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Miscibility Behaviour of Blends of a Thermoplastic Polyester Polyurethane with Vinyl Polymers

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SUMMARY: A method based on the intrinsic viscosities of transfer has been used to predict miscibility of polymer blends. This method has been applied to study the change in the phase behaviour of a microphase separated polyester polyurethane (PSPU) on blending with polyvinyl chloride (PVC), polyvinyl acetate (PVAc) and a vinyl chloride-vinyl acetate copolymer (VCVAc). The PVC/PSPU blends are found to exhibit complete miscibility over the entire composition range. PVAc/PSPU blends show immiscibility while VCVAc/PSPU blends show partial miscibility. Thermal analysis and scanning electron microscopic studies of the blend films have confirmed the results evaluated on the basis of the viscosity method.

Introduction

Viscometric methods have frequently been employed in the investigation of polymer-polymer miscibility[1-3]. Dilute Solution Viscometry (DSV) is concerned with accurate quantitative measurement of the increase in viscosity and allows determination of the intrinsic ability of a polymer to increase the viscosity of a particular solvent at a given temperature. Recently, a simple viscometric method has been proposed to predict the miscibility in polymer blends[4,5]. This method is applicable to ternary systems comprising of solvent S and polymers 2 and 3. The solvent S is the pure solvent for polymers 2 and 3. In this method, the intrinsic viscosity of polymer 2 is determined separately in a pure solvent ($[\eta]^{\circ}$) and also in a "mixed" solvent ($[\eta]^{*}$). The "mixed" solvent contains a fixed concentration of polymer 3 in solvent S. The

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difference, $[\eta]^* - [\eta]^\circ = \Delta[\eta]$, the intrinsic viscosity of transfer, gives a measure of the interaction between polymers 2 and 3 in solvent S. Depending on the strength of the interaction, the magnitude of $\Delta[\eta]$ varies. Hence, $\Delta[\eta] < 0.1$ dl/g, suggests very little or no interaction and hence immiscible blends. A high positive value of $\Delta[\eta]$ i.e. ≥ 0.1 dl/g, indicates an increase in the hydrodynamic volume due to strong associative interactions and hence miscible blends.

Thermoplastic polyurethanes are segmented, multiblock copolymers characterised by a limited miscibility between the short, hard polyurethane segments and the alternating long and flexible polyether and polyester segments6,7). The hydrogen bonding interactions between the diisocyanate blocks and diol extenders give these materials high modulii at the use temperatures, making them commercially important materials. Literature offers diverse results concerning the miscibility behaviour of blends of these thermoplastic polyurethanes (TPU) with other polymers8-10). This is mainly due to the different synthetic variations possible in the thermoplastic polyurethanes.

We report here, the change in phase behaviour of a microphase separated polyester polyurethane (PSPU) on blending with polyvinylchloride (PVC), polyvinyl acetate (PVAc) and a vinyl chloride - vinyl acetate copolymer (VCVAc) using the dilute solution viscometric technique. Thermal analysis and Scanning Electron Microscopy have been used as complementary techniques in determining the phase behaviour of the blends.

Experimental

Polymers

The characteristics of the polymer samples used in the present work are listed in Table 1. The chemical structure of the polyester polyurethane was elucidated by ^1H and ^{13}C – NMR spectra recorded on a 300 MHz Varian NMR Spectrometer in deuterated chloroform. The hard segments comprised of 4,4' – diphenylmethane diisocyanate (MDI) with 1,4-butane diol as chain extender while polyethylene adipate served as the soft segments. The VCVAc copolymer is a random copolymer containing 13 % vinyl acetate.

Table 1. : Characteristics of Polymer samples used

Polymer	Source	M_n
PVC	NOCIL, India	46,000
PVAc	BDH, England	65,000
VCVAc	Aldrich , USA	46,000
PSPU	Quimal Int., USA	31,000

Preparation of Blend Films

Films were cast on teflon - coated aluminium plates from 5% (w/v) solutions of the polymers in tetrahydrofuran (THF) as solvent. Five different compositions of the blend films were made and dried under vacuum at 60°C for 3 weeks.

Dilute Solution Viscometry Measurements

2% (w/v) solutions of each polymer in THF were prepared. Polymer blend solutions having 10, 30, 50, 70 and 90% PSPU were made, keeping the total blend concentration constant for all systems. A "mixed" solvent containing 0.5 g/dl PSPU in THF was prepared. Viscosity measurements were made on a Schott Gerate AVS 400 instrument using a suspended – level Ubbelohde capillary viscometer at 30° ± 0.05°C. Plots of reduced viscosities versus weight fractions of one of the polymers were made. Intrinsic viscosities of polymers in pure and "mixed" solvents ($[\eta]^{\circ}$ and $[\eta]^{*}$), and $\Delta[\eta]$ were estimated.

Thermal Analysis Measurements

The glass transition temperatures of homopolymers and blends were measured on a Mettler DSC instrument calibrated using an Indium standard. 5-7 mg of each sample was sealed in an aluminium pan and scanned over a temperature range of – 100° to + 150°C, at a heating rate of 10°C / min. An inert nitrogen atmosphere was maintained throughout the DSC run. The low temperature T_g was measured by cooling the DSC cell with liquid nitrogen to –100°C. The T_g value was taken as the step transition value which is obtained as the inflexion point of the slope change in heat flow (in mW) versus temperature (in °C). The measurements were repeated after a couple of months and were found to be reproducible. Thus the kinetic effect seems negligible.

The thermal stability of the polymers and blends was studied on a DuPont 9900 Thermal Analyser. The T_{50} values indicating the temperature at 50% weight loss of the samples were taken as an index of thermal stability.

Scanning Electron Microscopic Studies

The phase behaviour of the samples was examined on a JEOL JSM 6400 scanning electron microscope. The samples were cryogenically fractured and sputtered with a gold-palladium alloy using an EMSCOPE SC 500 sputter coater. The sputtered samples were then studied at different accelerating voltages and different magnifications.

Results and Discussion

Intrinsic Viscosities of Transfer

Figures 1, 2 and 3 depict the change in reduced viscosities versus concentration for all blends in pure and "mixed" solvents. Table 2 lists the values of $[\eta]^{\circ}$, $[\eta]^{*}$ and $\Delta[\eta]$ for the blends. In pure solvent, the reduced viscosity of PVC increases linearly with concentration. Addition of a small amount (0.05g) of PVC to the "mixed" solvent (PSPU + THF) leads to an appreciable increase in viscosity. The intrinsic viscosity in the "mixed" solvent is drastically higher than that in the pure solvent giving $\Delta[\eta] = 0.21$ dl/g. Such a large increase in the intrinsic viscosity is directly dependent on the structure and conformation of polymer molecules in solution and is a measure of the effective hydrodynamic specific volume of the polymer. Thus, a high positive value of $\Delta[\eta]$ implies strong attractive interactions between PVC and PSPU chains indicating miscibility on the basis of the proposed method.

Table 2 : Intrinsic Viscosities for different blend systems at 30°C.

Blend System	$[\eta]^\circ$ dl/g	$[\eta]^*$ dl/g	$\Delta[\eta]$ dl/g
PVC/PSPU	0.55	0.76	0.21
PVAc/PSPU	0.19	0.26	0.07
VCVAc/PSPU	0.24	0.29	0.05

In case of PVAc/PSPU blends, at very low concentrations of PVAc, there is an increase in the reduced viscosity of the “mixed” solvent. But, as the concentration of PVAc increases, the viscosity decreases steadily, possibly due to the contraction of macromolecular coils. A similar trend is observed for the VCVAc/PSPU blends. The values of $\Delta[\eta]$ for these systems being less than 0.1 dl/g, these can be regarded as immiscible systems.

Thermal Analysis Studies

All blend films of PSPU with PVC and VCVAc, cast from THF, are transparent and optically clear. The DSC and TGA data for these blends are given in Table 3. The PVC/PSPU blends show only one T_g over the entire composition range. The T_g increases steadily as concentration of PVC in the blend increases. Thus, the presence of a single, composition – dependent T_g, indicates complete miscibility for the PVC/PSPU blends. This is contrary to Piglowski et al’s8) results which predicted immiscibility for a similar system. Blends of PVC with poly(ethylene adipate) were found to exhibit two T_g’s9). Later, Woo et al10) concluded miscibility based on the heat of mixing data of PVC – polyester blends.

Table 3. : DSC and TGA data for PVC/PSPU blends and VCVAc/PSPU Blends

PSPU	PVC/PSPU		VCVAc/PSPU	
% wt.	T_g°C	T_{50} °C	T_g °C	T_{50} °C
0	78	335	60	302
10	53	290	63	300
30	38	332	30	336
50	24	385	18, 75	395
70	02	403	-5, 75	401
90	-14	403	- 19	405
100	-20	405	- 20	405

The VCVAc/PSPU blends show partial miscibility on the basis of DSC studies. Blends having low VCVAc content (upto 50%) show the presence of two T_g's. However, the T_g due to the polyester segments increases steadily as the VCVAc content of the blends increases, and finally blends containing more than 70% VCVAc show only a single T_g. The increase in the T_g of the polyester segments indicates that the local environment of these blocks is altered due to some positive interactions with VCVAc.

The thermal stability of PVC and VCVAc is increased by incorporation of PSPU. Thus, PSPU acts as a heat stabiliser for PVC and VCVAc. All blend films of PVAc/PSPU system show phase separation in THF and hence are regarded as immiscible systems.

Scanning Electron Microscopy Studies

The polyester polyurethane shows an interesting microphase separated structure at 15 kV and 1000X magnification. Microphase separation is clearly visible even though no staining is used. The micrograph reveals a continuous polyester matrix in which the hard PU segments are dispersed (plate 1).

Incorporation of a small amount (30%) of PVC in PSPU leads to an ordered, one – phase, lamellar structure with fibrils perpendicular to these lamellae (plate 2). This ordered structure is suggestive of good mixing of the PVC and PSPU chains at molecular level indicative of miscibility by SEM studies.

PVAc/PSPU blend shows gross phase – separation and hence immiscibility (plate 3). VCVAc/PSPU blend also reveals a highly ordered, lamellar structure suggesting miscibility for this composition (plate 4).

Conclusions

The approach of intrinsic viscosities of transfer accurately predicts miscibility for the PVC/PSPU blends giving a high $\Delta[\eta]$ value. This is further confirmed by the single composition – dependent T_g for all blends by DSC and the ordered structure in the SEM micrographs.

PVAc/PSPU blends are found to be immiscible by all the techniques used in the present work. VCVAc/PSPU blends show partial miscibility by the DSC and SEM techniques. Further viscosity studies of these blends need to be done to determine the validity of our approach.

Due to the complex behaviour of the TPU's and the different synthetic variations possible, comparison with literature becomes difficult. However, the method of intrinsic viscosities of transfer does provide a direction for predicting miscibility in polymer blends.

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