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Miscibility Evaluation of Polystyrene and Poly (Methyl Methacrylate) Blends: Analysis of Mechanical, Thermal, Morphology, and Viscoelastic Properties

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Abstract

Partially miscible blend of polystyrene (PS) and poly (methyl methacrylate) (PMMA) was successfully prepared employing melt blending technique. The materials were blended at temperature above upper critical solution temperature (UCST) to obtain miscibility, as observed from cloud point measurements. The complex modulii and viscosity derived from melt rheology analysis as a function of angular frequency were also used to study the effect of PMMA loading on the miscibility of PS/PMMA blend. The cross-sectional morphology suggested partial miscibility, which was further confirmed from the intermediate behavior of the blend as compared to its constituents, pertaining to mechanical and thermal properties as well as melt rheology and viscoelastic characteristics.

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Abbreviations: PMMA, poly (methyl methacrylate); **PS**, polystyrene; **UCST**, upper critical solution temperature

INTRODUCTION

The combination of two or more chemically and structurally different polymers gives rise to blends with a range of properties, not deliverable by any of the constituents alone. Blending usually results in immiscible or partially miscible blends. A stable interface is a pre-requisite for partially miscible blends to be used in any application. The interface of such blends is considered as a third matrix or phase whose width is dependent on the inter-diffusion of constituent polymer matrices.[1,2] Miscible polymer blends exhibit single phase behavior while immiscible polymer blends exhibit two or more distinct phases at all compositions and temperatures. PS and PMMA form two distinct phases giving rise to immiscible system, which has been widely investigated for their phase separation. From the application point of view, miscibility is not a prerequisite since blends represent an easy way to design a new polymeric material. It is well known that PS and PMMA lead to heterogeneous (phase separated) blends due to the immiscibility between components at high molecular weights.[3] However, at lower molecular weights, they are expected to show UCST behavior. Also, incorporation of nanofillers within polymer blends is expected to have synergistic effects pertaining to mechanical, thermal, fire performance as well as rheological behavior.

In the present study, an attempt has been made to examine the miscibility characteristics of PS and PMMA blends prepared using melt blending technique, an area wherein many studies have not been undertaken. The miscibility window was studied from cloud point determination. Various blend compositions were studied for their performance through mechanical properties, thermal properties and cross sectional morphology. The processability, flow behavior and miscibility of the blends were studied in detail from the viscoelastic behavior and parallel plate rheometry.

MATERIALS AND METHODS

General Purpose Polystyrene (PS) (Grade-SC 203 LV), Poly(methyl methacrylate) (PMMA) of Grade IH-830-LG, obtained from M/s Shah Polymers (India) were used as the base matrices. PS and PMMA were melt-blended in a microcompounder (XPlore, 15 ml, M/s DSM, Netherlands). The processing temperature was maintained at 210°C with 100 rpm screw speed for 13 min. The whole process was carried out under nitrogen atmosphere to avoid any possible oxidative degradation. PMMA and PS pellets were dried at 65°C for 12 h prior to melt blending. Samples as per ASTM standards were prepared using the mini injection jet coupled with microcompounder with mold temperature at 60°C.

PS and PMMA were dissolved in *N*,*N*-dimethylformamide and heated to higher temperatures wherein the blends formed a complete transparent solution to study the cloud point. This solution was then cooled at a rate of 1°C/min and the temperature at which the solution turned cloudy or exhibited turbidity was noted. The procedure was repeated for different compositions with varying PMMA loading. A cloud point curve was drawn through the cloud point observed for different compositions.

The tensile properties of PMMA, PS and their blends were studied using universal testing machine (LR 100K, M/s Instron Instruments Ltd., UK), for analyzing the effect of various organic modifiers on the matrices. All the samples were prepared as per ASTM D 638 standards with dimensions 127 × 32 × 3 mm. The izod impact properties were measured as per ASTM D 256 (63.5 × 12.7 × 3 mm dimension with a v-notch of 45°). Subsequently, the measurements were carried out in an Impactometer (M/s CEAST, Italy) attached with a notch cutter. SEM analysis was carried out using EVO MA15 (M/s Carl Zeiss SMT Ltd., Germany) at 20 kV. PS/PMMA blend and its nanocomposite were analyzed for their miscibility characteristics. The storage modulus (E') and damping factor ($\tan\delta$) of PS, PMMA and their blends under dynamic conditions were studied using Q 800, M/s TA Instruments (USA).

The samples were scanned at a fixed frequency of 1 Hz with a static strain of 0.3% and dynamic strain of 0.1%. PMMA and its nanocomposites were analyzed from –200 to +200°C wherein both α and β transitions were studied. Melt rheology characteristics of PMMA, PS and PS/PMMA blend were studied in the angular frequency range of 0.01 to 100 rad/sec at 210°C in a parallel plate rheometer (Mars III, M/s Thermofischer Scientific, Germany).

DSC analysis was carried out for PS, PMMA and PS/PMMA blend for determining their glass transition temperature (T_g). Samples (5–10 mg) were studied at the temperature range of 50–210°C at scanning rate of 10°C/min under nitrogen atmosphere to relieve any thermal history of the amorphous state employing Q 20, M/s TA Instruments (USA).

RESULTS AND DISCUSSION

Cloud Point Determination

In the case of PS/PMMA blends, which are majorly phase-separated, the styrenic part is expected to impart properties like strength, flame retardancy and solvent resistance, while PMMA would provide many excellent properties such as light weight, high light transmittance, chemical resistance, colorlessness, weathering corrosion resistance and good insulation. Figure 1 depicts the cloud point measured for various blend ratios of PS/PMMA to understand the miscibility window. All the blends displayed UCST (upper critical solution temperature) behavior wherein the two blend components are miscible at a temperature above 200°C for medium molecular weight components. Miscibility gaps were observed for the blends containing 30, 40 and 50 wt% of PMMA while the blend containing 70 wt% remained immiscible. The blends containing ~30 wt% of PMMA were partially miscible at processing temperatures. According to Hildebrand solubility theory, solubility parameters (δp) of individual matrices define the miscibility between them in the absence of any interfacial compatibilizer. Considering their solubility parameters and cloud point study, PS and PMMA having Hildebrand solubility parameters (δp), 17.4 and 18.6 MPa$^{1/2}$ respectively shall display partial miscibility at higher temperatures.

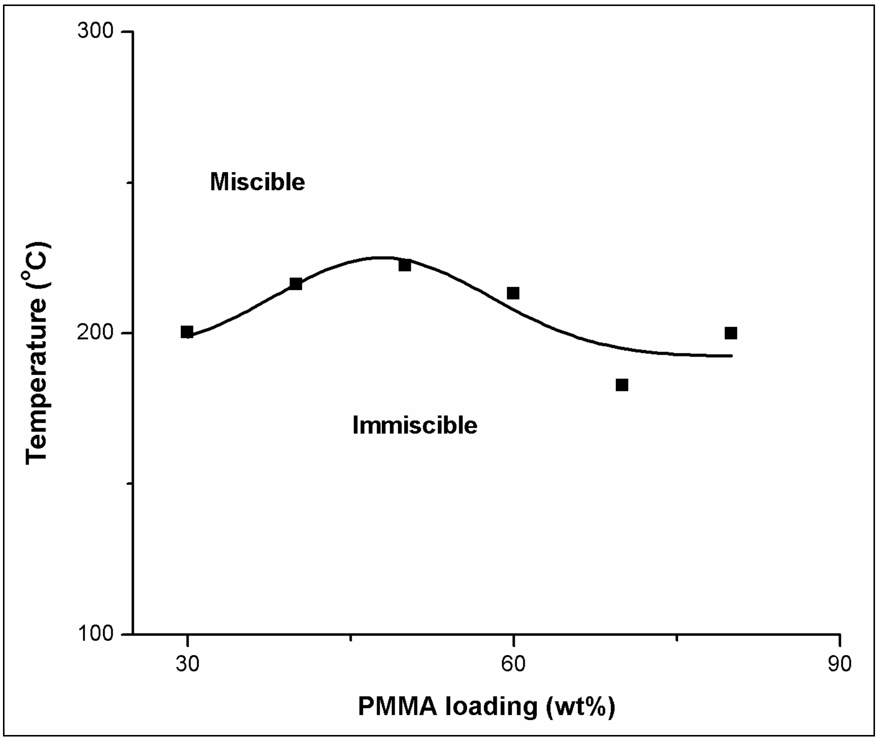

Fig. 1. *Cloud Point Measurement of PS/PMMA Blends at Different Blend Ratios.*

Mechanical Properties

Stress-Strain Behavior

The stress–strain behavior of PS, PMMA, PS/PMMA blends and its nanocomposite are depicted in Figure 2. All the blend compositions (PS/PMMA 70/30, 50/50, 30/70) displayed brittle failure similar to PS and PMMA (explained in earlier chapters). It was also noticed that with the incorporation of PMMA to the tune of 30, 50 and 70 wt% to PS matrix, the stress and strain at break of PS increased to an intermediate value between that of PS and PMMA. When the PMMA content was increased to 50 and 70 wt%, there was an increase in the strain at break while the stress reduced, which in turn decreased the tensile modulus. The effect of blending PMMA within PS was studied in terms of tensile modulus, tensile strength, strain at break and impact and is enumerated in Table 1. It could be noted that all the blends displayed intermediate results for all mechanical properties studied and that addition of PMMA has improved the mechanical integrity of PS.

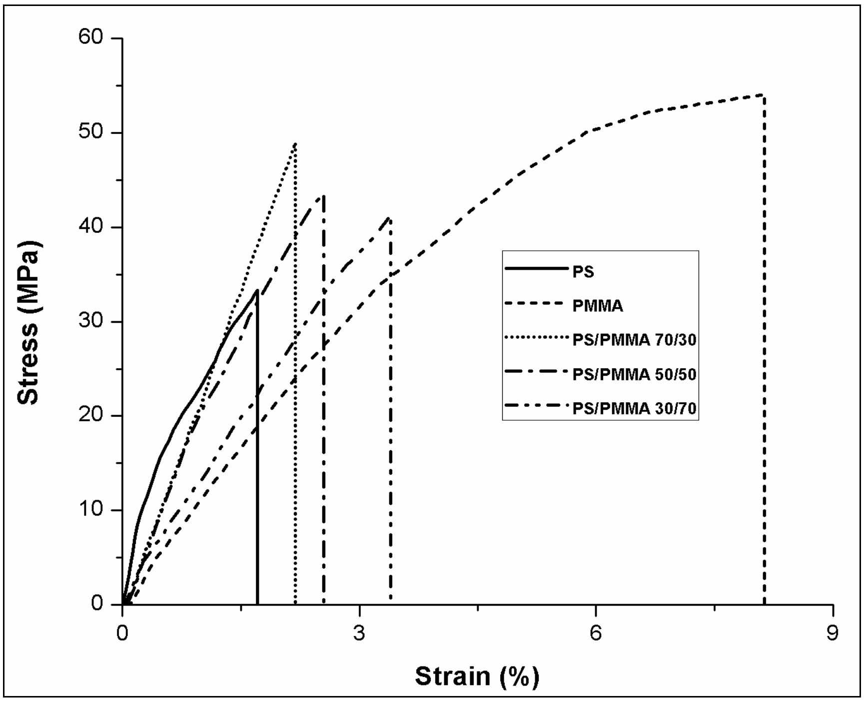

Fig. 2. *Stress–Strain Behavior of PS, PMMA and its Blends.*

Tensile Modulus, Tensile Strength, Strain at Break, and Impact Strength

The base matrices used in the study, PS and PMMA displayed tensile modulus of 845 and 1396 MPa, respectively. The tensile modulus of PS, PMMA and their blends, depicted in Table 1 show that the incorporation of tougher PMMA within highly brittle PS resulted in drastic improvement. Incorporation of 30 wt% of PMMA resulted in optimum increase in the modulus value to the tune of 59.76% to 1350 MPa as compared to that of 845 MPa for PS. However, a decrease in the tensile modulus was observed with an increase in the PMMA content to 50 and 70 wt% due to increased phase separation of the blend components as the dispersed and continuous phase were altered. This incompatibility may further be attributed to the earlier solidification of the PS matrix than the minor phase, PMMA resulting in lower interfacial tension and hence the poor internal stress transfer. The incorporation of nanoclay improved the tensile modulus owing to the inherently higher modulus of the nanofiller.

Similar results were obtained for tensile strength of the blends as compared to that of virgin polymer counterparts. The strength of PS was increased significantly when blended with PMMA, owing to the higher strength characteristics of the acrylic polymer. PS/PMMA blend with 30 wt% PMMA exhibited an optimum value of 48.04 MPa, equivalent to 99.2% increase as compared to that of PS. With the increasing PMMA content, the blends turned completely immiscible leading to poor interface and hence, the stress was not transferred effectively between the phases. The plastic deformation might have affected the phases separately and PS phase might have failed first leading to a decreased strength. A marginal increase was observed in the strain at break of PS/PMMA blends as compared to that of virgin PS. PS and PMMA chains are unable to move independent of their neighbors because of secondary bonds between the macromolecular chains and geometrical interaction between the molecules.

This leads to high resistance to deformation, resulting in decrease of strain at break in case of all the blend compositions studied. When the PMMA loading was increased, the strain at break was found to increase indicating the dominance of PMMA phase at higher loading.

Both PS and PMMA exhibited similar impact properties depicting, 24.85 and 24.20 J/m, respectively. All the blends indicated decreased energy dissipation and hence fracture toughness. Since both the matrices are amorphous and inherently brittle, the resultant blends also displayed similar phenomenon with a decreased magnitude of impact strength. This decrease may again be correlated with the sliding of polymer chains within the immediate vicinity of the counterparts. Also, the decrease in impact strength might be presumably due to the internal stresses in the sample during melt blending.[4] From the above results, it may be concluded that the rigidity of PS could be reduced via blending it with PMMA. Optimum performance was displayed by the blend with PMMA as minor phase (30 wt%).

Table 1. *Mechanical Properties of PS/PMMA Blends.*

Sample	Tensile Strength (MPa)	Tensile Modulus (MPa)	Strain at Break (%)	Impact Strength (J/m)
PS	33.22±0.97	845±15.68	1.71±0.09	24.85±0.59
PMMA	56.54±0.49	1396±25.89	8.32±0.68	24.20±0.98
PS/PMMA 70/30	48.04±0.85	1350±22.54	2.16±0.12	21.97±0.64
PS/PMMA 50/50	43.96±0.72	1307±19.84	2.58±0.15	19.81±0.85
PS/PMMA 30/70	41.46±0.38	1254±17.45	3.20±0.19	16.57±0.87

Cole–Cole Plot

The cole–cole plot of PS/PMMA blends with various compositions, viz., 70/30, 50/50 and 30/70 was studied and is represented in Figure 3. As observed from the plot, the 50/50 blend composition displayed two distinct relaxation mechanisms contrary to the behavior of other blend compositions. The high frequency relaxation may be correlated to that of PS matrix while the low frequency relaxation to that of the dispersed phase, PMMA. This might confirm phase-separation at higher PMMA content. Further, at 50/50 loading of PS and PMMA, both constituents are equally strong to display their distinct relaxation peaks, which would otherwise be dominated by the continuous phase.

A plot depicting G'' vs. G' (Figure 4) was plotted to study the miscibility characteristics of the blend. As explained by Han’s group, a miscible blend shows similar slope as compared to that of the constituents.[5] In the present study, it was observed that the blend showed a slope equivalent to that of PS and PMMA matrices. Thus, the blend composition, PS/PMMA 70/30 shall be considered as a co-continuous blend, from the rheological, morphological and thermal analysis.

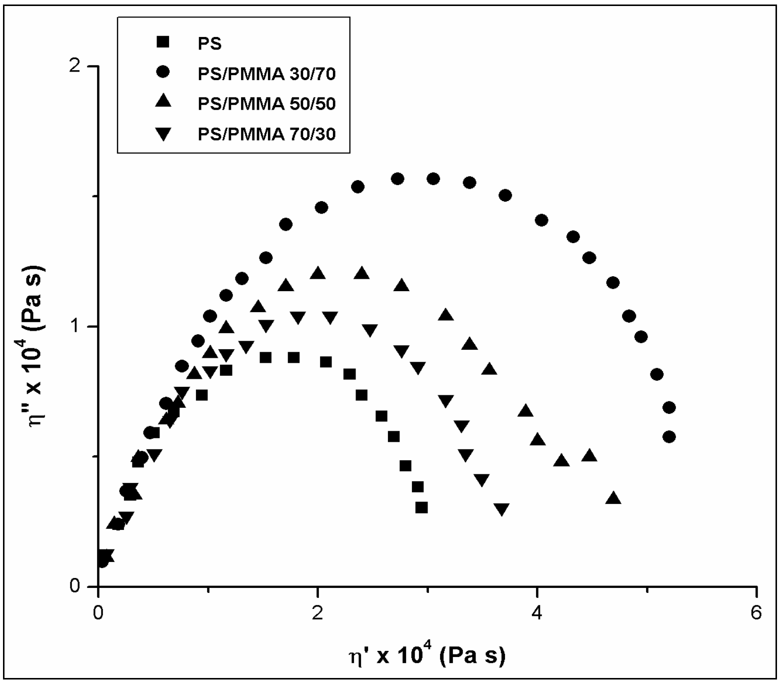

Fig. 3. *Cole–Cole Plot of PS and PS/PMMA Blends.*

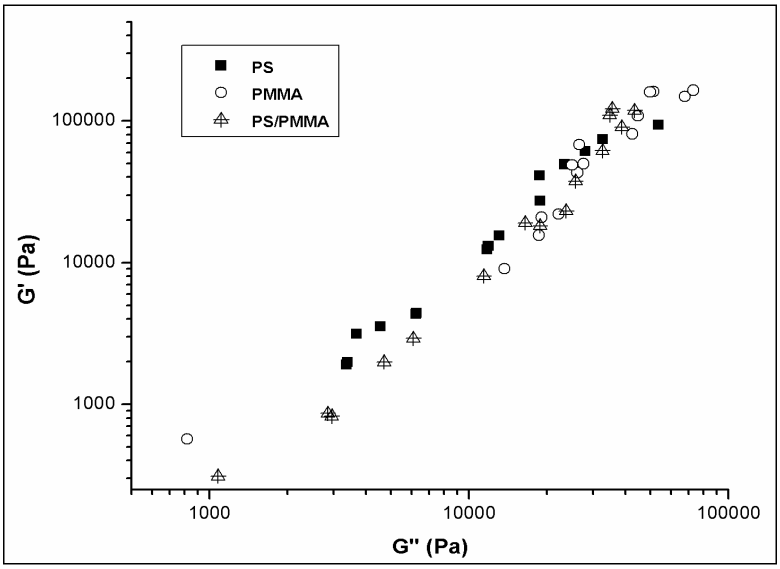

Fig. 4. *G" vs. G' Curve of PS, PMMA and PS/PMMA Blend.*

Cross-Sectional Morphology

From the SEM micrograph in Figure 5, it was noted that the blend surface showed more or less uniformly dispersed PMMA phase within the continuous PS matrix emphasizing better interfacial properties. The average particle size of PMMA was calculated to be 1.54 µm in the PS/PMMA blend. The observed well distributed morphology may be ascribed to the melt mixing carried out at temperature above UCST. This further confirms reduced interfacial energy between the two phases, PS and PMMA. However, the distribution of void size was not uniform throughout the bulk, indicating a small degree of phase separation between the blend constituents. This non-uniform size distribution may also be due to the shearing force exerted on the PMMA domain during mixing process.

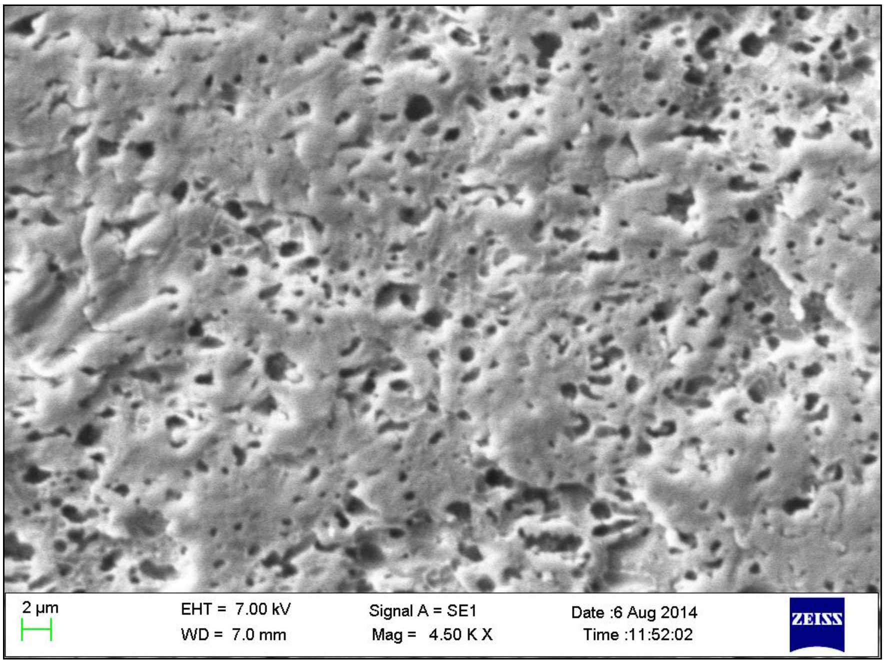

Fig. 5. *SEM Micrograph of PS/PMMA Blend.*

Viscoelastic and Melt Rheological Characteristics

The viscoelastic properties such as storage modulus E', and tanδ of PS, PMMA and PS/PMMA blend are depicted in Figures 6 and 7, respectively. As observed in the Figure 6, a stable plateau was observed till ~100°C for PS and PMMA, beyond which there was a drastic decrease in the modulus in case of PS while PMMA displayed a gradual decrease until 110°C.

This phenomenon may be attributed to the relaxation of macromolecular chains as a result of T_g of both the polymers. PS is more stable than PMMA, which is evident here from an increased magnitude of E′ to the tune of 25% (3000 MPa at 30°C) in case of PS, as compared with that of PMMA. In case of PS/PMMA blend, the modulus gradually decreased till 104°C after which a drastic decrease was observed. tanδ vs temperature curve depicted in Figure 7 may be correlated to the T_g of PS, PMMA and PS/PMMA blend. PS displayed a T_g around 102°C while the T_g of PMMA was around 120°C. As observed, the PS/PMMA blend displayed a T_g of 114°C intermediate to that of its constituents, PS and PMMA. These β-transition peaks revealed a decrease in free volume of PS with the incorporation of PMMA as the dispersed phase in the blend matrix. The chain mobility was also restricted due to formation of a compact structure that required more activation energy for segmental motion thereby leading to an increase in T_g of the blend.

Oscillatory shear dynamic moduli, G' and G'' of PS, PMMA, PS/PMMA blend and its nanocomposite are shown in Figures 8 as a function of angular frequency. Both PS and PMMA showed classical behavior of polymer melts with a Newtonian plateau at high frequencies and a terminal zone in the low-frequency region with low slopes for G' and G'' curves.

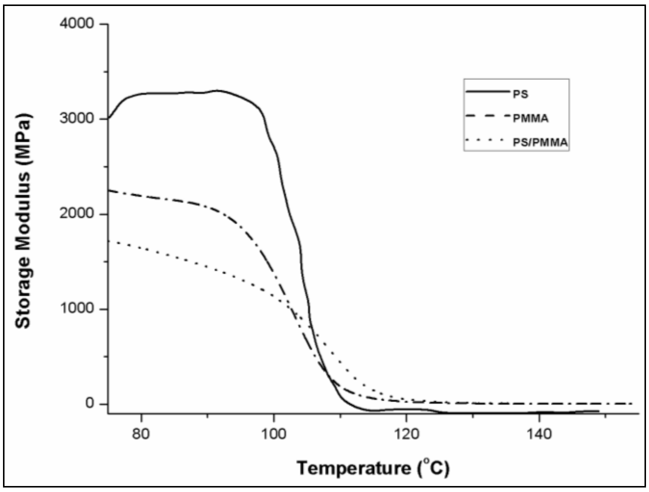

Fig. 6. *Variation in Storage Modulus of PS, PMMA, and PS/PMMA Blend.*

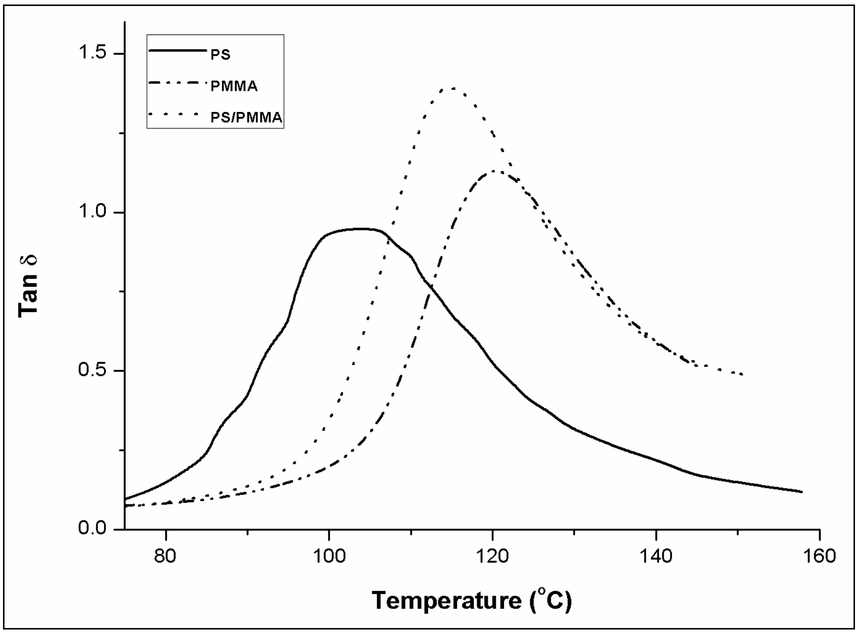

Fig. 7. *Variation in tanδ of PS, PMMA and PS/PMMA Blend.*

As observed from the Figure 8, PMMA showed higher modulus through the frequency range indicating improved melt strength as compared with PS. The modulus of PS/PMMA reached an intermediate value at higher frequencies beyond 0.13 rad/sec indicating reinforcement effect of PMMA phase within the continuous PS matrix. The modulus values were continuously increasing with the angular frequency in case of both PS and PS/PMMA blend while PMMA reached an almost constant value beyond 10 rad/sec. Similarly, PS/PMMA displayed G'' values lower than PS as well as PMMA till 0.11 rad/sec, beyond which intermediate values were noticed. The increase in the melt storage modulus of PS with the incorporation of PMMA at higher frequencies might be the result of a co-continuous structure in the blend. According to Kalfus *et al.*, the immobilization of polymer chains causes difference in strain dependence of the blends or composites.[6]

The complex viscosities (η^*) of PS, PMMA and PS/PMMA blend its nanocomposite as a function of angular frequency are plotted in Figure 9. The viscosities displayed in the figure showed a smooth transition to frequency-thinning behavior (shear-thinning) at high frequencies. The incorporation of PMMA within PS matrix led to increased melt viscosity than that of PS. The incorporation of PMMA also led to long relaxation times for the blend and consequently high sensitivity of the cloud points to change under shear flow.

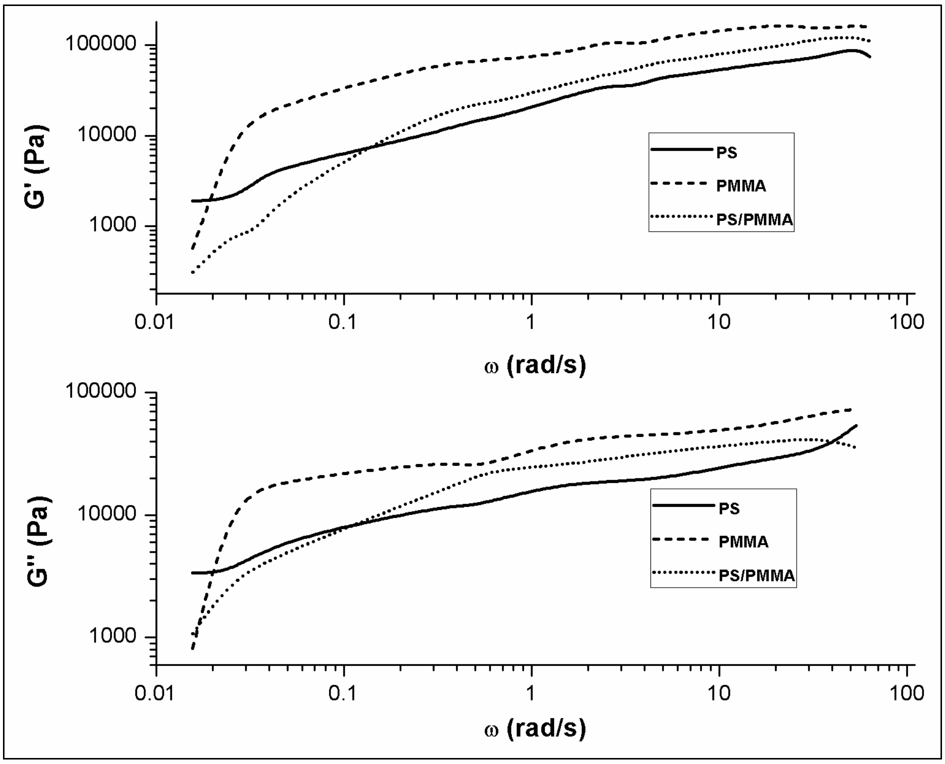

Fig. 8. *Variation of G' and G" of PS, PMMA and PS/PMMA Blend as a Function of Angular Frequency.*

The viscosity behavior of the blends ideally obeys the rule of additivity, which states that:

$\log\eta^*_{\mathrm{blend}}=\log\eta^*_{\mathrm{PS}}+\log\eta^*_{\mathrm{PMMA}}$

Where η^*_{blend} is the viscosity of the blend system, η^*_{PS} the viscosity of PS and η^*_{PMMA} is that of PMMA melt. However, the experimental results observed in the present study are contradictory to that of the theoretical explanation, which showed an intermediate viscosity for the blend. This may further be correlated to the findings of Vashishtha *et al*. [7] According to him, the viscosity of the blends may also depend on the compatibility of the component matrices. The reinforcing effect of PMMA might have helped in improving the viscosity of PS, despite the repulsion-interaction of these incompatible components.

Glass Transition Temperature

Figure 10 and Table 2 show the DSC thermograms of PS, PMMA and PS/PMMA blend. Miscible polymer blends show a single glass transition whereas multiple transition peaks are expected in case of immiscible blends.[8] As observed from the figure, the PS/PMMA blend exhibited a single broad transition at ~97°C, which may be correlated as the glass transition of the blend composition. Thus, the blend demonstrated an intermediate response towards T_g. In case of PS/PMMA incompatible blends, the PMMA chains rigidifies in the presence of PS, while the opposite occurs with the PS chains.[9] This may lead to an increase in the T_g of PMMA phase and a decrease for PS phase leading to an intermediate T_g value for the resultant blend. Further, this may also be attributed to the overlapping of 02 different transitions since the T_gs of PS (96°C) and PMMA (99°C) are too close to each other.

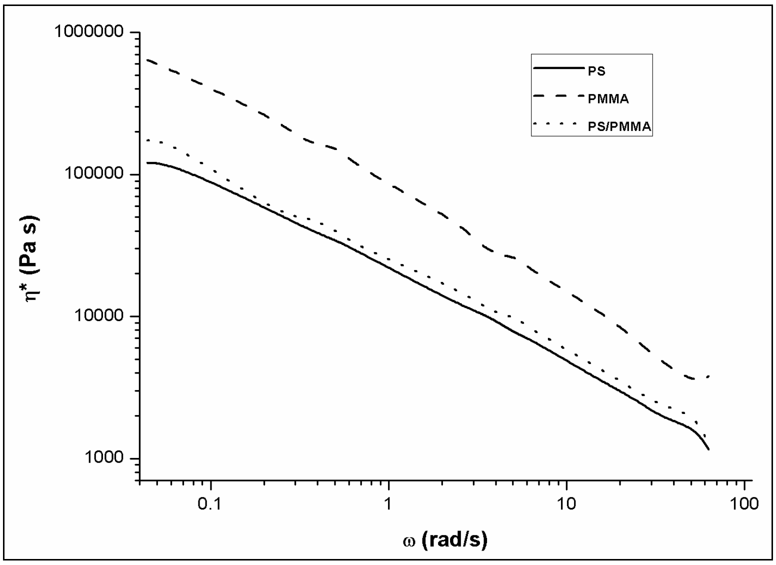

Fig. 9. *Complex Viscosity of PS, PMMA and PS/PMMA Blend as a Function of Angular Frequency.*

Table 2. *Glass Transition Temperature of PS, PMMA and PS/PMMA Blend.*

Sample	**T_g (°C)**
PS	96
PMMA	99
PS/PMMA	97

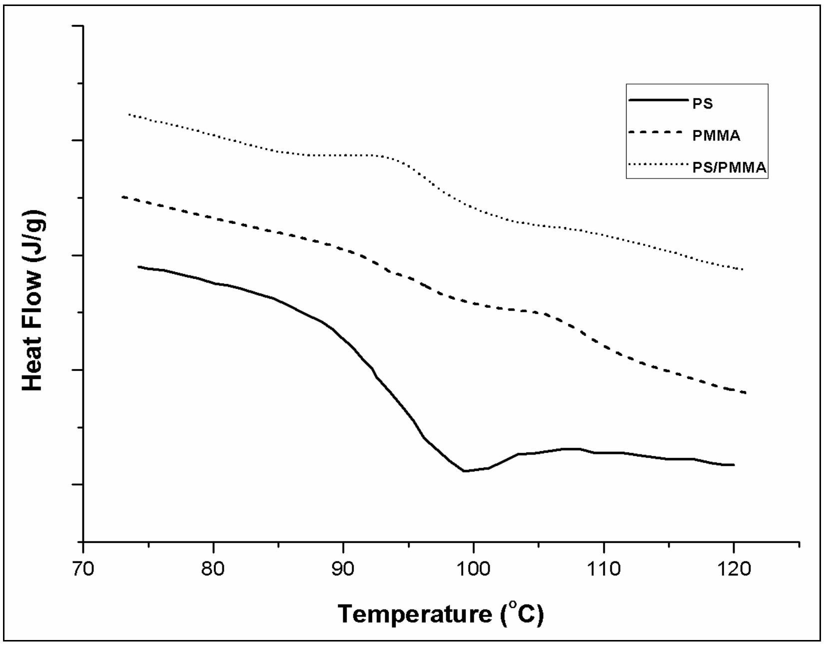

Fig. 10. *DSC Thermograms of PS, PMMA and PS/PMMA Blend.*

CONCLUSION

Melt blending technique under controlled conditions was effectively used for blending PMMA and PS. Cloud point measurement as well as cole–cole plot of complex modulii revealed partial miscibility of PS and PMMA phases in the blend, processed above UCST temperature. This was also evident from the well distributed morphology observed in the scanning electron micrographs. The viscoelastic and melt rheology characteristics also displayed an intermediate response to that of blend constituents, which again confirmed a partially miscible structure. The broad range of glass transition was visible in case of PS/PMMA blend owing to the overlapped individual transitions of PS and PMMA. Thus, melt blending at temperatures above UCST shall result in a partially miscible blend of otherwise immiscible PS and PMMA.

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