

Synthesis, Characterization and Negative Thermal Coefficient of Polystyrene - Poly (Methyl Methacrylate) Blends

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Abstract—Polystyrene modified PMMA blends were prepared by the extrusion moulding technique with different weight percentage. The prepared blends were characterized by FTIR (structural study) and SEM (surface morphology). The important characteristic peaks of pure PS and PMMA appearing in the spectra confirm the compatible blends results in flourishing the interface between the polymers. DC conductivity increases with increase in temperature as well as PMMA percentage up to 6 wt % and the highest conductivity is found to be 12×10^{-5} S/cm. This increase in conductivity is due to the increase in charge density and extended charge length which is confirmed by NTC plot. Therefore these materials have potential use in engineering and technological applications.

Keywords: Blends, Polystyrene, Poly(methyl methacrylate), Scanning electron microscopy, Negative thermal coefficient

1. INTRODUCTION

Polystyrene (PS) is a thermoplastic polymer that has many applications such as packaging, insulation, automotives, etc. However, disadvantage of this material is its brittleness at room temperature [1]. Nevertheless, it is known that the polymers break macroscopically in a brittle manner (e.g. poly(methyl methacrylate) PMMA, polystyrene, PS). On the other hand they show highly ductile deformation zones (e.g. crazes, shear yielding, etc.) with a maximum natural draw ratio [λ_{max}]; for polystyrene of about 4 and for PMMA of about 3. This means that these polymers are intrinsically tough (elongation at break of several hundred percent) [2, 3]. Hence the main goal for the toughness modification of the brittle plastics like polystyrene is to transfer their intrinsic toughness to the macroscopic scale [4 – 6].

In brittle polymers, toughening is achieved by incorporation of a small amount of rubber, which forms the dispersed phase embedded in the brittle polymer matrix [7]. However, due to intrinsic incompatibility and poor adhesion between several polymer pairs, there is a large deterioration in mechanical properties. One can avoid this problem by the introduction of phase compatibilisers or graft polymerisation [8, 9]. However,

the resulting polymer may be opaque due to the relatively large size of the dispersed phase. The conductivity of the polymer decreases because of cracks created in to the polymer surface due to its brittle nature which distorts the conduction path of the polymer chain [10 -13]. This can be improved by the introduction of additives in to the matrix during preparation of blends. We made an effort to improve its micro-structure and conductivity properties by adding small amount of PMMA into it. The prepared blends was characterized by FTIR, SEM and DC conductivity by using two probe methods with Keithely 2100 electrometer to measure the resistance of the polymer.

2. EXPERIMENTAL

All the chemicals used for synthesis were of Analytical Reagent (AR) grade. Polystyrene (PS) powder form Sigma Aldrich (Aldrich-81387) India has approximately molecular weight (173 000, Mw/Mn), Poly(methyl methacrylate) (PMMA) resin with a $M_w=108,500$ were supplied by Canus Plastics, acetone (TEDIA, 95%) were used as received without further purification. For conductivity measurements, the pellets were coated with silver paste on either side of the surfaces to provide electrical contacts.

2.1 Preparation of polystyrene – poly(methyl methacrylate) (PMMA) blends

Polystyrene (PS) and poly(methyl methacrylate) (PMMA) powder were dried for five hours at 100°C to ensure low moisture levels. Further the dried PS and PMMA were used to prepare the blends by extrusion moulding technique in a 500 ml step polymerization reactor in the presence of modified agent cocoamphodipropionate. 5 g of PS and PMMA was dissolved in N-methyl-2-pyrrolidone (25 ml) solvent at 50 °C with constant stirring and preserved in separate beaker. The different compositions of PMMA added in PS (2, 4, 6, 8 and 10 weight percent) were made by weighing the accurate quantities [14, 15]. The resulting mixture was sonicated (probe

type sonicator was used at lower amplitude of less than 50 % at 20 kHz) for 1 h to get a uniform dispersion of the PMMA. The mixed solution was added drop-wise in cold ethanol (anti-solvent) under constant stirring, in order to precipitate out the solid mass. The precipitated solid fibrous mass was then vortexed (turbulent motion) using an Ultra Turax at 15,000 RPM for 10 minutes, kept for 1 day and then filtered off. The obtained mass was dried in ambient condition and grinded using a mortar and pastel. Similarly pure PS and PMMA were processed, subjected to a pre-treatment process, as that of the blends. This grinded mass was pressed under teflon coated metal mould in a compression moulding machine (S.C Dey & Co., Kolkata, India). Upper and lower half portion of the compression moulds were maintained at 170 °C and a pressure of 2 ton was applied for 5 minutes to fabricate the blend films [16].

3. CHARACTERIZATION

The prepared PS - PMMA blends were characterized by using Fourier transform infrared spectroscopy (FTIR), the surface morphology of the blends were studied using scanning electron microscopy (SEM).

The FTIR spectra of PS and its blends were recorded on Perkin Elmer (model 783) IR spectrometer in KBr medium at room temperature. For recording FTIR spectra, sample powders were mixed with KBr in the ratio of 1:25 by weight and grounded to ensure the uniform dispersion of samples in KBr pellets. The mixed powders were pressed in a cylindrical dye to obtain clean discs of approximately 1 mm thickness [17].

The surface morphology of PS and PS / PMMA blends were studied by using Phillips XL30 ESEM scanning electron microscope (SEM). The thin film samples are coated on the carbon tape which is mounted on aluminium tab, conducting gold is sputtered on the sample to avoid charging at the sample surfaces and selected areas were photographed.

DC conductivity was measured by using two probe method with Keithely 2100 electrometer to measure the resistance of the polymer blends. The samples were prepared in circular disc of 10 mm diameter and 1 mm thickness by pressing with hydraulic press (De - Luxe Trading Company, India. Ltd). The samples were coated with silver paste on either surface for better contact between electrodes and sample surface.

4. RESULTS AND DISCUSSION

Fig. 1 (a, b) shows the FTIR spectra of original PS and PMMA samples. The IR spectrum of PS showed absorption bands at 3026 and 2849 cm^{-1} corresponding to aromatic and aliphatic C-H stretching respectively. The peaks at 1601 and 1493 cm^{-1} are assigned to aromatic C=C stretching. The C-H deformation vibration band of benzene ring hydrogen's (5 adjacent hydrogen's) appeared at 758 cm^{-1} . Ring deformation vibration was observed at 700 cm^{-1} . The C-H stretching

vibrations of ring hydrogen's are seen from 3000 and 3100 cm^{-1} . The IR spectrum of PMMA showed absorption bands at 2951 and 1736 cm^{-1} due to $-\text{CH}_3$ asymmetric stretching and C=O stretching respectively [18 - 20]. The vibrational bands at 1483 and 1449 cm^{-1} are attributed to CH_2 scissoring and CH_3 asymmetric stretching or deformation of PMMA. The characteristic peak at 1390 cm^{-1} appears due to OCH_3 deformation of PMMA. The bands appearing at 1273 and 860 cm^{-1} are corresponding to C-O stretching and C-O-C stretching of PMMA. The absorption bands corresponding to CH_2 twisting, wagging and rocking modes of PMMA appear at 1192, 950 and 750 cm^{-1} respectively. The FTIR spectra of PS/PMMA blends are shown in Fig. 1 (c). The peaks at 1732 and 1149 cm^{-1} in all the blends represents the C=O and $-\text{OCH}_3$ stretching of PMMA. The peaks at 1600 and 698 cm^{-1} in all the blends represents the C-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 stretching 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 of polymer blends.

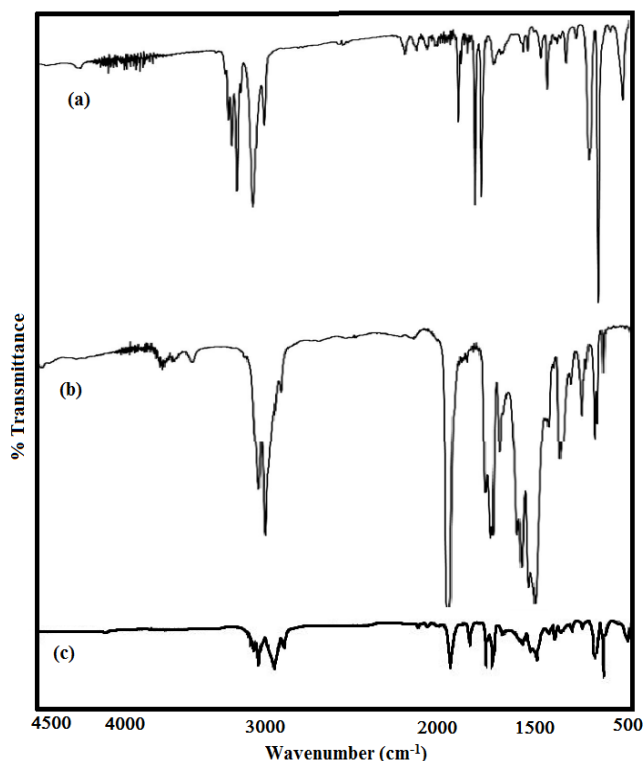


Fig. 1:(a -c) FTIR spectra of neat PS, PMMA and PS/PMMA blends

Fig. 2 (a, b) shows the SEM image of neat polystyrene indicating that the film surface is rough and rigid due to its non-Newtonian fluid with viscoelastic properties and ductility.

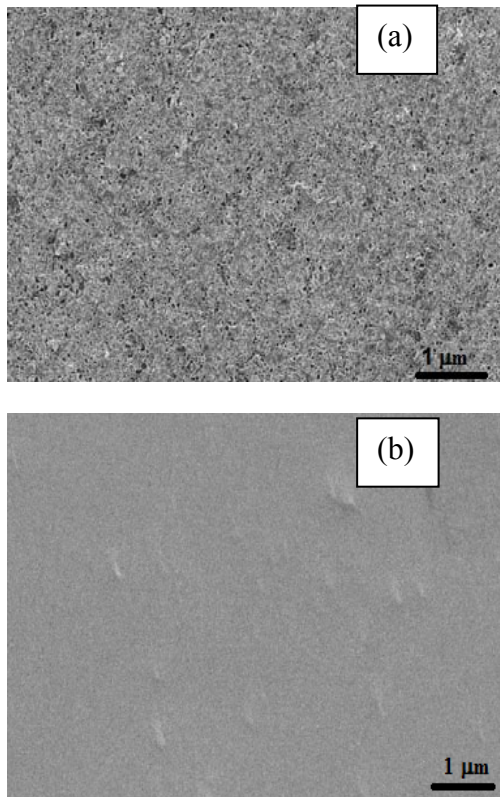


Fig. 2:(a, b) SEM image of neat PS and PS/PMMA blends

The microstructure and compatibility of PS – PMMA blend is improved, results downy the surface causes more smoother compared to pure PS.

3.1 DC Conductivity

The Dc conductivity of the PS -PMMA blends was studied at various temperatures from 40 to 160 °C as shown in Fig. 3. It is observed that the conductivity increases with increase in temperature as well as PMMA concentration in the polymer matrix. The observed conductivity increases with three steps similar to Nevil Mott semiconductor plot [21 -24]. It is observed that initially conductivity is constant up to 80 °C after that it gradually increases with increase in temperature till 160 °C. The conductivity increase with increase in PMMA concentration may be due to the increase in the electron density. Among all the blends, 6 wt % shows the high conductivity of $12 \times 10^{-9} \text{ S/cm}^{-1}$ due to the elongation of polymer chain length confirmed by NTC plot. It is also interesting to note that up to 6 wt % blend, the activation energy increases with increase in PMMA concentration indicating that it is significantly affecting the charge transport properties in polymer blends. The negative thermal coefficient (NTC) (α) of the PS – PMMA blend is shown in Fig. 4 as a function of various weight percentage of PMMA [25]. Generally the negative thermal coefficient (α) refers to blends that display decrease in the electrical resistance with increase in dopant concentration.

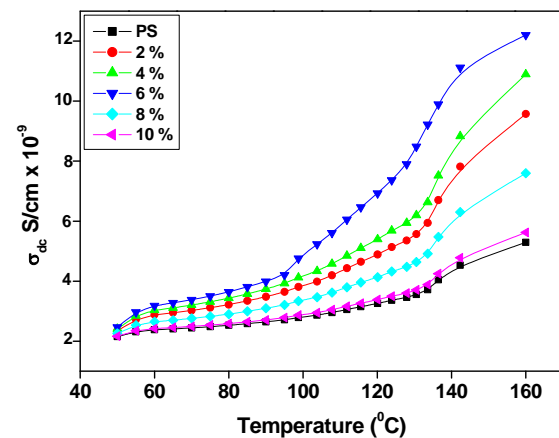


Fig. 3:DC conductivity of neat PS and its blends

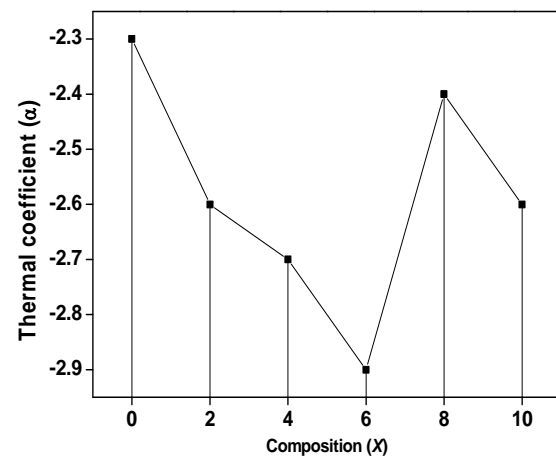


Fig. 4: Negative thermal coefficients (α) of neat PS and its blends

It is observed that the negative thermal coefficient increases with increase in PMMA weight percentage in PS indicating that there was decrease in electrical resistance due to the extended chain length of the polymer upon increase in temperature [26, 27]. It is also observed that there is a small change in the NTC values among blends, on increasing the temperature as well as dopant concentration. The α value linearly increases with increase in filler concentration up to 6 wt % composition after that its value decreases.

5. CONCLUSION

Polystyrene modified PMMA blends were prepared by the extrusion moulding technique with different weight percentage (2, 4, 6, 8 and 10 wt %). The prepared blends were characterized by FTIR spectra and the important peaks are found at 1732 and 1149 cm^{-1} in all the blends representing the C=O and $-\text{OCH}_3$ stretching of PMMA. The peaks at 1600 and

698 cm^{-1} in all the blends represents the C-C stretching and ring deformation of polystyrene. SEM image shows that the surface become smoother and it can be noticed that PMMA and PS interface is compatible due to the surface modified agent. DC conductivity increases with increase in temperature as well as PMMA percentage up to 6 wt % and the highest conductivity is found to be 12×10^{-9} S/cm. This increase in conductivity is due to the increase in charge density and extended charge length which is confirmed by NTC plot. Therefore, these materials have potential use in engineering and technological applications.

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