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Miscibility of polysulfone and poly(ether sulfone) with tertiary amide polymers

S. H. Goh*, S. Y. Lee, H. W. Goh, Xiping Ni

Department of Chemistry, National University of Singapore, Singapore 119260,
Republic of Singapore

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Summary

The miscibility of polysulfone (PSf) and poly(ether sulfone) (PES) with three tertiary amide polymers has been studied. PES is miscible with poly(*N*-methyl-*N*-vinylacetamide) (PMVAc) and with poly(*N*,*N*-dimethylacrylamide) (PDMA) but not with poly(2-methyl-2-oxazoline) (PMOx). Miscible PES/PDMA blends show lower critical solution temperature behavior. However, PSf is immiscible with all the three tertiary amide polymers. Previous studies have shown that both PES and PSf are miscible with poly(*N*-vinyl-2-pyrrolidone). PES is also miscible with poly(2-ethyl-2-oxazoline) but PSf is not. Therefore, PES is more readily miscible with tertiary amide polymers as compared to PSf.

Introduction

Sulfone polymers such as polysulfone (PSf) and poly(ether sulfone) (PES) are strong, rigid and tough materials with excellent dimensional stability. There has been considerable interest in the miscibility of blends of sulfone polymers. PES is miscible with several other polymers such as poly(ethylene oxide) (PEO) (1,2), poly(hydroxyether of bisphenol-A) (phenoxy) (3,4), poly(hydroxyether of phenolphthalein) (5), poly(ether ether ketone) (6,7), aramide (8,9) and polyimide (10-12). PSf is miscible with PEO of low molecular weight but it is immiscible with phenoxy (13).

It is of interest to note that both PES and PSf are miscible with poly(*N*-vinyl-2-pyrrolidone) (PVP), a tertiary amide polymer (14,15). However, PES is miscible with another tertiary amide polymer poly(2-ethyl-2-oxazoline) (PEOx) but PSf is not (16,17). Our recent studies have shown that among the tertiary amide polymers, PVP exhibits the best miscibility with other polymers (18-21). In this communication, we report the miscibility of PES and PSf with three other tertiary amide polymers, namely, poly(*N*-methyl-*N*-vinylacetamide) (PMVAc), poly(*N*,*N*-dimethylacrylamide) (PDMA) and poly(2-methyl-2-oxazoline) (PMOx).

$-C_6H_4-SO_2-C_6H_4-O-$ (PES) $-C_6H_4-C(CH_3)_2-C_6H_4-O-C_6H_4-SO_2-C_6H_4-O-$ (PSf)

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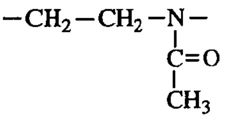
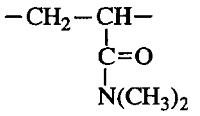
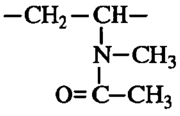
* Corresponding author


$-CH_2-CH_2-N(C(=O)CH_3)-$

PMOx


$-CH_2-CH(C(=O)N(CH_3)_2)-$

PDMA


$-CH_2-CH(N(CH_3)C(=O)CH_3)-$

PMVAc

Experimental

Materials

PES (high molecular weight grade) and PSf (reported molecular weight = 50 kg/mol) were obtained from Aldrich. PDMA (M_n = 12 kg/mol and M_w = 20 kg/mol) and PMVAc (M_n = 3.3 kg/mol and M_w = 3.7 kg/mol) were prepared by free radical polymerization as reported previously (18,19). PMOx (M_n = 12 kg/mol and M_w = 19 kg/mol) was prepared by ring-opening polymerization as described before (21).

Preparation of blends

Various binary blends were prepared by solution casting from *N*,*N*-dimethylformamide (DMF). Initial removal of DMF was done on a hot-plate at 90°C. The blends were then dried *in vacuo* at 100°C for two weeks. All the miscible blends were examined for the existence of lower critical solution temperature (LCST) behavior using the method described previously (22).

Tg measurements

The glass transition temperatures (T_gs) of various samples were measured with either a TA Instruments 2920 or a Perkin-Elmer DSC-4 differential scanning calorimeter using a heating rate of 20°C/min. Each sample was subjected to several heating/cooling cycles to obtain reproducible T_g values. The initial onset of the change of slope in the DSC curve is taken to be the T_g.

FTIR measurements

Samples for Fourier-transform infrared (FTIR) measurements were prepared by casting the DMF solution onto KBr discs and then dried *in vacuo* at 100°C for 2 weeks. Spectra were acquired on a Bio-Rad FTS-16 spectrophotometer at a resolution of 2 cm^{-1}. In view of the hygroscopic nature of these tertiary amide polymers, spectra were recorded at 120°C using a SPECAC high-temperature cell.

Results and Discussion

All the PES/PMVAc blends were transparent. Each of the blends showed a composition-dependent T_g. The optical clarity and the existence of a single T_g show that PES is miscible with PMVAc over the entire composition range. The miscible blends did not show phase separation upon heating to 300°C, the highest temperature attained by the apparatus. The T_g-composition curve as shown in Figure 1 can be fitted by the Gordon-Taylor equation

$$T_g(\text{blend}) = (w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2)$$

where w_i and T_{gi} are the weight fraction and T_g of component i in the blend, respectively, and k is an adjustable constant. The curve in Figure 1 is fitted with a k value of 0.42.

All the PES/PDMA blends were also transparent and each of them showed a composition-dependent T_g. Therefore, PES is also miscible with PDMA. However, all the miscible PES/PDMA blends became phase-separated upon heating, showing LCST behavior. The T_g-composition curve and the cloud point curve are shown in Figure 2. The T_g-composition curve of the blends can also be fitted by the Gordon-Taylor equation using a k value of 0.48.

In contrast, all the PES/PMOx blends were opaque, indicating the heterogeneous nature of the blends. Furthermore, DSC measurements showed the existence of two T_gs in each blend with values close to those of PES and PMOx. Thus PES is immiscible with PMOx.

On the other hand, all the binary blends of PSf with PMVAc, PDMA or PMOx were opaque. Each of the blends was found to exhibit two T_gs with values close to those of PSf and the tertiary amide polymer. It is evident that PSf is immiscible with the three tertiary amide polymers. The miscibility behavior of various blends is summarized in Table 1.

Table 1. Miscibility of sulfone polymer blends

	PES	PSf
PVP	Miscible (ref 14)	Miscible (ref 15)
PMVAc	Miscible	Immiscible
PDMA	Miscible (L)	Immiscible
PEOx	Miscible (L) (ref 16)	Immiscible (ref 17)
PMOx	Immiscible	Immiscible

L: blends showing LCST behavior

Several conclusions can be drawn from the results. Firstly, PES is more readily miscible with tertiary amide polymers than PSf does. PES is miscible with four of the five tertiary amide polymers but PSf is only miscible with PVP. The presence of the bisphenol-A unit in the PSf segment apparently reduces the ability of PSf to interact with other polymers. Secondly, PVP is more readily miscible with sulfone polymers as compared to the other tertiary amide polymers. This is consistent with our recent studies on the miscibility and complexation ability of tertiary amide polymers (18-21). Thirdly, the presence of LCST behavior in PES/PDMA and PES/PEOx blends indicates at least qualitatively that PDMA and PEOx interact less strongly with PES as compared to PVP and PMVAc. This is also in agreement with our previous findings that PVP and PMVAc are able to interact more strongly with hydroxyl-containing polymers than PDMA and PEOx do (18-21). We have attributed the better miscibility and complexation ability of PVP and PMVAc to the greater accessibility of their amide carbonyl groups (20). The carbonyl groups of PVP and PMVAc are two bond-lengths away from the main chain while those of PDMA, PEOx and PMOx are only one bond-length away from the polymer chain. Fourthly, it is noted that PEOx but not

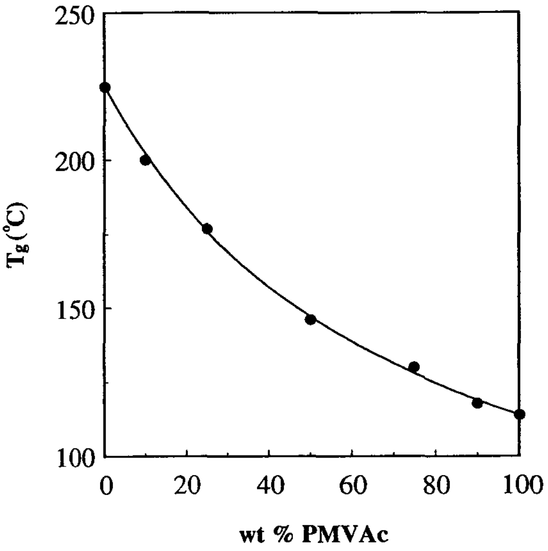


Figure 1. T_g-composition curve of PES/PMVAc blends.

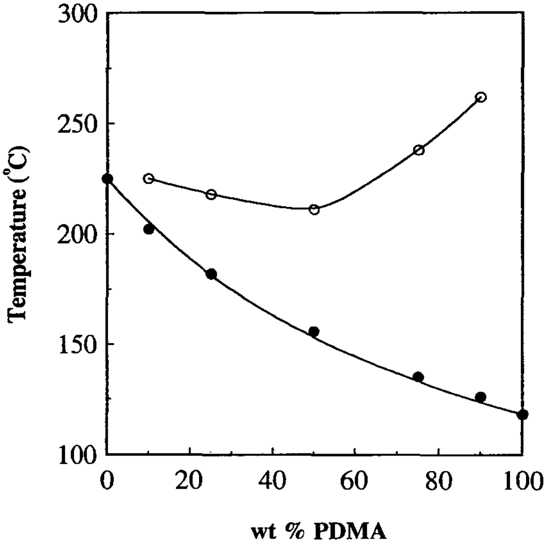


Figure 2. T_g-composition curve (●) and cloud point curve (○) of PES/PDMA blends.

PMOx is miscible with PES. Our recent study has shown that PEOx interacts more strongly with phenoxy than PMOx does, but PMOx interacts more strongly with poly(p-vinylphenol) and with poly(2-hydroxypropyl methacrylate) than PEOx does (21). Therefore, the pendant ethyl group of PEOx does not always pose a greater steric hindrance to intermolecular interaction as compared to PMOx.

It has been suggested that the intermolecular interactions in miscible PES blends are weak (10,11,14). FTIR studies on PES/PEO blends showed the involvement of sulfone and ether groups of PES in intermolecular interactions with the terminal hydroxyl groups of PEO (2). We have also made FTIR measurements on miscible PES/PDMA and PES/PMVAc blends. In miscible blends of tertiary amide polymers, the amide carbonyl bands show a low-frequency shift or develop a shoulder at a lower frequency (18-21). However, in the miscible PES/PDMA and PES/PMVAc blends, there are no significant shifts of the amide carbonyl bands, indicating that the interactions between tertiary amide polymers and PES are rather weak. The changes in the sulfone and ether bands of PES are also difficult to detect. The FTIR spectra of PES/PDMA blends are shown in Figure 3 as an illustration. The sulfone band is at 1152 cm^{-1} while the two ether bands are at 1242 and 1106 cm^{-1}. Only when the blend contains a high PDMA content do these bands show a slight shift. The present work supports the earlier suggestion that intermolecular interactions in PES blends are weak.

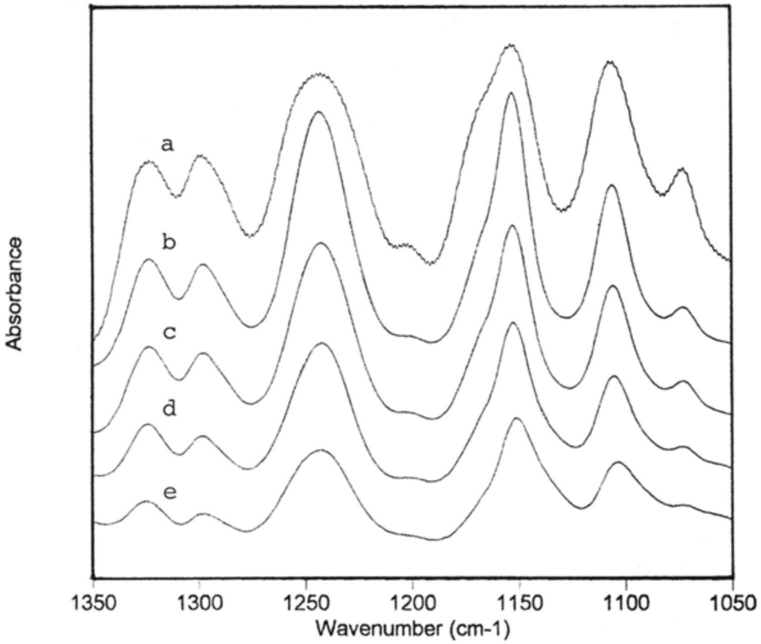


Figure 3. FTIR spectra of PES/PDMA blends. (a) PES; (b) 10% PDMA; (c) 25% PDMA; (d) 50% PDMA and (e) 75% PDMA.

In conclusion, PES is miscible with PMVAc and PDMA, and the miscible PES/PDMA blends show LCST behavior. PES is immiscible with PMOx; PSf is immiscible with PMVAc, PDMA and PMOx. Intermolecular interactions between sulfone polymers and tertiary amide polymers are weak.

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