

Miscibility and Thermal Studies of Isotactic Polystyrene and Poly (Cyclohexyl Methacrylate) Blends

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Abstract: Miscibility and thermal studies of isotactic polystyrene and poly (cyclohexyl methacrylate) blends (iPS/PCHMA) with different compositions were investigated by thermogravimetric method and differential scanning calorimetry (DSC). The thermogravimetric data under dynamic conditions (50–600°C) in an inert atmosphere shows the blends are miscible. Using DSC studies, a single glass transition temperature (T_g) for the blend confirm the miscibility of the compositions. The crystallization and melting enthalpy with composition deviates from additive rules. Comparison of the experimental and predicted results by the additive rule indicates the existence of the components interaction in the iPS/PCHMA blends. The addition of iPS improves the thermal stability of PCHMA for all compositions and the temperature ranges.

Keywords: isotactic polystyrene, poly (cyclohexyl methacrylate), miscible blends, thermal study.

I. INTRODUCTION

Miscibility of polymer blends is the subject of many researches from both theoretical and practical viewpoint. Most of binary blends consist of styrenic polymers (vinyl polymer with a pendant styrene or substituted styrene) and acrylic/methacrylic polymers (carbonyl-containing polymers) are immiscible. For example, the blends of PS with methacrylic polymers or polyacrylates are immiscible, however, miscible with poly(cyclohexyl methacrylate).[1], [2], [3]. The blend of PS/PCHMA shows miscible when the molecular weight of PS is relatively low, whereas higher molecular weight of PS make the blend immiscible.[1], [2]. Most of the studies have been reported for the blends corresponding to the atactic PS of melt mixing blends.[4], [5]. For the future industrial application, it is important to study the miscibility and thermal behavior for blends with isotactic content for controlling their properties, especially in solution blend.[6]. Theoretically, comparing with melt mixing, the solution mixing is beneficial to improve the compatibility of the two polymers and retard the macro-phase separation because of fast freezing of macromolecules.[7].

Usually, a miscible binary blend shows a single aging peak by DSC whose kinetics is in between those of the component polymers, whereas an immiscible blend exhibits two aging peaks corresponding to each of component polymers. Observing the aging peak is one of the quick and convenient methods that have been widely used for identifying the miscibility of polymer blends. However, there is general consensus that such experimental techniques alone, while very useful, cannot guarantee that a polymer blend is miscible in a molecular level. For a detailed and appropriate method to identify the miscibility between the components in a blend has been well developed. Several experiments are used to evaluate the miscibility of blends such as inverse-phase gas chromatography, light scattering, Hess's law calorimetric method, and the melting point depression. Among them the most widely convenient technique, the calorimetric method has been widely used due to the simplicity. It is well established that blending may greatly influence the thermal stability of the component polymers.[8], [9], [10]. Under degradation, considerable interactions may occur between components in the blend and/or their degradation products. The type of interaction depends on the degree of miscibility of the components and the ratio in the blend. Therefore, the purpose of this work is to investigate the miscibility of iPS and PCHMA and the influence of the blend composition on the thermal stability as a function iPS composition.

II. EXPERIMENTAL

Isotactic polystyrene with tacticity of 90%, molecular weight of $M_n=400,000$ and poly (cyclohexylmethacrylate) with $M_n=65,000$ were purchased from Scientific Polymer Products. The iPS/PCHMA blends of different mass fractions of polymers (100/0, 90/10, 80/20, 70/30, 50/50, 40/60, 30/70, 20/80, 10/90 and 0/100) were prepared by mixing in tetrahydrofuran (THF). The component polymers were first weighted and dissolved into THF with continuous stirring for 24 hours using a magnetic stirrer. Subsequently, the solution was poured into a petri-dish at room temperature. The solvent (THF) in the cast samples was first vaporized inside fume hood at a controlled temperature, followed by residual solvent removal in a vacuum oven for a week.

Thermogravimetric measurements were carried out on a TA instrument Q500 in order to control thermodegradation under a nitrogen atmosphere. Samples about 10 mg in weight were heated from room temperature to 600 °C for complete degradation at a heating rate of 5 °C/min.

The DSC experiments were performed using a TA instrument Q2000 differential scanning calorimeter where an empty aluminum pan employed as reference. The DSC was calibrated for temperature by indium with melting point of 156.6°C. For the DSC experiments, the scan was made with a heating rate of 10°C/min with a typical sample weight of 3 ± 0.1 mg. To prevent thermal degradation, nitrogen gas was circulated around the sample. The glass transition temperature (T_g), crystallization peak temperature ($T_{c,peak}$), melt temperature (T_m) and enthalpy of fusion (ΔH) were measured from room temperature to 300°C at a constant heating rate of 10°C/min.

III. RESULTS AND DISCUSSION

The dynamic heating of the iPS/PCHMA blends are shown in figure 1 as the thermogravimetric (TG) curves (residual mass versus temperature). These curves, obtained in the temperature ranges between 50– 600°C with a heating rate of 5°C/min. For simplicity few selected blends and for neat polymers, the residual masses with temperature are shown in figure 1a. Neat iPS has greater thermal stability than PCHMA, which is evidenced by the mean displacement of the weight loss curve to much higher temperatures as seen in figure. Three regions of temperature may be considered in investigating the thermal stability of iPS and PCHMA. The initial degradation of iPS starts at about 340°C. No significant change of mass loss was observed at this temperature and found solid iPS as stable. In the temperature ranges of 340–370°C, only negligible amount of mass losses; about 2% loss can be seen at 370°C, while between 393 to 423°C volatilization becomes very rapid and almost complete distillation occurs at 440°C. About 97 % mass losses at this temperature ranges. On the other hand the PCHMA degrade with three degradation step, an initial degradation of PCHMA starts at about 212°C, more mass losses at 298°C (~25% mass losses) and again it losses 65% at 347°C, and finally complete distillation occurs at 465°C that is few degree higher than that of distillation temperature of iPS. The derivative thermogram (DTG) is the rate of mass loss with temperature of these neat polymer and their blends are shown in figure 1b. PCHMA degrade in a triple-stage decomposition, which is represented by a triple peak in the DTG curves. The DTG curve of iPS shows the major degradation occurs from 370 and 450°C. The DTG peak value is increased upon the incorporation of iPS into PCHMA, indicating increasing thermal stability. At any temperature, PCHMA shows maximum weight loss when iPS shows the minimum, and intermediate for the blends. Thus it is clear and evidence that thermal stability of PCHMA increases as the iPS content increases.

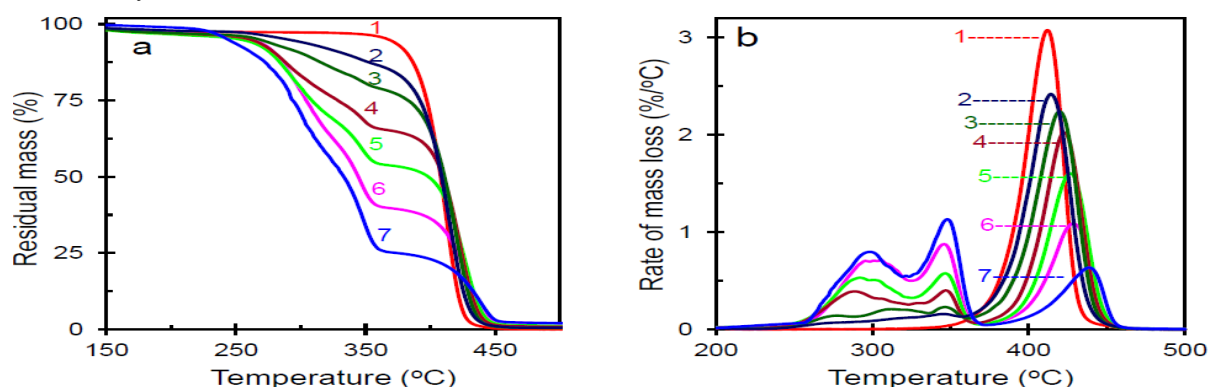


Figure 1: (a) Thermograms for residual mass with temperature; and (b) derivative of thermograms(rate of mass loss) with temperature for neat polymers and their blends are plotted for; (1) neat iPS, (2) 90/10, (3) 80/20, (4) 60/40, (5) 40/60, (6) 20/80 and (7) neat PCHMA.

DSC experiment was performed for the as-cast blend to reveal their thermal transitions, and to characterize the crystallization and melting behavior of iPS/PCHMA blends. For comparisons based on a uniform thermal history, all DSC thermograms take three runs and the result is followed from second runs after quenching from above the melt of the respective blend. Figure 2 shows the DSC heat flow for the iPS/PCHMA blends at a constant heating and cooling rate of 10°C/min from the melt. The DSC trace of neat iPS shows a significant crystallization and melting peak where both the peaks are influence by the PCHMA composition. In the blends, the crystallization peak temperature ($T_{c,peak}$) of iPS shifts to lower temperatures with PCHMA, indicating miscibility between this polymer pair. Such depression is due to the presence of non-crystalline PCHMA chains at the crystal growth front, may prevent the three-dimensional crystal growth of iPS. Wu et al. has reported in details about the crystallization temperature depression using dilution effect by non-crystalline part in the blends.[11].

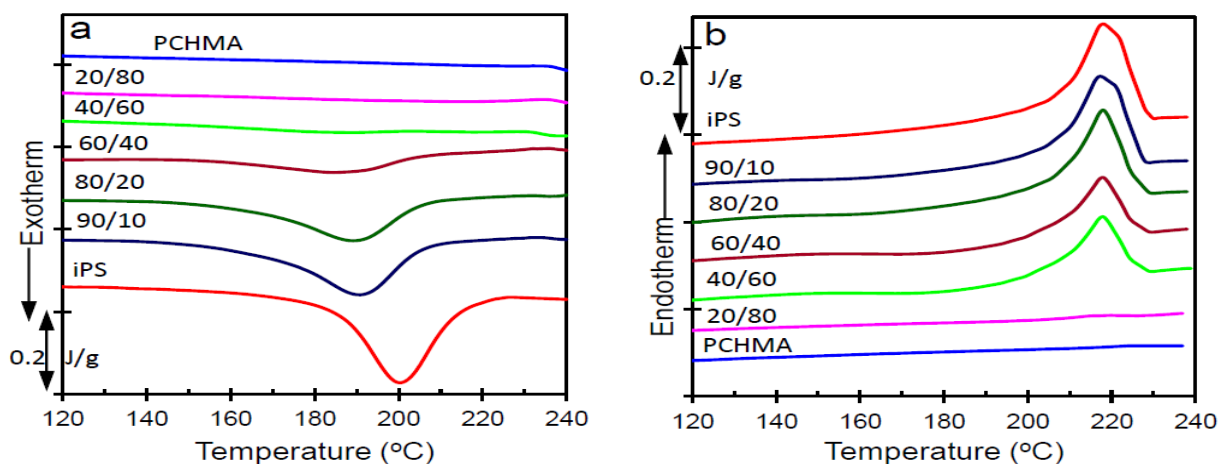


Figure 2: DSC scan for iPS/PCHMA blends with different compositions: (a) crystallization; and (b) melting cycle at the rate of 10°C/min.

The presence of non-crystalline PCHMA, retard the growth of iPS crystals and becomes much effective with the increase of PCHMA component in blends. The crystallization effect of PCHMA in iPS can be explained using the crystallization enthalpy; the total area of crystallization and melting peak. Figure 3 shows the crystallization and melting enthalpy of iPS as a function of PCHMA composition in iPS/PCHMA blends. It should be noted that the error in the experimentally determined enthalpies could not be rather large (ca. 2 %) in view of base line fluctuation problems. Within the entire content range of PCHMA, the melting and crystallization enthalpy does not follow the additive law drawn by broken line. The deviation from linearity infer the miscibility of the compositions in the blend.

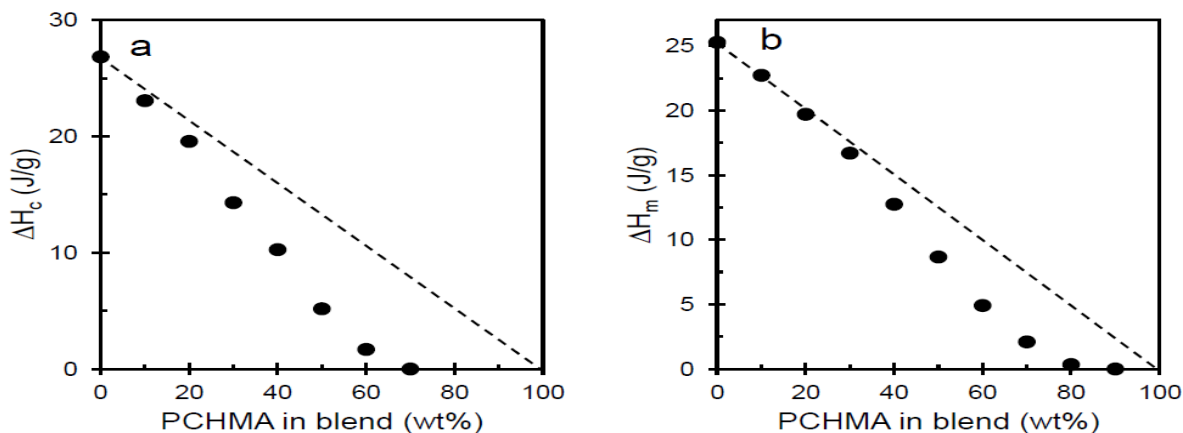


Figure 3: Composition of PCHMA dependence; (a) crystallization enthalpy; and (b) melting enthalpy for iPS/PCHMA blend system.

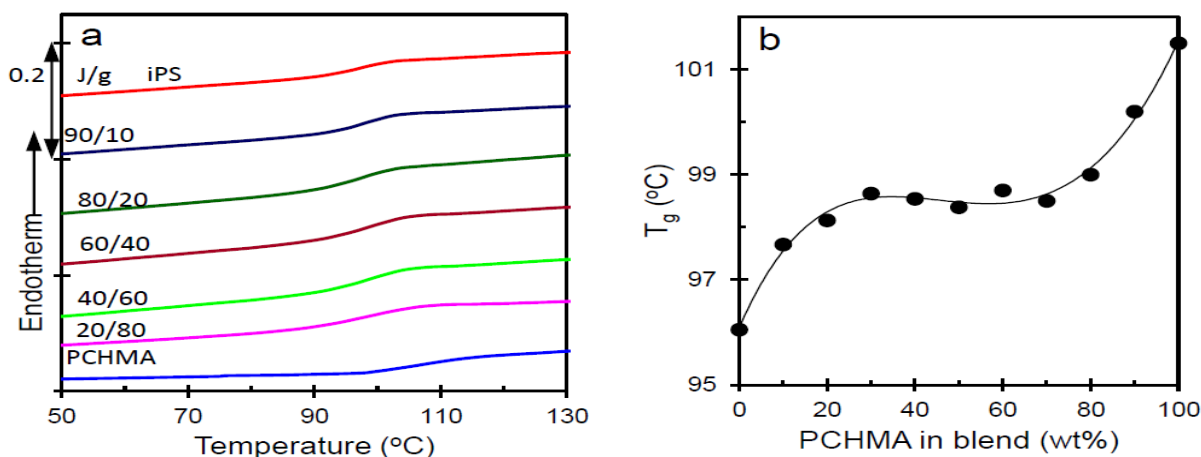


Figure 4: Composition dependence: (a) DSC curves; and (b) glass transition temperature for iPS/PCHMA blend system.

The miscibility of iPS and PCHMA was further investigated using differential scanning calorimetry (DSC). Investigation of glass transition temperature with composition usually shed more light on qualitative intersegmental interactions between the two components. The results are shown in Figure 4 as DSC curves for different compositions. On the DSC curve of iPS, the glass transition (midpoint about 96°C) can be noticed, while on the PCHMA curve, the glass transition can be noticed at 101.5°C. The change of the glass transition temperature with the blend composition is very interesting. The glass transition temperature increases first with PCHMA composition in iPS/PCHMA blends, showing a level off and then again increase with composition. The T_g composition relationship apparently suggests that the blend system is a miscible whose intermolecular interactions leading to miscibility depending on the compositions.

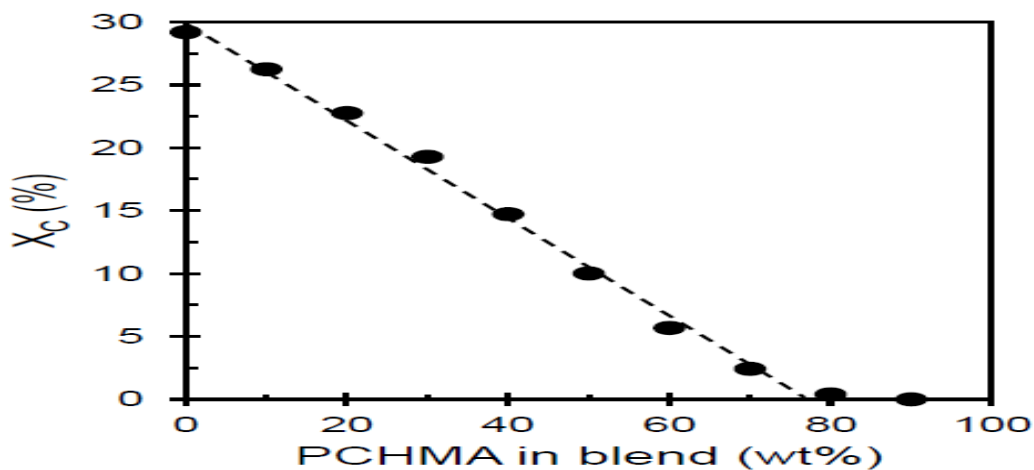


Figure 5: Composition dependence crystallinity for iPS/PCHMA blend system.

The crystallinity of iPS (X_c) is plotted with the composition in iPS/PCHMA blends, as shown in Figure 5. As the composition of PCHMA increases the crystallinity decreases and label off at high PCHMA. The linear decrease of crystallinity with PCHMA content is due to the increase of amorphous component in the blends. This is evident in all respects and is indicative of the homogeneous behavior consistent with the formation of a completely miscible blend.

IV. CONCLUSIONS

The miscibility and thermal studies of iPS/PCHMA blends were studied with different compositions by thermogravimetric and differential scanning calorimetry. The crystallization and melting enthalpy with composition deviates from linearity of additive law and the crystallinity decreases with composition in blends. Also a single glass-

transition temperature (T_g) with different composition-dependent was observed. All of these experimental results suggest that iPS and PCHMA are mixed at the molecular level within the blends at all compositions, confirming the miscibility of the blends. The addition of iPS into the blend improves the thermal stability of PCHMA for all compositions and the temperature ranges.

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