A study on miscibility of polysulfone and polydimethylsiloxane mixtures by viscometry

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The miscibility behavior of the blends of polysulfone (PSf) and polydimethylsiloxane (PDMS) was studied in dilute 1,2-dichloroethane solutions at 25 ^{0}C. The intrinsic viscosity and Huggins' parameter of the binary mixtures were determined from the intercept and slope of the linear straight line between specific viscosity and the overall polymer concentration at the studied compositions. From experimental results of the intrinsic viscosities of the mixtures, some miscibility parameters Δb , $\Delta b'$, $\Delta b''$, $\Delta[\eta]$ and β were obtained by applying the criteria proposed by the research groups Krigbaum and Wall, Catsiff and Hewett, Garcia et al. and Jiang and Han, respectively. The miscibility of mixtures was also studied by using differential scanning calorimetry and fourier transform infrared spectroscopy.

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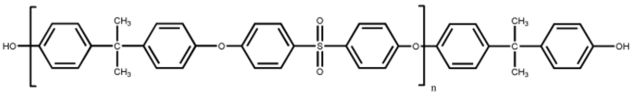
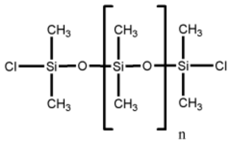
1. Introduction

Blending of polymers has given a new direction for developing novel materials. The mixing of structurally different polymers is more easier and economical way than synthesizing new copolymers. The manifestation of the superior properties of polymer blends depends upon the miscibility of its components at the molecular scale [1]. Thermodynamics and the study of phase separation in thin films of binary mixtures is important because most of the blend components are also highly incompatible with each other. The most commonly used techniques for investigation of polymer-polymer miscibility are thermal analysis [2-3], electron microscopy [4-5] and spectroscopy [6]. These techniques are very powerful for such applications, but they are somewhat expensive for most of the researchers. Therefore, other methods on investigation of polymer-polymer miscibility were proposed either using alternative properties or low cost equipment. Among them, viscometry is a very promising technique. Several works on polymer-polymer miscibility *via* viscometry have been investigated in recent years [7-14].

PSf is an amorphous thermoplastic high performance polymer has excellent chemical and thermal stability and exhibit superior mechanical properties. PSf has high glass transition temperature and has many usage areas eg. cookware appliance, electrical and electronic devices, plumbing uses, membrane technology, automotive and aerospace industry [15]. PDMS belongs to a group of polymeric organosilicon compounds that are commonly referred to as silicones [16]. PDMS is the most widely used silicon-based organic polymer, and is particularly known for its unusual properties. These include very low glass transtition temperatures (-123 ^{0}C), high thermal, UV and oxidative stability, low surface energy, hydrophobicity, high gas permeability, good electrical properties and physiological inertness or biocompability [17]. Its applications range from contact lenses and medical devices to elastomers; it is present, also, in shampoos (as dimethicone makes hair shiny and slippery), caulking, lubricating oils, and heat-resistant tiles. Their blends possess both good mechanical properties and the characteristics of silicone rubbers. Chemical structures of PSf and PDMS were given in Scheme 1.


(a)


(b)

Scheme 1. Chemical structure of PSf(a) and PDMS(b).

In this study, the miscibility of PSf and PMDS was evaluated by several techniques such as viscometry, differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). Viscometric analysis of polymer-polymer miscibility in dilute solution is based on the Huggins' equation which reflects the relationship between specific viscosity and polymer concentration.

2. Experimental

2.1. Theoretical background

For the ternary mixture of polymer (1), polymer (2) and a common solvent, at constant weight ratio of polymer 1 to 2 for a given composition, the well-known Huggins' equation is written as [18]

$$(\eta_{sp})_m / c_m = [\eta]_m + b_m c_m \tag{1}$$

where c, $(\eta_{sp})/c$, $[\eta]$ and b are concentration, reduced viscosity, intrinsic viscosity and viscometric interaction parameter of the polymer in the solution, respectively, while subscript "m" denotes "mixture".

Parameter b_m, which reflects the binary interactions between polymer segments is related to the Huggins' coefficient, k_H

$$b_m = k_H [\eta]^2 \tag{2}$$

The miscibility of the polymer (1) and (2) is estimated by comparison of the experimental and ideal values of b_m and $[\eta]_m$.

Krigbaum and Wall [19] have defined the ideal value of the interaction parameter b_m^{id} as

$$b_m^{id} = b_{11}w_1^2 + b_{22}w_2^2 + 2b_{12}^{id}w_1w_2 \tag{3}$$

and the b_{12}^{id} as a geometric mean;

$$b_{12}^{id} = b_{11}^{1/2}b_{22}^{1/2} \tag{4}$$

Catsiff and Hewett [20] have defined the ideal value of the interaction parameter $b_{12}^{id'}$ as an arithmetic mean

$$b_{12}^{id'} = (b_{11} + b_{22})/2 \tag{5}$$

On the other hand, Garcia et al. [21] have stated that the Eq.(3) proposed by Krigbaum and Wall was mathematically erroneous and have defined the ideal value of the interaction parameter $b_{12}^{id''}$ as

$$b_{12}^{id''} = b_1w_1^2 + b_2w_2^2 \tag{6}$$

Furthermore, Garcia et al. have also proposed another miscibility criterion based on the difference between the experimental and ideal values of $[\eta]_m$ assuming that the intrinsic viscosity can be treated as an excess property. The value of $[\eta]_m^{id}$ has defined as

$$[\eta]_m^{id} = [\eta]_1 w_1 + [\eta]_2 w_2 \tag{7}$$

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities of corresponding polymers.

Jiang and Han [22] have proposed another miscibility criterion, β for polymer-polymer miscibility defined as

$$\beta = \frac{2w_1w_2[\eta]_1[\eta]_2}{(w_1[\eta]_1 + w_2[\eta]_2)^2}\Delta k \tag{8}$$

Where

$$\Delta k = k_{12} - \sqrt{k_1k_2}\ ;\ k_1 = b_1/[\eta]_1^2\ ;\ k_2 = b_2/[\eta]_2^2\ ;$$

$$k_{12} = b_{12}/[\eta]_1[\eta]_2 \tag{9}$$

2.2. Materials and instrumentation

Methanol (Besa Chemistry) was technical grade and distilled before use, N-methyl pyrrolidone (NMP) (Riedel-de Haen), chloroform (Merck KGaA) and toluene (Riedel-de Haen) were reagent grade and used without further purification. 4,4'-Dichlorodiphenyl sulfone (DCDPS) (Merck KGaA) and 2,2-Bis(4-hydroxyphenyl)propane (Bisphenol A) (Merck KGaA) were recrystallized from toluen and dried in vacuo overnight before use. Potassium carbonate (K_2CO_3) (Fluka) was grinded to fine powder and dried in a vacuum oven at 80 ^{0}C for 8 h before the polymerization.

PDMS ($\rho = 0.99$ g.cm^{-3}) were provided by ABCR GmbH. and used without further purification, Bisphenol A based PSf ($\rho = 1.24$ g.cm^{-3}) was synthesized according to the procedure given in the next section.

The number average molecular weights of the polymers were determined as 3250 and 8350 gmol^{-1} for PDMS and PSf, respectively, by gel permeation chromatography. GPC measurements were performed with an Agilent model 1100 instrument consisting of a pump and refractive-index and UV detectors and three Waters Styragel columns (HR4, HR3, and HR2). DSC measurements were performed on about 5 mg samples with a Perkin Elmer Pyris DSC 6 Series. The DSC curves were recorded at a heating or cooling rate of 10 ^{0}C min^{-1} in two scans between 123 and 523 K. The second scans were reported in the paper.

FTIR spectra were collected using a Perkin Elmer Spectrum One FTIR spectrometer with a diamond micro-ATR accessory. The individual polymer samples were placed onto the ATR crystal and the anvil was hand-tightened to apply pressure. FTIR spectra of 8 scans at 4 cm^{-1} resolution were added and averaged to obtain the single-beam background and sample spectra.

All viscosity measurements were performed at 25 ^{0}C using an Ubbelohde-type capillary viscometer in a constant temperature bath controlled with ± 0.02 ^{0}C by a Huber type electronically controlled thermostat. For each measurement, 5 cm^3 stock solution was loaded into the viscosimeter and diluted by adding 2 cm^3 1,2-dichloroethane to yield five lower concentrations. The elution time of each solution was taken as an average of five readings agreed to within ± 0.5%.

2.2.1. Synthesis bisphenol A based PSf

Accurately weighed 12.5560 g (0.055 mol) Bisphenol A and 14.3585 g (0.050 mol) DCDPS and were added to 500 mL 3-neck flask. 11.4023 g (0.0825 mol) K_2CO_3 used to generate *in situ* phenoxide ion of Bisphenol A. The flask walls were rinsed with 100 mL NMP and 60 mL toluene was applied to remove the water by azeotropic distillation. The reaction mixture was stirred at 300 rpm rate with constant purge of dried argon and heated to reflux under Dean-Stark apparatus. It is maintained at reflux till no more water droplet is observed for 5 hours. While toluene was being removed *via* Dean-Stark apparatus, the reaction temperature increased to 155 ^{0}C. The reaction mixture became yellow color and temperature was raised slowly to 190 ^{0}C by controlled removal of toluene. Polymerization has been maintained for 24 hours, after this period flask content was cooled to room temperature and the viscous solution was diluted with 50 mL NMP in order to remove salts *via* filtration. Then, the solution was precipitated in a methanol/water mixture (10:1, vol:vol). After the separation by filtration, the polymer was reprecipitated in the above mixture and finally dried in a vacuum oven at 50 ^{0}C for 8 h.

2.2.2. Preparation of PSf-PDMS blends

Stock solutions of the binary and ternary PSf-PDMS blend systems were freshly prepared by dissolving appropriate amount of polymers in 1,2-dichloroethane into a concentration of 0.500 g/25 cm^3 solutions.

3. Results and discussion

Reduced viscosities in different compositions of PSf/PDMS: 0/100, 20/80, 40/60, 60/40, 80/20 and 100/0 were measured at 25 ^{0}C. Fig. 1 shows the Huggins' plots for the pure components and their blends at 25 ^{0}C. The linear relationships were observed for the polymers and their blends studied.

The values of $b_m^{\exp}$ and $[\eta]_m^{\exp}$ are determined from the slope and intercept of the linear straight line plotted according to Eq.(1) for solutions containing one of the polymer in binary mixtures or both of them at a given ratio in ternary mixtures. The data were collected in Table 1.

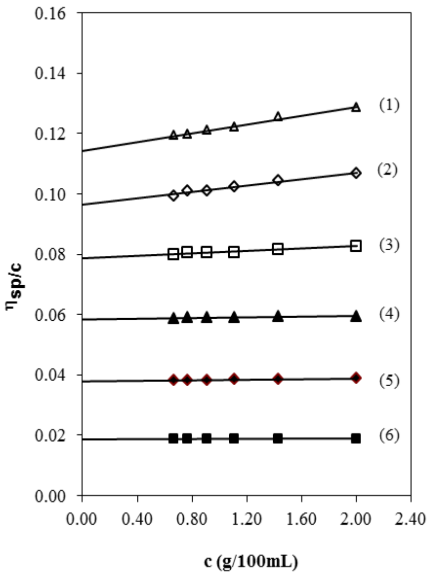


Fig. 1. Reduced viscosity values (η_{sp}/c)against total concentrations of the pure polymers of PSf, PDMS and their mixtures at 25 ^{0}C in 1,2-dichloroethane at the compositions of PSf/PDMS: 100/0 (1), 80/20 (2), 60/40 (3), 40/60 (4), 20/80 (5) and 0/100 (6) by weight.

Table 1. Experimental dilute solution viscosity data of the blends and constituent polymers at 25 ^{o}C in 1,2-dichloroethane.

PSf/PDMS 25 ^{o}C in 1,2-dichloroethane	$b_m^{\exp}$ (cm^6/g^2)	$[\eta]_m^{\exp}$ (cm^3/g)	r^2
100/0	0.0073	0.1144	0.9801
80/20	0.0052	0.0965	0.9734
60/40	0.0019	0.0787	0.9862
40/60	0.0006	0.0585	0.9533
20/80	0.0004	0.0380	0.9293
0/100	0.0002	0.0185	0.9275

According to the miscibility criterion Δb was described by Krigbaum and Wall, the polymer blend is miscible if $\Delta b = b_m^{\exp} - b_m^{id} > 0$ and attractive molecular interactions are present or immiscible if $\Delta b = b_m^{\exp} - b_m^{id} < 0$ and repulsive molecular interactions are considered. In the case of $\Delta b = 0$, neither attractive nor repulsive molecular interactions are present between components of the polymer blend. The other miscibility criterion of a blend, $\Delta b'$ was found from Eq.(5). Catsiff and Hewett were proposed that $\Delta b' > 0$ shows miscibility and $\Delta b' < 0$ shows immiscibility. The miscibility criterion on $\Delta b''$ and $\Delta[\eta]$ were described by Garcia et al. and found from Eqs. (6) and (7), respectively. According to Garcia et. al, if $\Delta b'' = b_m^{\exp} - (b_m^{id})'' > 0$ and $\Delta[\eta] = ([\eta]_m^{\exp} - [\eta]_m^{id}) < 0$ the system is miscible, and if $\Delta b'' = b_m^{\exp} - (b_m^{id})'' < 0$ and $\Delta[\eta] = ([\eta]_m^{\exp} - [\eta]_m^{id}) > 0$, the system is immiscible. Jiang and Han were described the parameter β as a new miscibility criterion that is, $\beta > 0$ if attractive intermolecular interactions and miscibility exist whereas $\beta < 0$ if the repulsive intermolecular interactions and immiscibility exist between polymers in the mixture.

All miscibility criteria of PSf/PDMS blends obtained using viscosity measurements were given in Table 2. According to the signs ($\Delta b < 0$, $\Delta b' < 0$, $\Delta b'' < 0$, $\Delta[\eta] > 0$ and $\beta < 0$) PSf/PDMS blends are immiscible at studied compositions**.** The magnitudes of the parameters are close to zero which implies the absence of any interactions between the components of the blend. However, the change of the magnitude of the parameter β with composition is totally different than others. It can be seen from the Table 3 the magnitude of the β decreases gradually with increasing PDMS content although other parameters do not present any meaningful variation.

The decrease of β suggests the blend is becoming more immiscible with increasing PDMS content. No studies are encountered in literature on determination of miscibility of PSf and PDMS blends. However, the microphase separation of some block copolymers of PSf and PDMS were studied by their T_g measurements earlier [23-25]. It was observed very low molar mass oligomers produce single-phase PSf-PDMS block copolymers while higher molar mass oligomers ($M_n \geq 5000$ g/mol) give two phase systems [23]. In another study, it was reported the block copolymers of PSf and PDMS are immiscible and undergo microphase separation if the molar masses of blocks are higher than 5000 and 3000 g/mol for PSf and PDMS, respectively [24]. Hamcuic et al revealed also two T_gs were obtained only for the block containing higher molar mass PDMS-blocks (M_n > 6500 g/mol) indicating immiscibility with increasing PDMS content [25]. Thus, it can be expected the PSf/PDMS blends should be more immiscible with increasing PDMS content. Therefore, it is obvious the values of parameter β are in agreement with literature data of PSf-PDMS block copolymers

Table 2. Numerical values of polymer-polymer interaction coefficient for PSf/PDMS blends.

PSf/PDMS at 25 °C in 1,2-dichloroethane	Δb (cm^6/g^2)	$\Delta b'$ (cm^6/g^2)	$\Delta b''$ (cm^6/g^2)	$\Delta[\eta]$ (cm^3/g)	$-\beta$
80/20	0.000	-0.001	0.001	0.001	0.001
60/40	-0.001	-0.003	-0.001	0.003	0.046
40/60	-0.001	-0.002	-0.001	0.002	0.124
20/80	0.000	-0.001	0.000	0.000	0.140

The FTIR/ATR spectra of PSf, PDMS and their blends in the compositions of 80/20, 60/40, 40/60, 20/80 were presented in Fig. 2. As can be seen from Fig. 2, the typical peaks of FTIR/ATR spectra of the films are centered at aromatic C-H stretching vibration ($\nu_{C\text{-}H}$) at 3070 cm^{-1}, aromatic C=C stretching ($\nu_{C=C}$) at 1584 cm^{-1}, 1503 cm-1 and 1487 cm^{-1} for PSf and Si-O-Si band (broad) at 1020-1090 cm^{-1} ($\nu_{Si\text{-}O\text{-}Si}$), and 798 cm^{-1} ($\nu_{Si\text{-}CH3}$) for PDMS.

It is useful to detect the changes in aromatic regions absorption bands of PSf in order to determine composition of blends. It can be easily observed that transmission values of aromatic regions absorption bands of PSf decreased linearly and transmission values of absorption bands of PDMS increased progressively with increasing of ratio of PDMS in blends. However, no significant changes in its FTIR spectra were observed with the all studied blends in comparison with the pure PSf and PDMS.

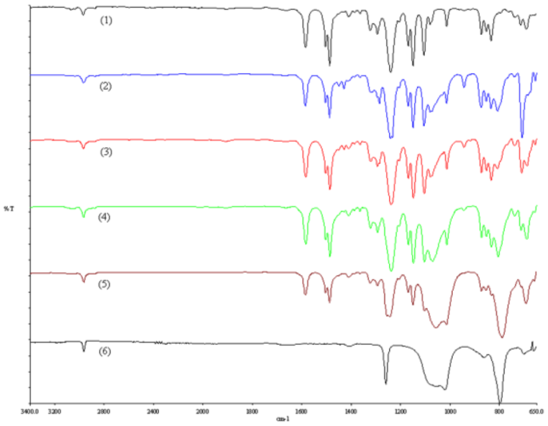


Fig. 2. FTIR/ATR spectras of PSf/PDMS (100/0) (1), PSf/PDMS (80/20) (2), PSf/PDMS (60/40) (3), PSf/PDMS (40/60) (4), PSf/PDMS (20/80) (5) and PSf/PDMS (0/100) (6).

The T_gs of the blends were determined from the cast films by means of DSC. Triple T_g values were found for PSf/PDMS blends. PSf (T_g =155) and PDMS (T_g = -122) have very distinct T_g values polymers and according to DSC results, different mixture ratio having blends of these polymers shows a third different T_g value. Thermograms of PSf/PDMS blends indicate that blends contain three different zone first one is PDMS rich domain, second one is miscible zone and third one is PSf rich domain. These results indicate partial miscibility of PSf/PDMS blends. It means that there are no attractive or repulsive forces between the components of the blend.

Table 3. Glass transition temperatures of PSf, PDMS and their blends in the compositions of 80/20, 60/40, 40/60 and 20/80.

Blends	**T_g (^{0}C)**		
PSf/PDMS	**1. PDMS Rich Domain**	**2. Miscible Zone**	**3. PSf Rich Domain**
100/0	-	-	155
80/20	-66	94	146
60/40	-81	84	131
40/60	-94	73	123
20/80	-112	65	114
0/100	-122	-	-

4. Conclusions

The miscibility of PSf/PDMS blends was investigated by viscometry, FTIR and DSC. The triple T_gs of the blends indicate the components of the blend are partially miscible in the solid state at the studied compositions. According to the obtained values of miscibility criteria proposed by Krigbaum and Wall (Δb), Catsiff and Hewett ($\Delta b'$), Garcia et al., ($\Delta b''$ and $\Delta[\eta]$) there are neither attractive nor repulsive interaction between the polymeric components of the blend in 1,2-dichloroethane solution. The values of miscibility criterion proposed by Jiang et al. (β), indicates immiscibility increasing with PDMS content. This result is in agreement with literature [23-25]. DSC and FTIR measurements do not indicate attractive interaction between components, also. In conclusion, it can be stated viscometry is a reasonable method to obtain quantitative data in determination of miscibility of polymer blends and the criterion β reflects the degree of miscibility or immiscibility better than other criteria at least in this study.

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