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Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

DSC STUDIES OF THERMALLY INDUCED PHASE SEPARATION OF HYDROGEN BONDED POLYMER BLENDS

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Abstract

The thermally induced phase separation behavior of hydrogen bonded polymer blends, poly(*n*-hexyl methacrylate) (PHMA) blended with poly(styrene-*co*-vinyl phenol) (STVPh) random copolymers having various vinyl phenol contents, was studied by temperature modulated differential scanning calorimetry (TMDSC). The enthalpy of phase separation was determined to be about 0.5 cal g^{-1} for one of the blends. A phase diagram was constructed from the TMDSC data for one of the blends. The kinetics of phase separation was studied by determining the phase compositions from the glass transition temperatures of quenched samples after phase separation. Subsequently, the phase separated samples were annealed at temperatures below the phase boundary to observe the return to the homogeneous state.

Keywords: glass transition temperature, hydrogen bonding, kinetics of phase separation, phase diagram, poly(*n*-hexyl methacrylate), poly(styrene-*co*-vinyl phenol), TMDSC

Introduction

Although thermally induced phase separation of polymer blends has been studied extensively during the past twenty years, there is only limited information on phase compositions. Among the techniques used for studying phase behaviors [1–9], two methods of determining phase compositions have been reported in the literature, NMR relaxation time [6, 10] and glass transition temperature (T_g) measurements. The calorimetric method has appeal because the experiments are relatively straightforward and because the method also enables the measurement of demixing enthalpy. The latter quantity is usually small in magnitude, often less than 1 cal g^{-1}, but the advent of Temperature Modulated Differential Scanning Calorimetry (TMDSC) has alleviated much of the experimental difficulty [11]. This motivates our investigation of the kinetics of phase composition changes. In the course of the study, the enthalpy of phase separation was also determined.

Aside from the obvious requirements that phase separation should take place at temperatures well below the onset of thermal degradation and that the T_g's of the component polymers should be far apart, the successful application of DSC to the determination of phase compositions is contingent on another condition. The calibra-

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tion curve relating T_g to blend composition should not contain regions in which a small uncertainty in the experimental T_g value causes a large error in the estimated phase composition. A case in point is the polystyrene/poly(vinyl methyl ether) (PVME) blend; the T_g values change by only 11°C when the blend compositions vary from 100 to 70% PVME [10]. Therefore, phase compositions deduced from T_g values will not be reliable in this region. Additionally, it is desirable that the return to single phase upon cooling takes place at a reasonable rate so that the kinetics of rehomogenization can also be examined. With the above considerations in mind, we have studied blends of poly(*n*-hexyl methacrylate) with poly(styrene-*co*-vinyl phenol)s containing various concentration of vinyl phenol. The vinyl phenol moiety was introduced in the random copolymer as a hydrogen bond donor to enhance miscibility. Since the phase diagrams of polymer blends can be shifted along the temperature axis by changing the density of hydrogen bonding [12], we have varied the vinyl phenol contents in our systems so that the phase diagram is located at a convenient temperature range for studying phase separation. Of the many blends examined, a particular combination of poly(*n*-hexyl methacrylate) and a styrene copolymer containing 7 mol% of vinyl phenol fulfills all the requirements outlined above. The results are reported below.

Experimental

Poly(*n*-hexyl methacrylate) (PHMA) was purchased from Aldrich Chemical Company, Inc., with a reported molecular weight (Mn) of 400000 g mol^{-1}. The glass transition temperature was measured by DSC to be –4°C. Poly(styrene-*co*-vinyl phenol) (STVPh) random copolymers with 3 (STVPh3), 7 (STVPh7), and 10 (STVPh10) mol percent vinyl phenol, respectively, were synthesized in our laboratory [13]. The molecular weights (Mn) of STVPh3, STVPh7, and STVPh10 were 40000, 33000, and 32000 g mol^{-1} determined by gel permeation chromatography (GPC) as polystyrene equivalents, and the glass transition temperatures were 108, 110 and 113°C, respectively. Solutions (3% w/v) of PHMA and STVPh were prepared by dissolving the individual polymers in toluene. Blends of various compositions, expressed in weight ratios, were made by mixing appropriate amounts of these solutions. Films for subsequent experiments were obtained by casting the solution on glass slides followed by slow evaporation of the solvent at room temperature, and vacuum drying at 60°C for 7 days to ensure the removal of the residual solvent in the samples.

Thermogravimetric analysis (TGA) studies were carried out on a Hi-Res$^{\text{TM}}$ 2950 TGA from TA Instruments with a 10°C min^{-1} heating rate under nitrogen purge. For certain samples, the high-resolution mode was activated with appropriate sensitivity and resolution. A TA 2920 Modulated$^{\text{TM}}$ DSC which can be operated in both standard and modulated modes was used for this study. In MDSC, the cells are subjected to a linear heating rate, when averaged over time, but with a sinusoidal modulation. Besides the accurate determination of heat capacity, MDSC increases both the sensitivity and resolution of the measurement [11] so that close or overlapped transitions can be effectively resolved. [14, 15]. About 4 mg of each sample was used throughout the experiments under helium purge. A heating rate of 3°C min^{-1} with an oscillation amplitude of 0.68°C and a period of 80 seconds was adopted when the TMDSC mode was activated. The glass transition temperature of the polymer was identified from the derivative of the heat capacity signal ($\mathrm{d}C_p/\mathrm{d}T$). The TA 3100 Thermal Solution software was used for data analysis and calculation.

An optical microscope (Nikon Optiphot) equipped with a hot stage (Mettler FP-82) and a Nikon FX-35A camera was used to observe the morphologies of polymer blends. A 1°C min^{-1} heating rate and nitrogen purge were used to observe the phase transitions of blend samples.

Results and discussion

The phase behavior of polymer blends comprising amorphous polymers is experimentally accessible in a 'window' which is bounded at high temperatures by the thermal degradation temperatures of the polymer blends and at the low temperatures by the glass transition temperatures of the system [16]. The thermal degradation temperatures of our blends were determined by TGA to be about 230°C, well above the phase separation temperatures which, as we shall see later, were much higher than the T_g's of the blends. Thus, there is a great deal of latitude in choosing a desired temperature for the study of the kinetics of phase separation.

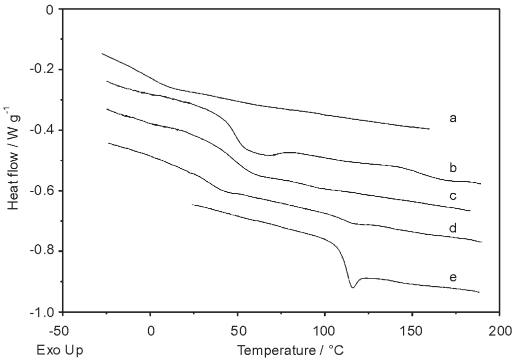

Fig. 1 DSC curves (heating rate 20°C min^{-1}) of (a) PHMA, (b) 50/50 STVPh10/PHMA, (c) cooled from 190°C at a rate of 20°C min^{-1}, (d) quenched from 190°C, (e) STVPh10

The 50/50 STVPh3/PHMA blend showed two glass transitions, thus immiscibility [17]. However, STVPh7 and STVPh10 were found to be miscible with PHMA over the entire range of blend compositions. The 50/50 STVPh10/PHMA blend was first investigated using the standard DSC mode with a heating rate of 20°C min^{-1}. A single T_g was observed at 50°C accompanied with a broad endotherm which most likely represents a physical aging phenomenon in the first scan, followed by an endothermic peak beginning at around 150°C (Fig. 1). The onset of the endothermic event was designated as the phase separation temperature because heterogeneity was observed by microscopy at a slightly higher temperature. After the phase separated sample was quenched from 190 to –170°C by immersing the sample pan directly into liquid nitrogen, two T_g's at 35 and 112°C were found in the second scan, i.e., there were two phases. On the other hand, when the phase separated sample was cooled at 20°C min^{-1}, a single T_g close to that of the original specimen was recorded, that is, phase mixing had taken place. A small phase transition near 75°C in Fig. 1c probably is the glass transition of the STVPh10-rich phase but the heat capacity jump is very small and does not warrant elaboration. The above experiment underscores the importance of preserving the phase separation state by rapid cooling. For the STVPh10/PHMA blend in question, there is no guarantee that the quenching procedure we adopted preserved the phase separated state.

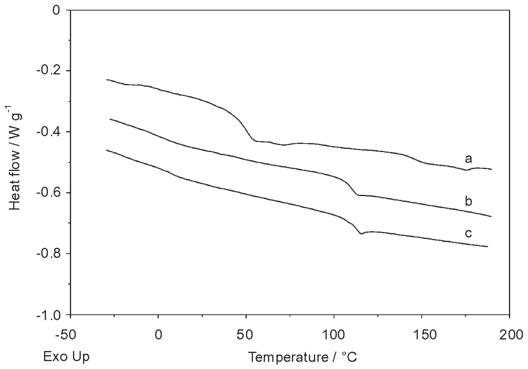

Fig. 2 DSC scans of 50/50 STVPh7/PHMA polymer blend (heating rate 20°C min^{-1}) first heating (a), heating after cooled from 190°C at a rate of 20°C min^{-1} (b), heating after quenched from 190°C (c)

To solve the problem of preserving the phase separated state during cooling, we investigated blends of STVPh7 with PHMA in hopes that the smaller number of hydrogen bond donors in the system would reduce the driving force, and hence the rate, of phase mixing. The thermograms of 50/50 STVPh7/PHMA blend showed a T_g at 44°C and an endotherm beginning at 139°C, about 11°C lower than the value for the STVPh10/PHMA blend (Fig. 2). The lower phase separation temperature was consistent with the weaker intermolecular interaction mentioned above. Interestingly, this weaker intermolecular interaction also retards phase mixing as we have hoped. The heating scan for the quenched, phase separated sample is represented by curve c. The corresponding heating curve for the same phase separated sample cooled at a lower heating rate of 20°C min^{-1} was given by curve b which was nearly superposable on curve c. This suggests that the phase compositions in the two samples are indistinguishable in the context of DSC measurements. This observation gave assurance that quenching essentially preserved the phase separation state in the heterogeneous region. Therefore we chose the 50/50 STVPh7/PHMA blend as the candidate for sys-

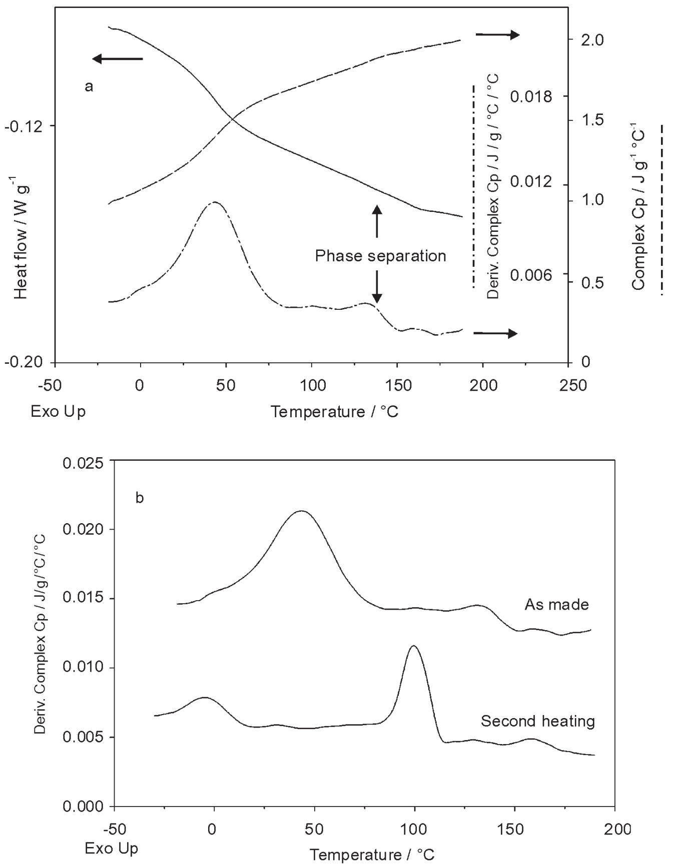

Fig. 3 MDSC scans of 50/50 STVPh7/PHMA polymer blend (a), dC_p/dT signals of as made sample and second heating scans after quenching from the two-phase region (b)

tematic study of phase separation and phase remixing. Because of its high sensitivity and resolution, TMDSC was used in the following experiments.

In Fig. 3a, the TMDSC scan of the 50/50 STVPh7/PHMA was shown from –20 to 180°C. The increase in heat capacity in the 30~60°C region signified a glass transition but the transition temperature was more conveniently identified at 43°C from the reversing heat flow signal with the help of dC_p/dT curve. As the temperature increased, a deviation from the baseline of the curve occurred at 130°C. The onset of this endothermic event can also been seen clearly in the derivative curve. After quenching the sample directly into liquid nitrogen from 190°C, the dC_p/dT signal of the subsequent heating scan showed two main distinctive peaks (Fig. 3b), which related to separated phases, followed by a baseline shift due to further phase separation process.

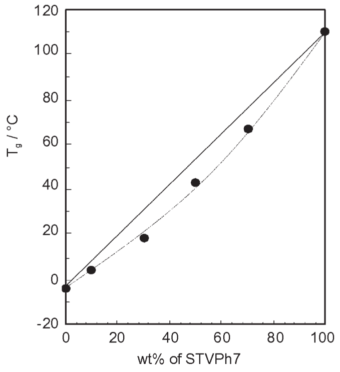

Fig. 4 Glass transition temperatures of STVPh7/PHMA blends

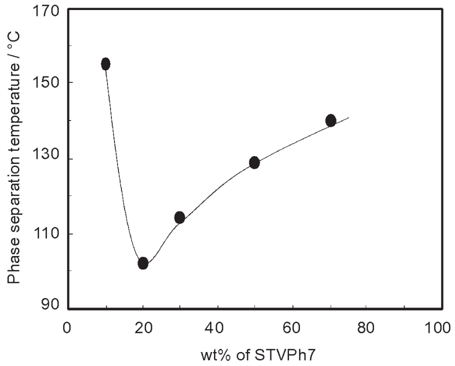

Fig. 5 Phase diagram of STVPh7/PHMA from MDSC measurements

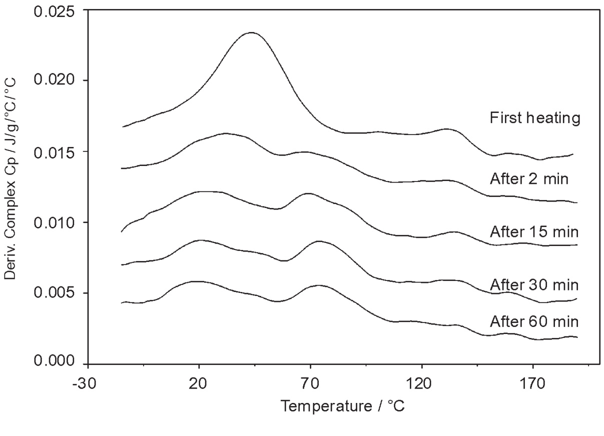

Fig. 6 dC_p/dT signals of 50/50 STVPh/PHMA blends maintained at 140°C for different time periods

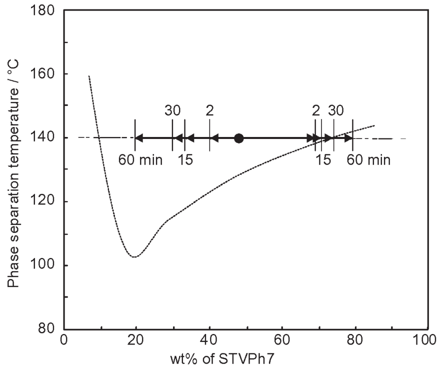

Fig. 7 Phase separation of the STVPh7/PHMA blend (50:50 wt% initial composition) at 140°C for different time periods. Phase boundary is represented by the dashed curve

The dependence of the glass transition temperatures on the compositions of the STVPh7/PHMA blends was shown in Fig. 4. Phase compositions in heterogeneous samples were estimated from this calibration curve. The phase separation temperatures for different blend compositions were shown in Fig. 5. Under the experimental conditions, the onset of phase separation detected by baseline shift in the curve was generally lower than the temperature at which discrete domains can be seen in optical microscopy; however, the latter is in reasonable agreement with the temperature of maximum deviation from the baseline (Fig. 3a). The enthalpy of demixing was calculated from the area of the endotherm to be 0.54 cal g^{-1} for the 50/50 blend which compares favorably with the values reported in the literature for other miscible blends.

The kinetics of phase separation was studied by maintaining the sample at a constant temperature of 140°C for different time periods. The results are shown in Fig. 6. Samples were preheated to 80°C in the DSC cell and allowed to reach temperature equilibrium. A series of temperature-jump experiments were initiated by raising the

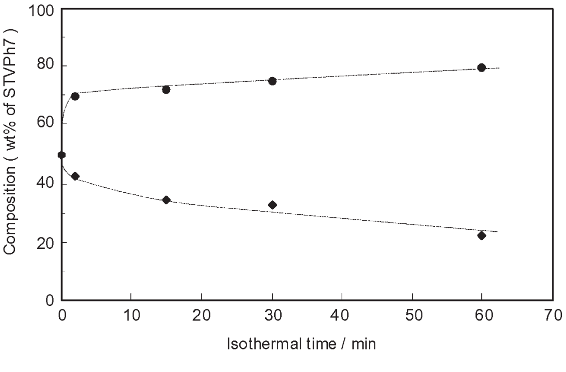

Fig. 8 Different compositions of annealed 50/50 STVPh7/PHMA blend at 140°C for different time periods. (♦– PHMA-rich phase, • – STVPh7-rich phase)

temperature quickly, within 1.5 min, to 140°C (two-phase region) and maintained at that temperature for up to 60 min. The phase separated blends were quenched to the subambient by liquid nitrogen and then MDSC scans were activated. As shown in Fig. 6, the high temperature T_g (STVPh7-rich phase) moved progressively with time to higher values and the low temperature T_g (PHMA-rich phase), to lower values. The phase compositions estimated from the calibration curve of T_g *vs*. composition are given in Fig. 7 in relation to the phase diagram. It was interesting to note that the STVPh7-rich phase seemed to have reached its limiting composition after 60 min but the PHMA-rich phase has not. The implication that phase separation was not yet complete was supported by the observation that although the endotherm at around 130°C decreased with the duration of experiment, it had not vanished completely after 60 min.

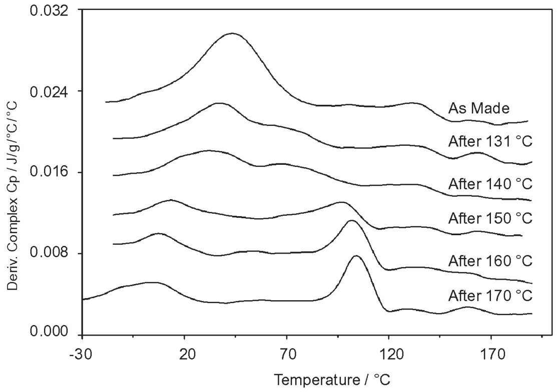

Fig. 9 dC_p/dT signals of 50/50 STVPh7/PHMA blend after heating for 2 min at different temperatures

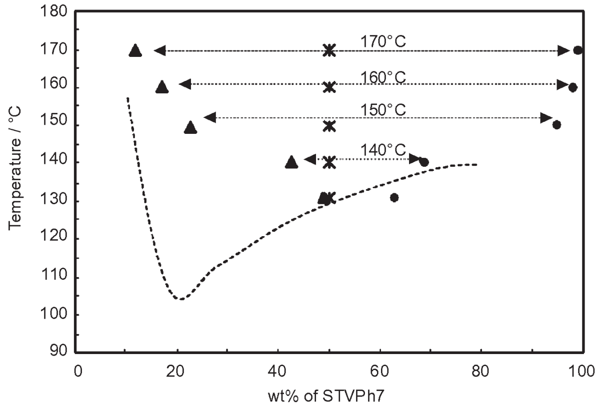

Fig. 10 Phase behavior of STVPh7/PHMA blends after 2 min at different temperatures. * – Initial, overall concentration, • – STVPh7-rich phase, ▲ – PHMA-rich phase, ---- MDSC phase diagram

The data in Fig. 7 are replotted in Fig. 8 as a function of time. The composition changes can be represented by two smooth curves. It is of interest to note that although the STVPh7-rich phase must have traversed the boundary between unstable and metastable regions of the phase diagram, there is no detectable discontinuity in the rate of composition change.

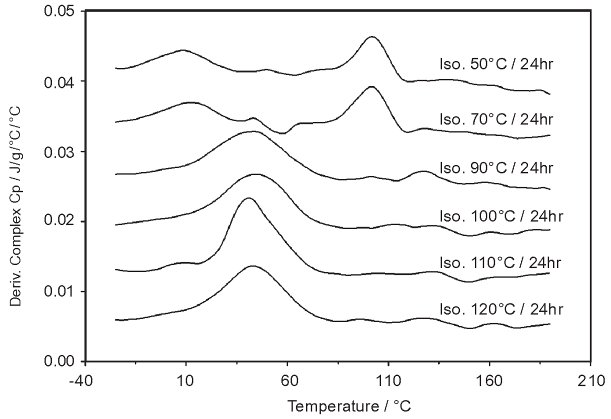

Fig. 11 dC_p/dT signals of 50/50 STVPh7/PHMA blend with different thermal treatment after phase separation at 160°C for 2 min

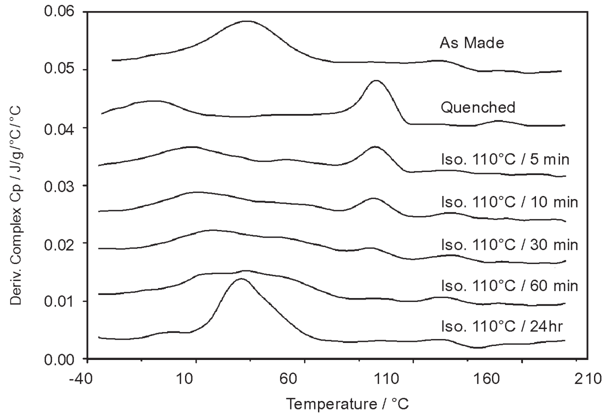

Fig. 12 dC_p/dT signals of 50/50 STVPh7/PHMA blend with different thermal treatment after phase separation at 160°C for 2 min

When the blend was allowed to undergo phase separation at five different temperatures for two minutes each, the results are shown in Fig. 9. At 131°C, the two T_g's were not well-separated and the baseline shift at 130°C remained quite large. At higher temperatures, the two T_g's, representing STVPh7-rich and PHMA-rich phases, moved increasingly apart from each other. At the same time, the baseline shift became smaller. The phase composition changes were shown in Fig. 10. It was quite evident that, after 2 min at 170°C, the compositions of the two phases had approached the values at the phase boundaries.

We next conducted a series of experiments in which a phase-separated sample (2 min at 160°C) after quenching was annealed at temperatures not far below the phase boundary to see whether a return to the single-phase state was possible. Annealing for 24 h at 50 or 70°C did not result in a single T_g, but annealing at 90, 100, or 110°C did (Fig. 11). Interestingly, annealing at 110°C resulted in a sharp derivative peak but the peak broadened after annealing at 120°C probably because the temperature was too close to the phase boundary. When the same sample was annealed at 110°C for different periods of time, the results in Fig. 12 showed clearly that a duration of 60 min was insufficient to produce a single T_g.

Conclusions

The phase separation behavior of hydrogen bonded polymer blends was studied by the thermal analysis technique. The enthalpy of phase separation for 50/50 STVPh7/PHMA blend is about 0.5 cal g^{-1}. The kinetics of phase separation of this blend was studied isothermally at 140°C. The composition of the STVPh7-rich phase appears to have reached its final value after 60 min, but the composition of the PHMA-rich phase is still short of its limiting value. The phase compositions change smoothly with time and there is no discontinuity in the curve even though the STVPh7-rich phase must have crossed the boundary between unstable and metastable region. Annealing of a phase separated sample at temperatures not too far below the phase boundary promotes the return to the single-phase state.

* * *

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