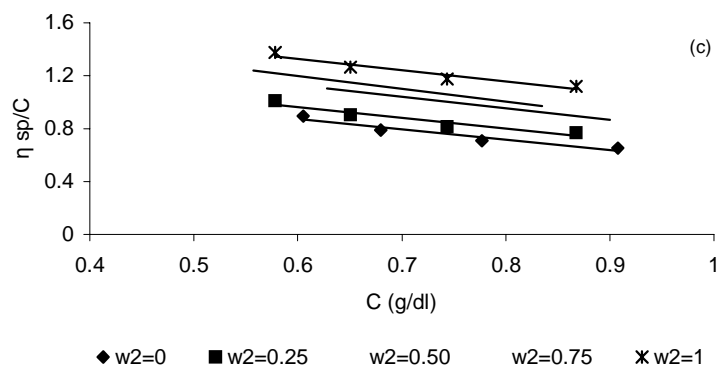


Fig. 1. Reduced viscosity dependence on polymer mixture concentration and Huggins Linearization at different weight fractions of PS for the ternary system (a) Benzene(1)/PS(2)/PDMS(3), (b) Toluene(1)/PS(2)/PDMS(3) and (c) THF(1)/PS(2)/PDMS(3) at 25°C

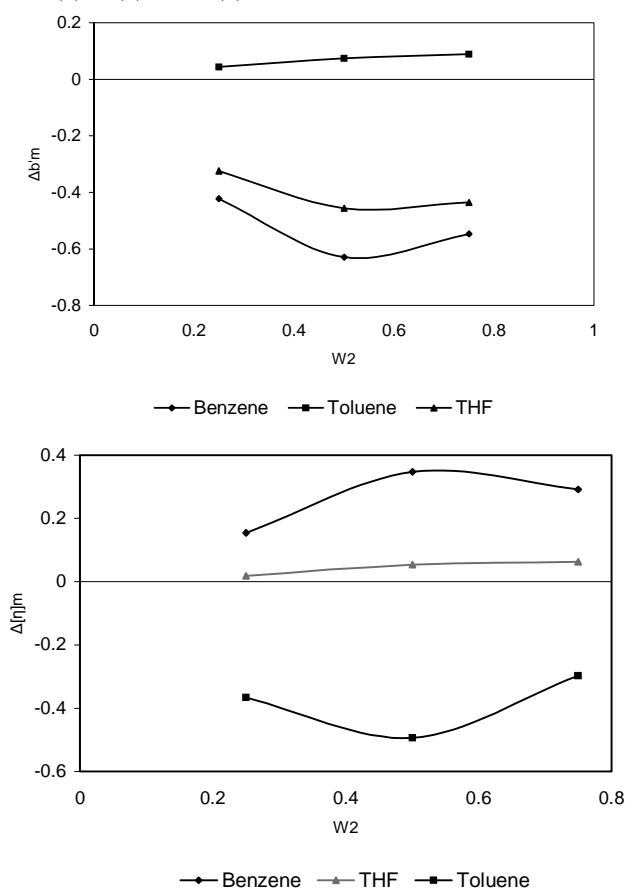


Fig. 2. Plots of different compatibility magnitude as a function of mixture composition for the polymer mixture in different solvents

## Conclusion

The intermolecular interaction between PS and PDMS in solution is greatly associated with the solvent from which PS/PDMS blends dissolved. In Toluene, the attractive intermolecular interaction between PS and PDMS existed; on the contrary, in either THF or benzene, the repulsive intermolecular interaction between PS and PDMS existed. These different intermolecular interactions can be used to interpret the phase behavior of PS/PDMS blends cast from different solvents.

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