

MORPHOLOGY AND DIFFUSION STUDY OF POLYSTYRENE WITH POLY (VINYL METHYL ETHER) BLEND

Ali Asghar Bhutto^{1,*} and Barbara J. Gabrys²

¹Department of Physics, Government Degree and Postgraduate College Larkana, Sindh, Pakistan, email: phpgaab@hotmail.com.

²Department of Continuing Education, University of Oxford, Kellogg College, Oxford OX1 2JA, UK.

Abstract: The morphology and diffusion of polystyrene (PS) with poly (vinyl methyl ether) (PVME) blend have been investigated by light microscopy on both solvent-casting and mechanical blended samples. Both amorphous polymers are miscible and exhibit lower critical solubility temperature behavior. These preliminary results show that the microstructure of solvent cast samples is different than the microstructure of samples prepared by mechanical mixing. Diffusion between these two polymers was found to be very slow, indicating that a homogeneous blend cannot be achieved during a commercial polymer processing cycle.

Keywords: Morphology, Diffusion, Polystyrene and Poly (vinyl methyl ether)

INTRODUCTION

During the last two decades, the phenomenon of inter-diffusion in miscible polymer blends has been the subject of many investigations and is of interest for several applications such as welding and blending of polymers [Kausch and Tirell 1989]. When two miscible polymers come into contact with each other, mutual diffusion across the interface between the two polymers may occur. The composition inhomogeneities decrease (theoretically) due to the inter-diffusion, until a homogeneous molecular mixture of both components is reached. The kinetics of such processes has been investigated in model systems of planar double layer films using neutron reflectometry, ellipsometry, and small angle X-ray and neutron scattering [Takahashi *et al.* 1994, Geoghegan *et al.* 1999 and Shearmur *et al.* 1998]. Light microscopy of polymer–polymer diffusion has been reported by Parker and Vesely [1986] and in situ diffusion measurements by Vesely 1997.

The typical and well-known polymer mixture exhibiting a lower critical solution temperature (LCST) is polystyrene (PS) and poly (vinyl methyl ether) (PVME) blend. Earlier studies [Nishi *et al.* 1975, Kapnistos and Hinrichs 1996 and Tsujita *et al.* 1992] have demonstrated that these two amorphous polymers are miscible at low temperature over the entire range of compositions. In this work the miscibility and phase behavior of this blend has been studied by light microscopy.

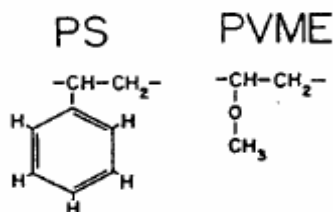
MATERIALS AND METHODS

MATERIALS

PS were obtained as powder from Exxon Chemicals of USA with $\bar{M}_w = 300,000 \text{ g mol}^{-1}$ and $\bar{M}_w / \bar{M}_n = 1.06$. Poly (vinyl methyl ether) PVME, was

* Author for Correspondence.

purchased from Scientific Polymer Products, Inc. (Ontario, New York), as a 50% (wt%/wt%) solids solution in toluene. Its molecular weight $\bar{M}_w = 95,000$, quoted by the company as determined by gel permeation chromatography (GPC). Both polymers were used without further purification. The chemical structures of these polymers are shown below:



SAMPLE PREPARATION

Polymer samples of PS, PVME and PS/PVME of different compositions were prepared by solvent casting, using 1% solution in toluene. Reported 50:50 PS/PVME concentration ratio means weight percentage. In order to remove the residual solvent, all films were put into a vacuum oven at a temperature above the (single) glass transition temperature of the blends. The temperature was slowly increased up to 60°C , and the final temperature was maintained for 3 days. Finally the dried films were left at room temperature in the oven until used. The mechanical blending was performed on a laboratory mixer with a temperature control for 3 gram batches, or by hand mixing the polymers on a glass slide, using a hot stage with a thermocouple for smaller batches.

The solvent or melt cast film samples for optical examination were prepared using glass slides and cover slips to sandwich the films. The films for light microscopy were sufficiently thin for the required resolution, i.e. less than $5\text{ }\mu\text{m}$. Light microscope (*Leitz Laborlux*) was used to examine the morphology of the (solvent – cast and mechanically blended) samples and also for the study of the diffusion layers. Polarized light and differential interference contrast were used. The resolution of a light microscope is high enough to resolve objects less than a micron in size. This technique cannot resolve small phases in miscible blends, which are of the order of $100 - 200\text{ nm}$, but is useful for study of larger phases obtained by mechanical blending and for study of diffusion layers. Samples for transmission light microscopy must be of even thickness and thinner than the required resolution. Samples were prepared in this work by pressing the polymer between a glass slide and a cover slip at elevated temperature, to reduce the viscosity. Some samples were prepared by cutting, using a microtome with a glass knife.

For diffusion studies using light microscopy, samples were prepared by following procedure: A thin PS film was produced by compression-molding the polymer powder in between heated platens; after molding, a small amount of PVME was placed on the upper surface of the PS thin

film in preparation for annealing. A vacuum oven was used for this purpose, and the temperature set below or above the glass transition temperature of PS. Annealing was performed on a number of samples for a range of annealing times.

After annealing, the boundary of PS/PVME was assessed by examination of thin sections. These sections were cut at room temperature perpendicular to the PS/PVME boundary, using a microtome with a glass knife, and examined under the light microscope, equipped with an eyepiece graticule calibrated using a stage micrometer (one millimeter divided into hundredths of a millimeter scale replacing the sample). Unfortunately the diffusion layer was too soft (plasticized) and difficult to cut without distortion. For accurate measurements in-situ observation of diffusion on a hot stage (Linkam) was performed. Thin samples were prepared by melting small amount of PS and PVME between two circular glass discs, 0.17 mm thick. An interface formed and diffusion of PVME into PS could be observed in a similar way as described in Morrissey & Vesely [2000] and Vesely [1997].

RESULTS AND DISCUSSION

Mixing of the two polymers PS and PVME by solvent casting in toluene resulted in optically clear samples. This observation indicates that PS/PVME blends present a single homogeneous amorphous phase at room temperature, i.e., phase separation did not occur, at least on a scale with dimension of phase domains exceeding the wavelength of visible light. Solubility of PVME in PS indicates that diffusion should occur.

Parker and Vesely [1986] have used polarized light microscopy and electron microscopy to measure and identify the inter-diffusion layer in the blends poly (vinyl chloride) / poly (caprolactone) (PVC/PCL). Similar analyses by light microscopy experiment have been tried on PS/PVME system. A small amount of PVME was placed on the top of thin PS film produced by compression molding. The light microscopy experiments were carried out after heating the samples above or below the glass transition temperature of PS.

Light microscopy of mechanically blended PS/PVME (50:50) sample at 180°C shows phases of PS dispersed in PVME (Fig. 1). It has been expected that on annealing at 110°C the PS phase will dissolve in PVME. Instead the PS phase conglomerated into larger, spherical particles (Fig. 2). This confirms the results obtained by phase separation studies using DSC [Bhutto 2003]. A single T_g of the blend was observed only after annealing for one day at 110°C. Fig. 2 shows that there is a high surface tension between both phases and that the diffusion is not symmetrical, i.e. PS is swelling with PVME, but not dissolving in it. The phase diagram for mechanical blending and diffusion is, therefore, different than the phase diagram measured using solvent, which produces a homogeneous mixture at this temperature (Fig. 3). After short annealing at 150 °C phase

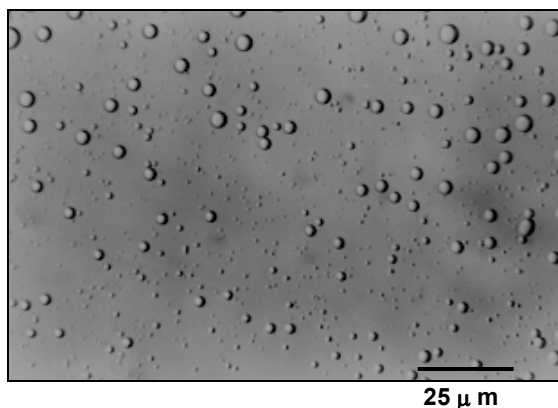


Fig. 1: Light micrograph (X 500) for PS/PVME 50:50 composition of mechanically blended sample at 180 °C.

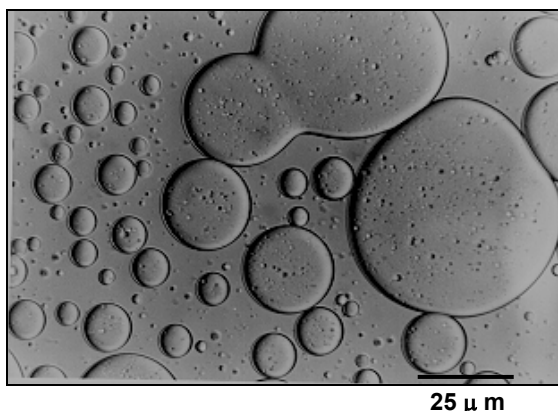


Fig. 2: Light micrograph (X 500) for PS/PVME 50:50 composition of mechanically blended sample annealed at 110°C for 1 hour.

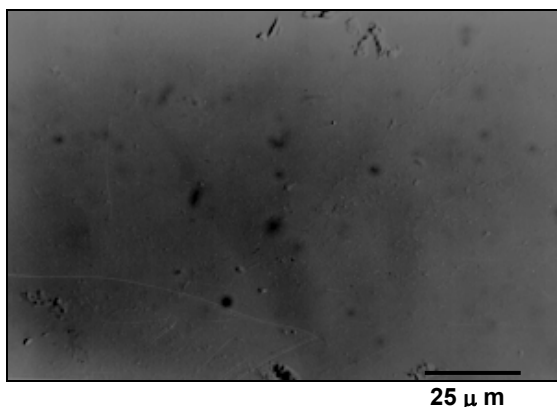


Fig. 3: Light micrograph (X 500) for PS/PVME 50:50 composition of solvent cast samples annealed at 110°C. No phase separation can be detected.

separation is however occurring as expected from DSC results [Bhutto 2003]. These results have shown that only one T_g is present for all blends

prepared by solvent casting and at high temperature (above 150°C) phase separation represented by two T_g of homopolymers. The phases are large and growing with annealing time (Fig. 4).

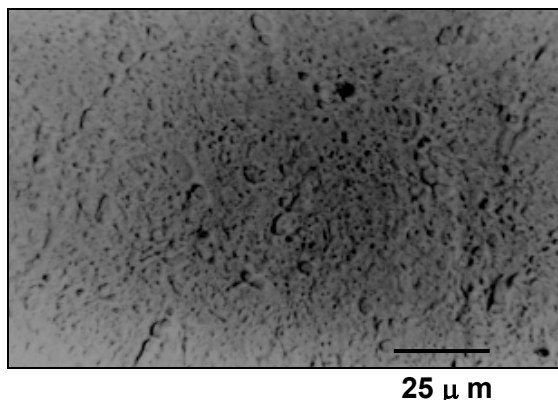


Fig. 4: Light micrograph (X 500) for PS/PVME 50:50 composition of solvent cast samples annealed at 150°C for 15 min. Phase separation is visible.

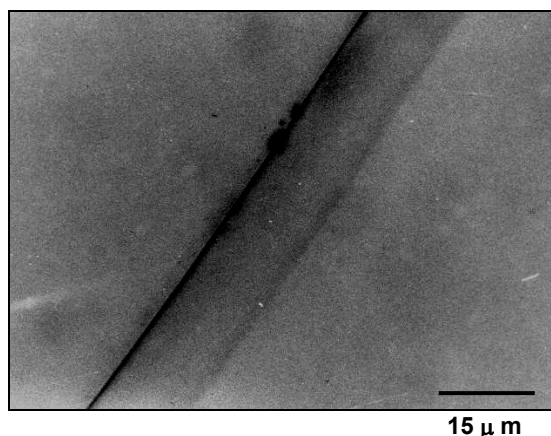


Fig. 5: Light micrograph of the PVME diffusion into PS. The diffusion front after 336 hours at 80°C is clearly visible.

Jabbari and Nicholas [1993] using ATR-FTIR spectroscopy observed that inter-diffusion was not dominated by either component, but was controlled by the rate of swelling of PS by PVME at 85°C below the glass transition of PS. The inter-diffusion was non-Fickian and time dependent. Our attempt to reveal the rate of diffusion by light microscopy has confirmed these conclusions. Difficulties with sample preparation using microtome of PS swollen by PVME could not have been overcome, however direct observation of diffusion in thin films (Fig. 5) have shown that the diffusion rate is very slow (15 μm after 336 hours at 80°C). This has implications for polymer processing; phases formed at processing temperature (high, to reduce viscosity) will need a long time annealing at elevated temperature to disperse the phases.

CONCLUSIONS

Miscibility and phase behavior in blends of PS and PVME have been investigated by light microscopy. The blends prepared in this work are miscible in the amorphous state over all the composition range at low temperature as judged from the transparency of blend films.

Blends prepared by mechanical mixing have different behavior. After mixing, two phases are observed by light microscopy. These results indicate that the microstructures of solvent cast samples and samples prepared by mechanical blending are different. The diffusion of PVME in PS was found to be very slow, which indicates that in practice it is difficult to make homogeneous blends with systems showing a LCST.

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