

# Certain Investigations on the Formulation and Characterization of Polystyrene / Poly(methyl methacrylate) Blends

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**Abstract:** Polystyrene (PS) / Poly(methyl methacrylate) (PMMA) blends with different ratios were prepared by solvent casting from toluene. The blend formation has been confirmed from Fourier transform infrared (FTIR) and Differential scanning calorimetry (DSC) studies. Thermal stability and toughness of the polymers were evaluated by Thermogravimetric analysis (TGA). The FTIR spectral results showed that PS and PMMA blend had no molecular interactions. The thermal properties of the prepared blends were investigated by DSC in order to analyze miscibility behavior through glass transition temperature. DSC analyses show that blends possess two distinct transitions due to heterophase nature.

**Keywords:** Polystyrene (PS), Poly(methyl methacrylate) (PMMA), Immiscible polymer blends, FTIR, Thermal properties, DSC.

## Introduction

Polymer blends are a mixture of chemically different polymers or copolymers with no covalent bonding between them. Polymer blends are classified as three types, namely, homologous, miscible and immiscible blends. Chemically identical polymers with differing molecular masses constitute homologous polymer blends. Miscible polymer blends exhibit single phase behaviour and immiscible polymer blends exhibit two or more phases at all compositions and temperatures. Preparation of polymer blends has been received considerable importance in the recent past owing to the shorter time and lower cost of the product development than those of a new polymer [1]. The performance of a polymeric material can be improved by selection of suitable ingredients and their ratios. Polymer blending imparts certain new characteristics leading to the formation of new materials with enhanced physical, chemical and

mechanical properties [2, 3]. Blending of two polymers having different properties is usually producing a new polymeric material. These new polymeric material may possess the properties of both the polymers. The properties of polymer blends such as toughness, strength, etc have close relationships with their internal microphase morphology [4-6].

PMMA has been found to form an immiscible blend with polystyrene. Miscibility is not a prerequisite for blends applications; it is an easy way to design a new polymeric material. Polystyrene is a well known amorphous polymer with good thermal and radiation resistant properties. PS is available with a wide range of formulations. The styrenic part may impart the properties like toughening, flame resistance and solvent resistance. Commercially available polystyrene is mostly atactic type and amorphous in nature. The use of polystyrene is limited because of its susceptibility to degradation from UV radiation,

chemical attack from aromatic, and chlorinated hydrocarbons may also cause problem in application areas.

PMMA is a transparent polymeric material possessing many excellent properties such as light weight, high light transmittance, chemical resistance, colorlessness, weathering corrosion resistance and good insulation. It is amorphous in nature and it has good mechanical property. Therefore, superior mechanical properties can be achieved via blending of PMMA with polystyrene. PS and PMMA are known to be immiscible, exhibiting phase separation and compatibilizers are required [7].

In the present work, PS/PMMA blends were prepared with different weight ratios to investigate their structural features and miscibility behavior through FTIR spectroscopy and DSC studies. Thermal stability of these blends was investigated by TGA studies.

## **Experimental**

### **Materials and blends preparation**

Commercial grades of PS and PMMA were purchased from Modern Scientific Company, Coimbatore and used as received. A series of polymer blends of PS and PMMA were prepared from the common solvent toluene as follows. Polymer solutions were prepared by dissolving PS/PMMA in various weight ratios (0/100, 20/80, 40/60, 50/50, 60/40, 80/20, 100/0 w/w) in toluene. The solutions were mixed at room temperature and stirred for 12 hours. The solutions were then poured into the glass plates and toluene was slowly evaporated under ambient conditions. The resulting polymer blends were dried in a hot air oven at 70°C for a period of two days.

### **Measurements**

Solubility of the prepared polymer blends was tested with various organic solvents viz., chloroform, cyclohexane, chlorobenzene, dimethylformamide, dimethyl sulphoxide and tetrahydrofuran. About 2-3 mg of the polymer sample was treated with 5 ml of solvent and kept aside for 6 hr with occasional shaking. If the polymer is insoluble in cold condition, the mixture was heated and cooled. Very thin transparent films of polymer / polymer blends were prepared by solution-casting over Teflon sheets. The

FTIR study was carried out on this films using FTIR spectrometer (Schimadzu). The glass transition temperatures were measured with a Perkin-Elmer Pyris-6 DSC apparatus at a heating rate of 20°C/min under nitrogen atmosphere over the temperature range of 30 to 440°C. The reported  $T_g$  values were based on the second run after heat relaxation upto 120°C. The glass transition temperature was taken as the initial onset of the change of slope in the DSC curve. The thermal stability of the polymers was studied by thermogravimetric analysis (TGA). Thermogravimetric studies were carried out using MettlerTG-50 instrument. The heating rate was 20°C/min in air atmosphere over temperature range from 50°C to 700°C.

## **Results and Discussion**

### **Solubility**

The solubility of polymers and polymer blends were tested in various organic solvents. The polystyrene is soluble in all the solvents used viz, chlorobenzene, tetrahydro furan, chloroform, DMF, DMSO and cyclohexane. The PMMA is also soluble in all the solvents tested except cyclohexane. The same trend was observed in the polymer blends also. Polymer blends show improved solubility in cyclohexane. Hence a wide range of solvents can be applied for processing of polymer blends. The solubility properties of the polymers and polymer blends are reported in Table 1.

### **FTIR analysis**

FTIR spectroscopy is one of the powerful tools for identifying and investigating the presence of various functional groups in polymers [8, 9]. **Figures 1 and 2** show the FTIR spectra of original PS and PMMA samples. The IR spectrum of PS showed absorption bands at 3026 and 2849  $\text{cm}^{-1}$  corresponding to aromatic and aliphatic C-H stretchings respectively. The peaks at 1601 and 1493  $\text{cm}^{-1}$  are assigned to aromatic C=C stretchings. The C-H deformation vibration band of benzene ring hydrogen's (5 adjacent hydrogen's) appeared at 758  $\text{cm}^{-1}$ . Ring deformation vibration was observed at 700  $\text{cm}^{-1}$ . The C-H stretching vibrations of ring hydrogen's are seen from 3000 and 3100  $\text{cm}^{-1}$ .

**Table 1. Solubility Behaviour of Polymers and Polymer Blends**

Solvent→ Polymer↓	Chlorobenzene	THF	$\text{CHCl}_3$	DMF	DMSO	Cyclohexane
PS	++	++	++	-+	-+	++
PMMA	++	++	++	++	-+	--
PS/PMMA blend	++	++	++	-+	-+	+-

++ : Soluble    +- : Partially soluble    -+ : Soluble at hot condition    -- : Insoluble

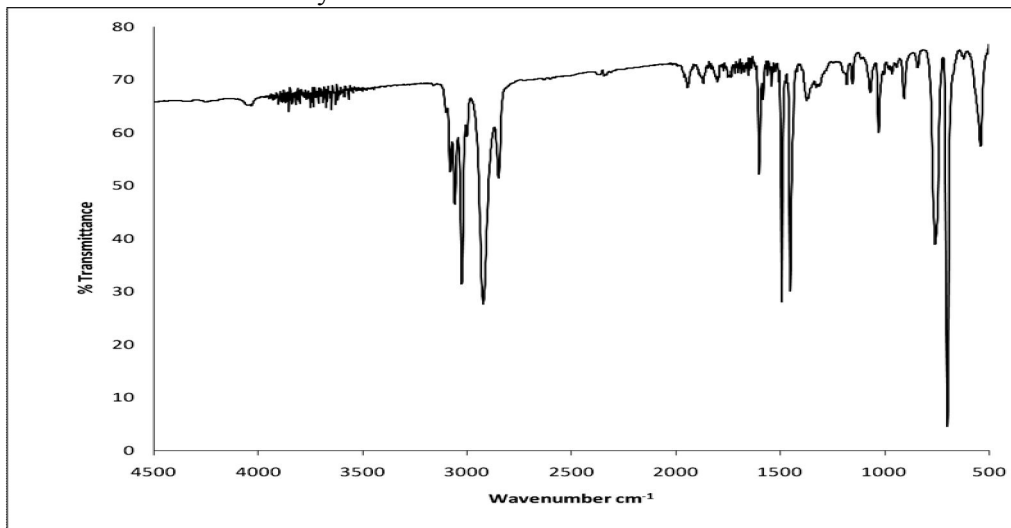


Figure 1. FTIR spectrum of polystyrene (PS)

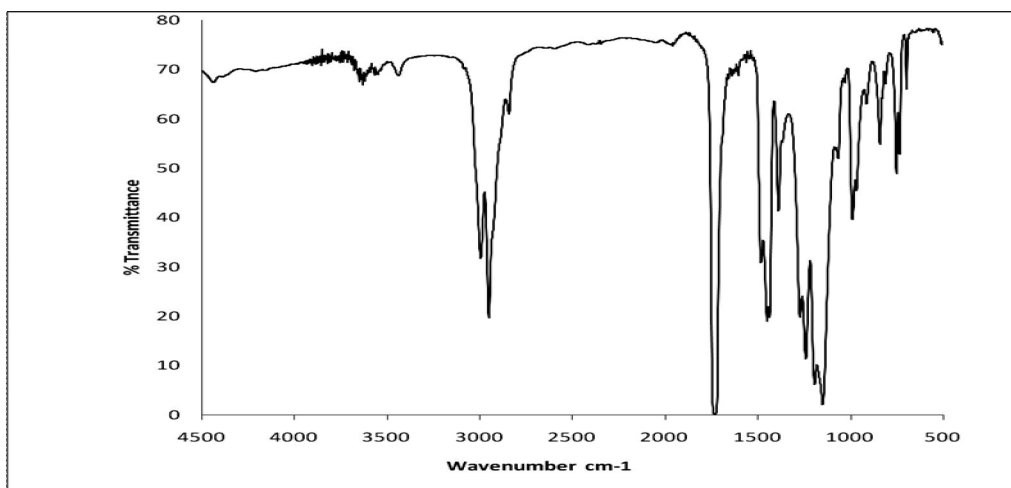


Figure 2. FTIR spectrum of poly(methyl methacrylate) (PMMA)

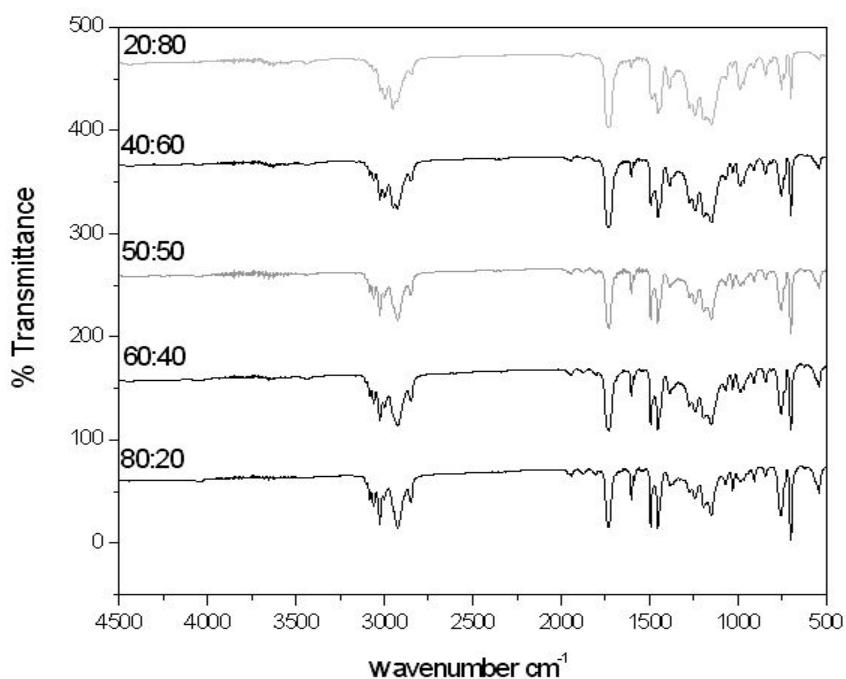


Figure 3. FTIR spectra of PS/PMMA blends

The IR spectrum of PMMA showed absorption bands at 2951 and 1736  $\text{cm}^{-1}$  due to  $-\text{CH}_3$  asymmetric stretching and  $\text{C}=\text{O}$  stretchings respectively. The vibrational bands at 1483 and 1449  $\text{cm}^{-1}$  are attributed to  $\text{CH}_2$  scissoring and  $\text{CH}_3$  asymmetric stretching or deformation of PMMA. The characteristic peak at 1390  $\text{cm}^{-1}$  is appeared due to  $\text{O}-\text{CH}_3$  deformation of PMMA. The bands appearing at 1273 and 860  $\text{cm}^{-1}$  are corresponding to  $\text{C}-\text{O}$  stretching and  $\text{C}-\text{O}-\text{C}$  stretching of PMMA. The absorption bands corresponding to  $\text{CH}_2$  twisting, wagging and rocking modes of PMMA are appeared at 1192, 950 and 750  $\text{cm}^{-1}$  respectively.

The FTIR spectra of PS/PMMA blends are shown in the Figure 3. The peaks at 1732 and 1149  $\text{cm}^{-1}$  in all the blends represents the  $\text{C}=\text{O}$  and  $-\text{OCH}_3$  stretching of PMMA. The peaks at 1600 and 698  $\text{cm}^{-1}$  in all the blends represents the  $\text{C}-\text{C}$  stretching and ring deformation of polystyrene. A thorough analysis of IR spectra of these blends show that decrease in transmittance of carbonyl and methoxyl stretchings with an increase of PS content and increase in transmittance of these peaks with an increase of PMMA content. These data clearly indicates the formation polymer blends.

When two polymers are completely miscible, there is a chemical interaction between them in a blend. This interaction leads to a considerable

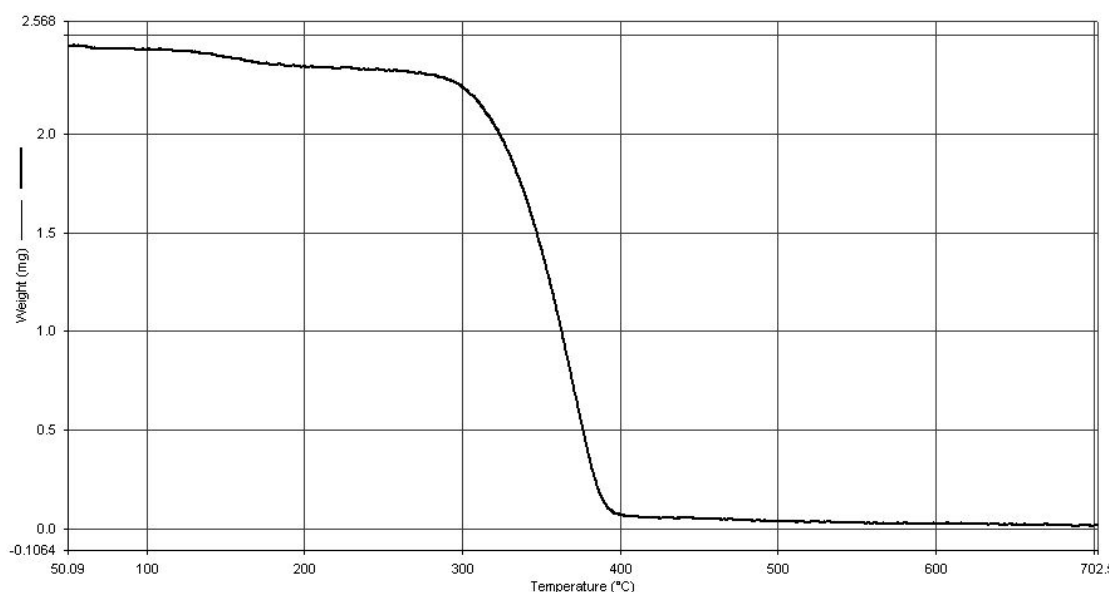
difference between the spectrum of the polymer in the blend. As there are no shifts of the peaks of any group in PS/PMMA spectra, it was confirmed that these blends show no chemical interaction between the constituent polymers and they remained as physical blends [10].

### TGA studies

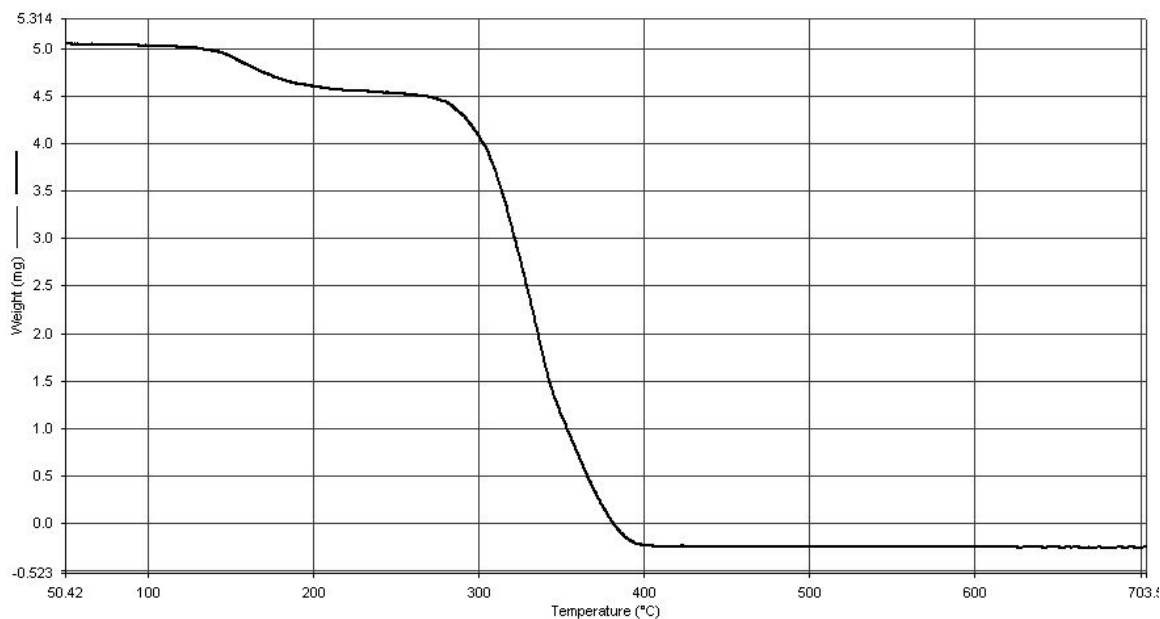
Thermogravimetric analysis was used to estimate the percentage weight loss of the polymers/polymer blends against temperature. The TGA curves of PS, PMMA and the representative 50:50 PS/PMMA blend are shown in Figures 4-6. Table 2 shows percentage weight loss at different temperatures. The temperature corresponding to 10% weight loss of polymers and the polymer blend are in the range of 237 to 305°C. The initial decomposition temperatures (IDT) of PS, PMMA and 50:50 PS/PMMA blend are 250, 140 and 250°C respectively. The major weight loss was obtained over the range of 250 to 400°C which corresponds to the structural decomposition of the polymers [11]. The decomposition temperature of polystyrene is higher when compared to that of PMMA. It indicates that polystyrene possess higher thermal stability than PMMA. The thermal decomposition temperature of 50:50 PS/PMMA blend lies between the polystyrene and PMMA.

**Table 2. TGA Data of Polymers and 50:50 PS/PMMA Blend**

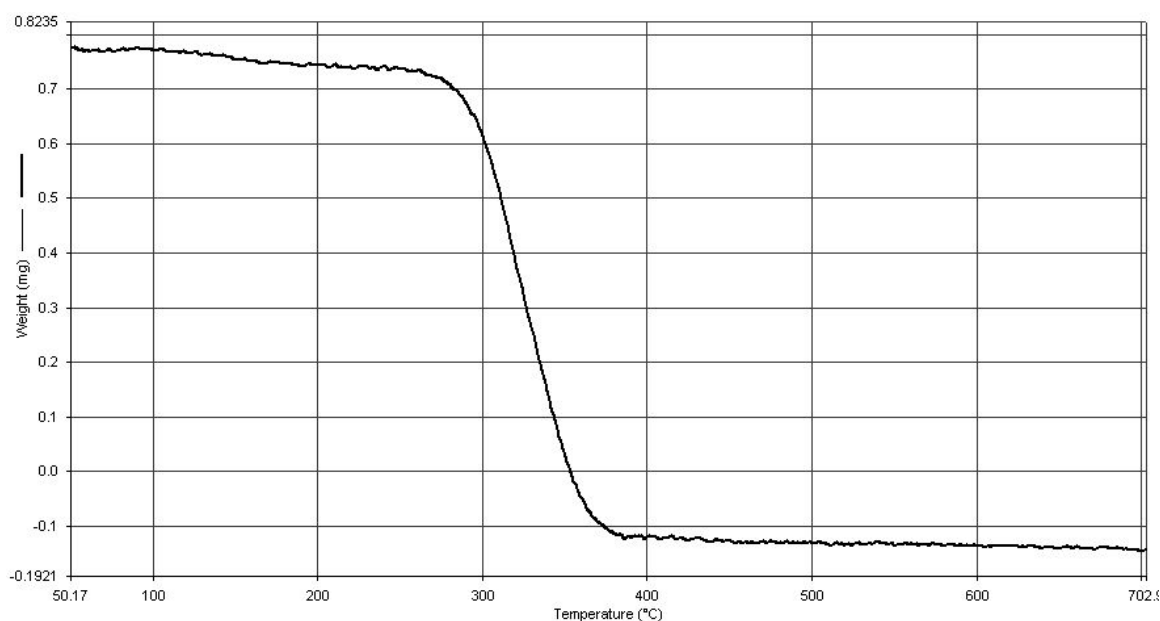
Polymer	IDT	Temperature ( $^{\circ}\text{C}$ ) corresponding to				
		10% Wt Loss	20% Wt Loss	30% Wt Loss	40% Wt Loss	50% Wt Loss
PS	250	305	326	339	348	356
PMMA	140	237	302	314	322	329
50:50 PS/PMMA Blend	250	285	300	308	314	320



**Figure 4. TGA trace of polystyrene (PS)**



**Figure 5. TGA trace of poly(methyl methacrylate) (PMMA)**



**Figure 6. TGA trace of 50:50 PS/PMMA blend**

### DSC studies

Thermal characterization of polymer blends is a well known method for determining the miscibility of polymer blends. The DSC thermograms of original PS, original PMMA and 50:50 PS/PMMA blend are given in Figures 7-9. Generally, polymer blends are miscible if their components form a single homogeneous phase at the molecular scale, or immiscible if they exhibit several distinct phases [12-15]. The DSC thermogram of the representative 50:50 PS/PMMA blend shows two distinct glass transitions. From the presence of multiple glass transition temperatures, it is

clear that the blends are immiscible. Further, the opaque nature of binary blends of PS and PMMA, cast from toluene indicates the phase separation [7]. The DSC thermograms of PS, PMMA and 50:50 PS/PMMA blend exhibited a broad melting peak in the range of 330-420°C. The melting range of polystyrene is 375-425°C. The polymer blend showed lesser melting temperature than the original PS, which indicates the incorporation of PMMA in the blend. Hence the toughness of PMMA may be increased via blending it with PS or rigidity of PS may be reduced via blending it with PMMA.

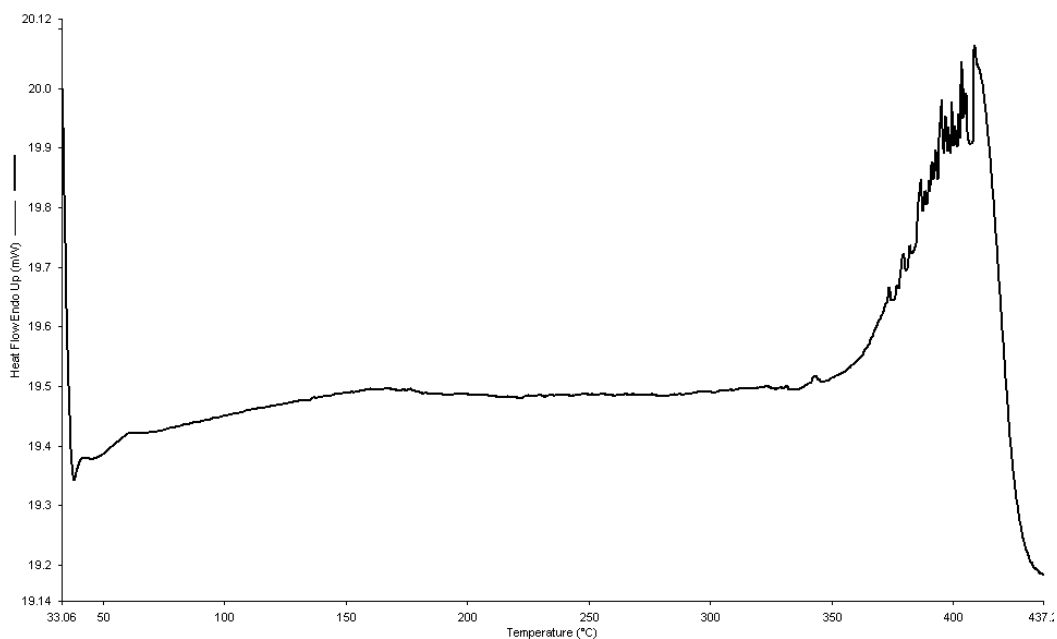


Figure 7. DSC thermogram of polystyrene (PS)

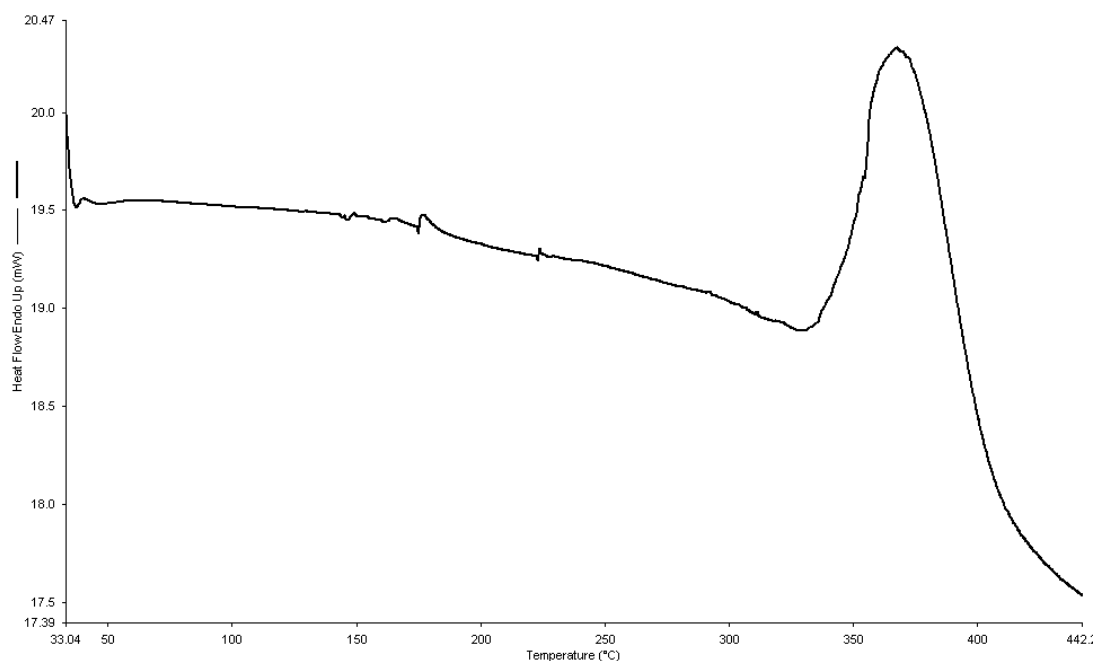
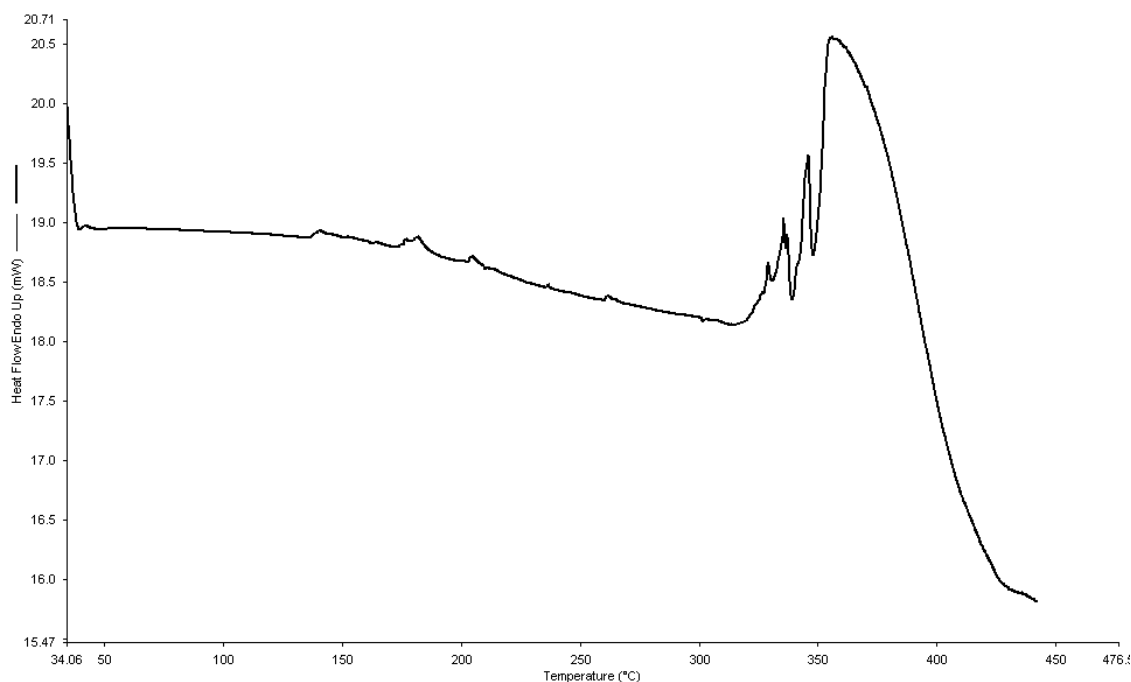


Figure 8. DSC thermogram of poly(methyl methacrylate) (PMMA)

## Conclusions

PS/PMMA blends were prepared by solvent casting technique. These blends were characterized by FTIR, TGA and DSC. The FTIR results of polymer blends indicate that there are no shifts of the peaks of any group in PS/PMMA spectrum; this confirms the formation of physical blend. The TGA studies reveal that blends possess intermediate stability than that of

component polymers. Hence toughness may be increased or decreased suitably. The immiscible character of the polymer blends was confirmed by DSC and the results evidenced that blend system was heterophase due to two distinct glass transitions. Hence PS/PMMA blends were immiscible and no specific intermolecular interactions was observed.



**Figure 9. DSC thermogram of 50:50 PS/PMMA blend**

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