Differential Scanning Calorimetric And XRD Studies Of Polysulfone / Poly (methyl methacrylate) Blends

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Abstract
Polymer blending was recognized in the last few decades as a most promising way to prepare new user -tailored materials. Differential scanning calorimetry (DSC) thermoanalytical methods were used to study the miscibility of polymer blends prepared from polymers having different glass transition temperatures. Knowledge of the glass transition temperatures (T_gs) as function of composition reflects miscibility (or lack of it) and is decisive for virtually all properties of polymer blend materials. In this study, we analyze the impact of blending on T_gs of polymer blends in various compositions. Among other techniques, DSC is preferred because it allows the detection of transitions in a wide range of temperatures (-90 to 550 ^0C) and ease in the quantitative and qualitative analysis of the transitions.

Keywords: Differential scanning calorimetry; Glass transition temperature; Blends

INTRODUCTION

Blending of polymers provide an economic alternative to synthesizing new polymers. Instead of synthesizing new materials, blending is preferred as a faster, easier and cheaper way of developing new materials [1,2]. Unfortunately the demands for many applications need a set of properties that no polymers can fulfill. One method to satisfy these demands is by mixing two or more polymers. Mixing two or more polymers to produce blends is a well-established route to achieve a certain amount of physical properties, without the need to synthesize specialized polymer systems. Homogeneous blends are relatively rare because the Gibbs free energy of mixing is positive due to change in entropy, as a consequence, high molecular weight polymer blending is practically negligible, with the enthalpy term being positive [3].

The polymer blends are widely utilized for a variety of applications as the particular thermo-physical properties of the individual components comprising the blend result in better overall properties. It is particularly the case of polymer blends used in the automotive industry where impact resistance, toughness, stiffness and paintability all become important issues. Blending of polymers yields a better overall product with the desired end use properties and characteristics.

Polymer blends are also used for container applications where there is a need for good impact resistance coupled with long term stability, barrier resistance and opacity.

Polymer blends may be classified into miscible or homogeneous and immiscible or heterogeneous. The study of polymer blends, began nearly two decades ago [2], revealed an enormous possibility of tailor–making the properties of polymer materials for various end–use applications. Large numbers of commercially produced blends are now in the market like HIPS (high-impact polystyrene), which is immiscible blend of polystyrene and polybutadiene, PET/PVA blend, whcih is immiscible blend of poly (ethylene terephthalate) and poly (vinyl alcohol) etc. and still larger are in the process of evolution.

Retolaza *et. al.* [4] have blended polysulfone with poly (ethylene terephthalate) (PET) and studied the thermal properties, morphology and mechanical properties of PSU/PET blends. The presence of a two–phase microstructure has been reported by Tyagi *et. al.* [5] for polysulphone/poly (dimethyl siloxane) copolymers by small–angle X–ray analysis.

A series of blends with various compositions was prepared on the basis of polysulfone, polyethersulfone and polyimide by Linares and

Acosta [3]. The blends were characterized by different techniques, including FTIR, DSC, DMA and tensile stress–strain measurements. The difference in results obtained by DSC and DMA measurements was explained on the basis of minute domains or micro heterogeneities in the samples which depending on the degree of sensitivity of the analytic device were detected or neglected. They concluded that the systems were compatible from a macroscopic point of view but from the molecular stance, they were immiscible. The effects of molecular weight of polysulfone on the morphology of bisphenol–A dicyanate (BADCy)/PSF blends were studied by Hwang *et. al.* [6]. They observed that the effect of viscosity was predominant, the viscosity of the blends at the onset point of phase separation increased with the increase of PSF molecular weight. The combined morphology and the BADCy particle structure were obtained with a smaller amount of high molecular weight PSF content. It was concluded that the viscosity of the blends at the onset point of phase separation is the critical parameter that determines the morphology of the blends.

Differential scanning calorimetry (DSC) has been applied to characterize the miscibility of PSF/PMMA blends at selected compositions. The T_g values of the virgin samples and the blends were measured using a temperature–modulated differential scanning calorimeter (TA Instruments, Model 2910) at IUC-DAE, Indore Centre. Samples weighing 4–12 mg were heated at a rate of 10 ^{0}C min^{-1}.

In DSC experiments, heat flows associated with transitions in the materials is measured as a function of temperature and time [7–9]. A heat–flux mode operated temperature modulated differential scanning calorimeter (MDSC^{TM})– TA Instruments Module 2910 has been used for the present work.

X–ray diffraction has played a central role in identifying and characterizing solids since the early part of this century. The nature of bonding and the working criteria for distinguishing between short range and long–range order of crystalline arrangements from the amorphous substance are largely derived from X–ray diffraction and thus it remains as a useful tool to obtain structural information. X–ray diffraction has been most commonly used for routine characterization as well as for detailed structural elucidation. Polymers are not simple covalent crystals of conventional solid–state physics. They can exist as crystalline materials as amorphous materials or as mixture of crystalline and amorphous materials so XRD becomes crucial for characterization of polymers and polymer blends [10–11].

Poly (methyl methacrylate) is a transparent thermoplastic material that is often used in place of glass. It has got vast applications including medical sciences. Polysulfone is tough, rigid, high-strength transparent thermoplastic polymer retaining its properties between –100^{0}C and + 150^0 C. It is a good membrane material. Its membranes are used in applications like hemodialysis, waste water recovery, food and beverage processing, and gas separation. We have prepared blends of PMMA and PSF. In this paper, differential scanning calorimetry (DSC) investigations in polysulfone, poly (methyl methacrylate) and polysulfone / poly (methyl methacrylate) (PSF/PMMA) polymer blends and XRD measurements are reported.

EXPERIMENTAL
Sample preparation
Polysulphone (PSF) supplied by Gharda Chemicals Ltd. Bharuch, Gujarat (India) and poly (methyl methacrylate) or (PMMA) supplied by HiMedia Laboratories Pvt. Ltd., Mumbai (India) were used for the study.

Thin films of PMMA, PSF and PSF/PMMA blends were prepared by solution cast method. Blends of PSF/PMMA in the ratio, 10:90, 30:70, 50:50, 70:30, 90:10 were prepared. For preparing blends of polysulphone and PMMA in variable proportions, the granules of PMMA and PSF were dissolved in common solvent i.e. dichloromethane, and stirred thoroughly for a few hours to ensure mixing. The solution was then put into flat–bottomed Petri dishes floating on mercury. The solvent was allowed to evaporate slowly over a period of 10–12 h. The films (thickness ~ 100 μm) so obtained were peeled off and dried in vacuum for 24 h in order to ensure the removal of the solvent. The cast films of PSF/PMMA blends were opaque in the entire composition range.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) has been applied to characterize the miscibility of PSF/PMMA blends at selected compositions. The T_g values of the virgin samples and the blends were measured using a temperature–modulated differential scanning calorimeter (TA Instruments, Model 2910). Samples weighing 4-12 mg were heated at a rate of 10^0 C min^{-1}. In DSC experiments, heat flows associated with transitions in the materials is measured as a function of temperature and time [11–12]. A heat–flux mode operated temperature modulated differential scanning calorimeter (MDSC^{TM})– TA Instruments Module 2910 at IUC-DAE, Indore Centre has been used for the present work. The glass transition, T_g, was taken as the mid point of the transition.

The experimental set–up is common to both DSC and MDSC modules. The difference lies in the thermal program used. The experimental chamber/sample holder, generally consists of a *cell*. The schematic of the 2910 TA cell is shown in the figure. 1.

The sample and the reference are placed on raised platforms cast on the thermoelectric Constantan disk, which serves as the primary means of heat transfer to the sample and the reference from the temperature programmed furnace. The temperature of the furnace is raised in a linear fashion while the resultant heat flow to the sample is measured by area.
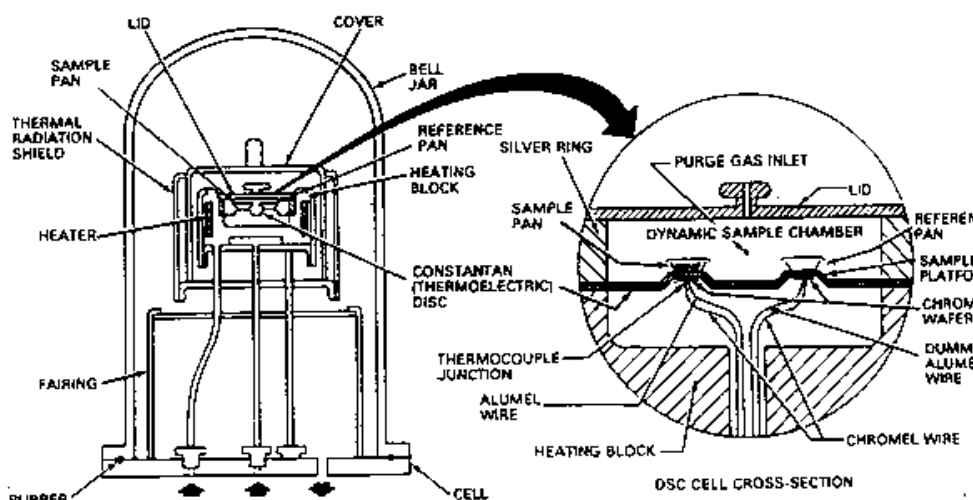

Figure 1: Cross section of the MDSC cell

thermocouples fixed to the underside of the disk platforms. These thermocouples are connected in series and measure the differential heat flow using the thermal equivalent of the Ohm's law.

The samples are generally powdered (for better contact and efficient heat transfer) and weighed in a microbalance. The aluminium sample pans and lids were chosen so that they were identical. The weighed samples were transferred into the pans and crimped.

The set–up is allowed a warm up time of one hour after power–on. The cell is flushed for a few minutes with purge gas argon or nitrogen at a high flow rate, to get rid of any minute impurities. The sample and the reference are then loaded and the

heating rate is chosen according to the nature of the sample and the process being observed.

XRD

The XRD measurements were taken at IUC-DAE, Indore Centre. The experimental set up used was a RIGAKU system. It has a horizontal gonimeter and a Rigaku Rotaflex X–ray diffractometer. The monochromator used was a post specimen flat graphite (200) crystal. The radiation detector used was a thallium doped sodium iodide scintillation counter. The diffraction experiments have been carried out at room temperature using Cu K_α radiation (λ=1.542Å). The X–ray diffraction patterns were collected in a step–scanning mode with $\Delta 2\theta$ =0.020^0 steps.

RESULTS AND DISCUSSION
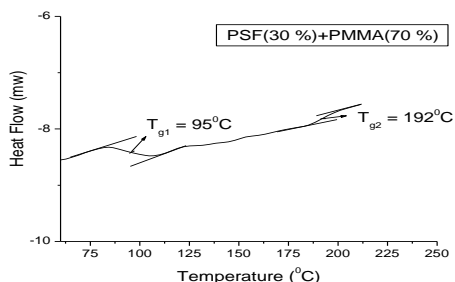
DSC measurements

Figure 2 shows the DSC curves for PSF, PMMA and PSF/PMMA blends. The T_g is defined as the midpoint of the transition of DSC measurements. The glass transition temperatures of the pure components, measured with DSC, are 99^0 C for PMMA and 194^0 C for PSF. The miscibility of the blends is characterized by the behaviour of the T_g. For blends having different percentage of PSF two T_gs are obtained. If the system was miscible, one T_g should be observed but we found T_{g1} and T_{g2} for all the compositions investigated, which is evidence given by DSC that the PSF/PMMA blends are immiscible. The two glass transitions observed for each immiscible blend have shifted from the component T_g values; this suggests the coexistence of a PSF rich phase and a PMMA rich phase in the blends.
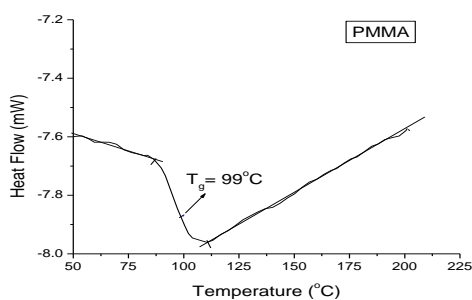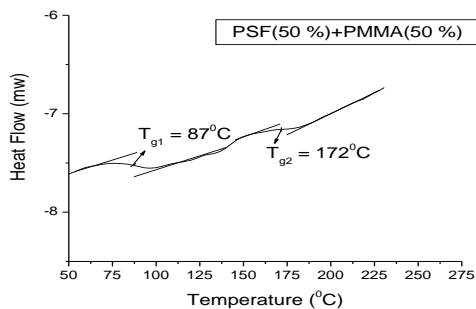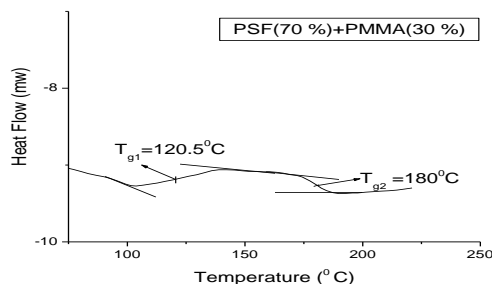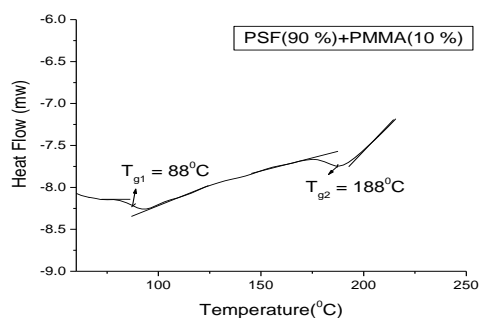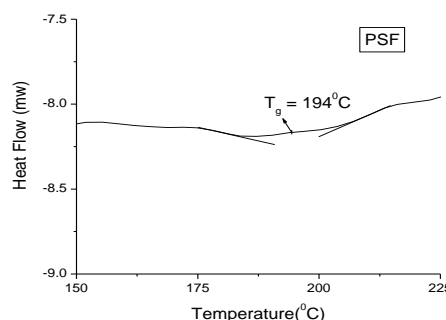
(a)
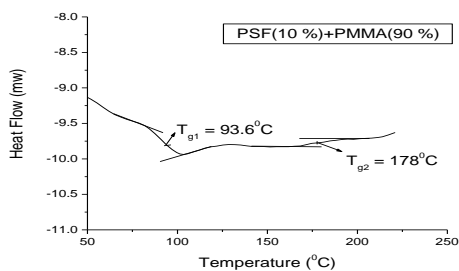
(b)

(c)

(d)

(e)

(f)

(g)

Figure 2. DSC curves for PSF/PMMA blends
(a) PMMA (b) 10/90 (c) 30/70 (d) 50/50 (e) 70/30
(f) 90/10 (g) PSF

XRD Measurements

Figure 3 shows the XRD pattern of virgin samples (PMMA & PSF) in addition to blends

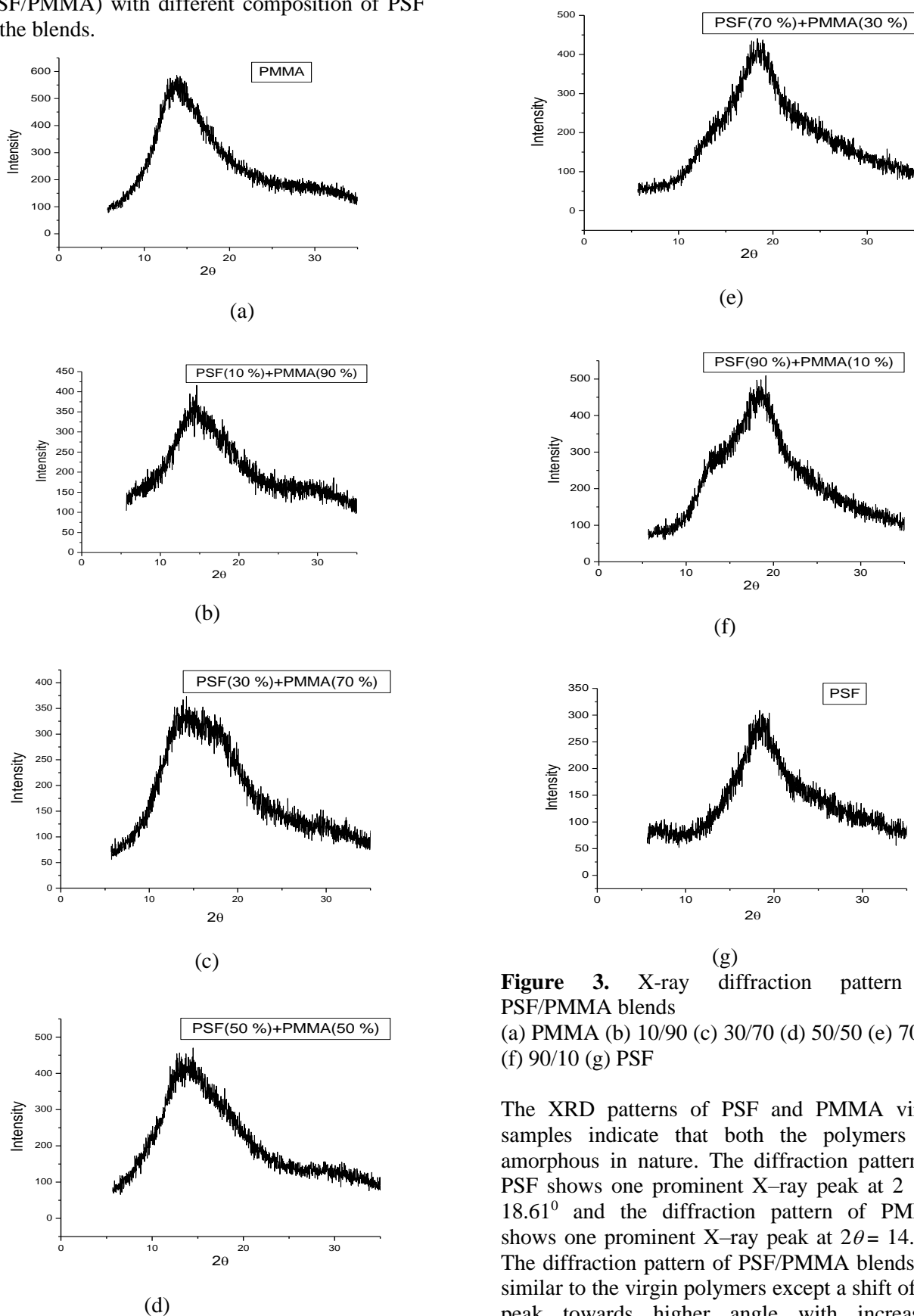(PSF/PMMA) with different composition of PSF in the blends.

(a)

(b)

(c)

(d)

(e)

(f)

(g)

Figure 3. X-ray diffraction pattern of PSF/PMMA blends
(a) PMMA (b) 10/90 (c) 30/70 (d) 50/50 (e) 70/30 (f) 90/10 (g) PSF

The XRD patterns of PSF and PMMA virgin samples indicate that both the polymers are amorphous in nature. The diffraction pattern of PSF shows one prominent X–ray peak at $2\theta = 18.61^0$ and the diffraction pattern of PMMA shows one prominent X–ray peak at $2\theta = 14.39^0$. The diffraction pattern of PSF/PMMA blends are similar to the virgin polymers except a shift of the peak towards higher angle with increasing percentage of PSF in the blend. Broadening of

XRD peak in the blend samples is also observed. The broadening of peak suggests an evolution of the blend towards a more disordered state [12].

The average crystal size, more commonly known as particle or grain size L, s related to b, the full width at half maximum (FWHM) of the peak (in radian) by the well known Scherrer formula

$$L = K \lambda / (b \cos \theta)$$

Where λ is the wavelength of X–ray beam, K is a constant, b is the full width at half maximum of the peak. The particle size in the blends varies between 10.6 and 18.2 as seen from table 1, which lies in between that of PMMA & PSF. Variation in the grain size in blends has been observed.

Table 1 XRD results for PSF/PMMA blends

PSF/PMMA	2 θ (θ = Bragg angle)	L (Å)
0/100	14.39	17.0
10/90	15.14	12.8
30/70	15.61	10.6
50/50	14.64	12.7
70/30	18.52	18.2
90/10	18.06	14.6
100/0	18.61	22.0

CONCLUSION

DSC measurements of PSF/PMMA blends for all the compositions under investigation show two T_g's. Existence of two T_gs is an evidence of immiscibility of these blends. DSC technique is very helpful in the microstructural analysis of polymeric systems. Brodening of XRD patterns show morphine nature of blends. No crystalline formation in the interfacial region between two co–continuous phases have been detected by XRD results.

Acknoledgement:

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