Analysis of the Multistep Solidification Process in Polymer Blends

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ABSTRACT: The multistep solidification process of various ternary blends has been correlated to the chain dynamics and crystallization kinetics of individual components. These blends include a noncrystallizable poly(propylene glycol), an acrylate, poly(methyl methacrylate-*co*-*n*-butyl methacrylate), and crystallizable polyesters such as poly(hexamethylene adipate) or poly(hexamethylene sebacate). When the sample temperature is lowered from the molten state, the contribution of each component in the solidification process can be readily recognized. The viscosity increase takes place in two steps. The initial increase is due to reduced segmental mobility. The second is due to the increase in crystallinity. On the basis of the data obtained for binary blends, the contribution of the crystallizable component in the viscosity change can be deduced. Although only minor structural differences exist between two polyesters, their phase diagrams differ considerably. As expected, these differences in phase diagrams led to different crystallization kinetics of the polyesters and associated solidification process.

Introduction

Polymeric ternary blends are widely used in very diverse applications.[1−4] Each component is employed because it has specific characteristics that lead to improved physical properties, ease in processing, or lower cost. For example, in our laboratories we have an interest in applications such as coatings, adhesives, or drug delivery systems. In each application, the solidification process or viscosity control of the blends is of interest. In adhesive applications, a functionalized polyether is mixed with crystallizable polyesters and an acrylate. The polyethers are employed to provide elasticity and impact strength at lowered temperatures. The acrylate and polyester crystallites are employed to control melt strength at elevated temperatures as well as cured strength. Because acrylate, a copolymer, is amorphous, its glass transition temperature is important. Since polyesters crystallize, the degree of crystallinity and crystallite size are important considerations. Thus, the crystallization process and its control are also important factors.

The ternary blends can vary in composition and individual components. In previous studies, we focused on the phase diagram of the blends,[5,6] morphological features developed, and reaction kinetics.[7,8] In the present study, we focus on factors that influence the viscosity of the blends at various temperatures. Film thickness is often an important parameter. Appropriate sample viscosity is crucial. It should be emphasized that crystallization kinetics is critically dependent on sample viscosity. The exact relationship is difficult to quantify. Obviously, viscosity depends on blend composition. Whether the sample is thermodynamically miscible can significantly influence the viscosity value.[9−11] The relationship is further complicated because both steps of the crystallization process, i.e., nucleation and crystalline growth, are dependent on the local concentration and segmental mobility. In this study, the viscosity of various ternary blends has been analyzed as a function of time and temperature profile. These studies were carried out in conjunction with real-time infrared spectroscopic measurements which are capable of measuring the crystallization process. It is thus possible to interpret the contribution of individual components to the change in overall sample viscosity.

In the previous study, phase diagrams of both binary and ternary blends of polyether, polyesters, and acrylate were investigated.[5] The evolution of morphological features in miscible or immiscible blends has also been characterized.[7] It was revealed that, depending on the local composition of crystallizable polymer in crystallizable/noncrystallizable binary blends, the crystallization kinetics and degree of crystallinity varied dramatically. In addition, a high-T_g acrylate component in ternary blends reduced segmental mobility and affected both miscibility and crystallization kinetics. Significant reductions in crystallization rates and degree of crystallinity were observed in ternary blends.[7] Depending on the phase diagram and thermal history, it is possible to obtain dramatically different sizes of phase-separated domains, different compositions within each phase, and different dispersions of large or small domains in the condensed state. The viscosity change in these blends from the initial liquid state to the final condensed state is related to formation of these crystalline features.

The viscosity and crystallization behavior of different ternary blends incorporating polyesters, poly(hexamethylene adipate) (PHMA) or poly(hexamethylene sebacate) (PHMS), noncrystallizable poly(propylene glycol) (PPG), and poly(methyl methacrylate-*co*-*n*-butyl methacrylate) have been characterized. The viscosity and crystallinity changes were studied at different degrees of supercooling (ΔT). The effect of a high-T_g third component, an acrylate, on the viscosity and crystallization process has also been studied. A typical phase-separated morphology of the PHMA/PPG/Acrylate ternary blend is shown in Figure 1, where the phase-separated domains are a PHMA-rich phase and the continuous matrix is a PHMA-poor phase. Morphological features such as domain size, crystallinity, and compositional distribution are expected to be quite different, depending on the composition as well as thermal history. Therefore, the relationship between the crystallization kinetics and change in viscosity in blends is a complex one.

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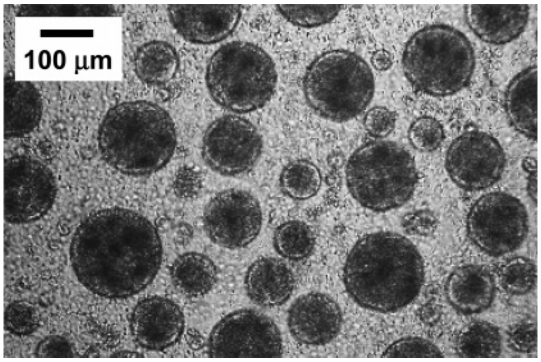

Figure 1. A typical phase-separated structure of the PHMA/PPG/P(MMA-*co*-*n*BMA) ternary blend.

Table 1. Correlation between Thermal and Infrared Band Intensity Data of PHMA and PHMS Crystallized Isothermally at Various Degrees of Supercooling

PHMA ($T_m^o = 58$ °C, $\Delta H_m^o = 151$ J/g)

ΔT (°C)	ΔH_m (J/g)	crystallinity (%)	IR band intensity at 973 cm^{-1}
23	85.55	57	0.102
18	81.26	54	0.091
15	74.28	49	0.081
13	66.60	44	0.072

PHMS ($T_m^o = 70$ °C, $\Delta H_m^o = 134$ J/g)

ΔT (°C)	ΔH_m (J/g)	crystallinity (%)	IR band intensity at 980 cm^{-1}
23	61.02	46	0.113
18	57.34	43	0.091
15	51.36	38	0.079
13	48.44	36	0.074

Experimental Section

As in previous studies,[5,7] poly(hexamethylene adipate) (PHMA, $M_n = 1575$ g/mol), poly(hexamethylene sebacate) (PHMS, $M_n = 1371$ g/mol), poly(propylene glycol) (PPG, $M_n = 1887$ g/mol), and a random acrylic copolymer of poly(methyl methacrylate-*co*-*n*-butyl methacrylate) [P(MMA-*co*-*n*BMA), $M_n = 18\,841$ g/mol] were utilized for blend studies. Both polyesters have primary OH groups at their chain ends, whereas PPG has secondary OH end groups. Equilibrium melting points (T_m^o) of PHMA and PHMS are 58 and 70 °C, respectively.[12,13] Since the melting points of these polyesters differ, the degree of supercooling ($\Delta T = T_m^o - T_c$, where T_c indicates the crystallization temperature) was used for crystallization analysis. The glass transition temperature (T_g) of P(MMA-*co*-*n*-BMA) is 85 °C. All blends were prepared by melt−mixing at 120 °C.

Temperature- and time-dependent viscosity development of blends was measured with a small-amplitude oscillatory shear using the cone and plate geometry of the Advanced Rheometric Expansion System (ARES, Rheometric Scientific Inc.). The instrument was operated using RSI Orchestrator (version 6.3.0). The frequency and applied strain were controlled at 1 rad/s and 1%, respectively. The blends were first melted at 120 °C for 3 min and then cooled to the predetermined temperature. The viscosity change was monitored as a function of time at a given temperature.

To investigate the crystallization process, time-resolved infrared spectral measurements were carried out using a Perkin-Elmer 2000 FT-IR spectrometer. Infrared spectra were obtained every 14 s. Spectral resolution was maintained at 4 cm^{-1}. In each case, the crystallization process as a function of time and temperature took place in a specially designed cell.

Thermal measurements of blends crystallized at various degrees of supercooling were conducted using a differential scanning calorimeter (DSC Q100, TA Instruments Inc.). The heating rate was 10 °C/min. The degree of crystallinity of binary or ternary blends was calculated by comparing the melting enthalpy (ΔH_m) of an isothermally crystallized sample with the equilibrium melting enthalpy of polyester (ΔH_m^o), as shown in Table 1.[12,13] Blend morphology was observed using an Olympus Vanox optical microscope equipped with a digital camera.

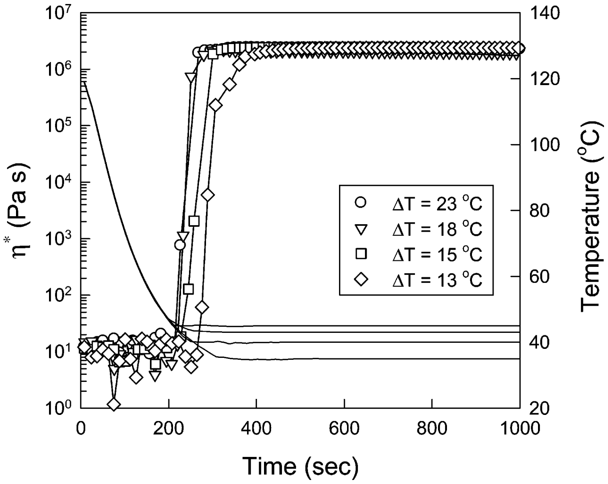

Figure 2. Time-dependent viscosity changes of the PHMA/PPG (1/1) binary blend under the cooling process from 120 °C to various ΔT's of 13−23 °C.

Results and Discussion

The morphological features and their development differ significantly for binary and ternary blends. Because of the relative interactions of individual components, the phase diagrams are also different.[5] To differentiate between contributions from the reduction in segmental mobility due to the presence of acrylate and from crystallinity of the polyesters, binary and ternary blends were studied separately. The miscibility behavior and associated morphological differences of PHMA/PPG and PHMS/PPG binary blends have been investigated.[5,7] It was revealed that the immiscible PHMA/PPG blends exhibited phase-separated morphologies for most compositions, while the miscible PHMS/PPG blends displayed homogeneous morphologies. This result is surprising as the two polyesters have very similar chemical structures.

The viscosity and crystallinity changes of the immiscible PHMA/PPG (1/1 by weight ratio) and miscible PHMS/PPG (1/1) blends when cooled from the melt are shown in Figures 2 and 3, respectively. The solid lines indicate the temperature profiles from 120 °C to the various temperatures. As described above, because of the different melting temperatures, the degree of supercooling, ΔT, was used. For both binary blends, there was no significant viscosity change during cooling from 120 °C to the predetermined ΔT, 13−23 °C. Sample viscosity increased only when samples began to crystallize. For the immiscible PHMA/PPG blend, the viscosities changed rapidly and reached a plateau value, independent of ΔT. No significant difference in the final viscosity indicates that the immiscible blends are totally solidified in the range of ΔT used. As shown in Figure 3, for the miscible PHMS/PPG blend, viscosity development as a function of time is quite different from the PHMA/PPG blend even though the blend composition is identical. The viscosity in this case at $\Delta T = 23$ °C increased quickly and reached a plateau value identical to that found for all PHMA/PPG blends. In contrast, viscosity values measured at lower supercooling, ΔT of 15 and 13 °C, increased slowly and reached lower plateau values. A few degrees of temperature difference near the melting temperature changed the viscosity behavior significantly in the miscible blend, quite unlike the

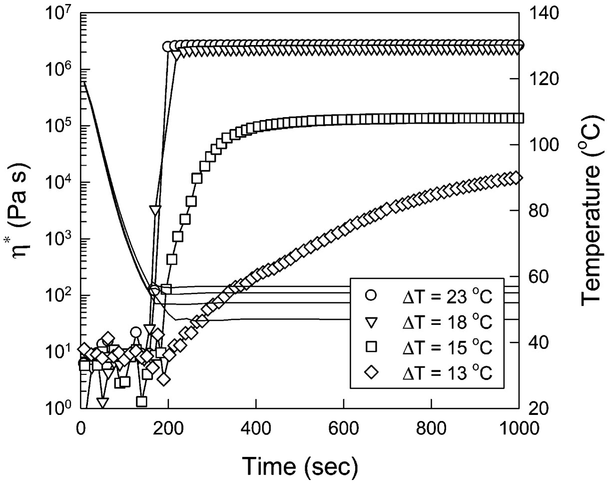

Figure 3. Time-dependent viscosity changes of the PHMS/PPG (1/1) binary blend under the cooling process from 120 °C to various Δ*T*'s of 13−23 °C.

immiscible PHMA/PPG blend. As observed previously,[5,7] the small differences in the chemical structures of the two polyesters led to astonishingly different phase diagrams and morphological features.

These viscosity differences must be attributed to differences in crystallization kinetics, the degree of crystallinity achieved, and morphological features obtained. To investigate the relationship between viscosity development and crystallization behavior, the crystallization kinetics of the immiscible and miscible binary blends were examined by infrared spectroscopy. Figure 4A shows typical time-resolved infrared spectra of the immiscible PHMA/PPG (1/1) blend at Δ*T* = 23 °C. The PHMA band at 973 cm^{-1}, assigned to CH_2 deformation vibration, is sensitive to the conformational order.[14] We also used this band to represent the degree of crystallinity. The intensity of the crystalline band at 973 cm^{-1} was obtained as a function of time. The intensity of the 973 cm^{-1} band normalized to the intensity of the C═O stretching band, which is independent of crystallization, can be used to assess changing crystallinity once calibrated to samples with a known degree of crystallinity. Since the change in enthalpy of these polyesters has been measured, spectroscopic measurements were calibrated to thermal measurements. The calibration samples are presented in Table 1.

The degree of crystallinity of PHMA/PPG blends at various Δ*T*'s could then be evaluated as a function of time, as shown in Figure 5. Crystallinity development becomes slightly slower with decreasing Δ*T* from 23 to 13 °C. The final degree of crystallinity obtained also decreases from 28% to 20% (nearly theoretical levels based on pure PHMA). The infrared spectra as a function of time obtained for the miscible PHMS/PPG (1/1) blend crystallized at Δ*T* = 23 °C are shown in Figure 4B for comparison. Similar to PHMA/PPG blends described above, the degree of crystallinity can also be obtained as a function of time. In this case, the integrated intensity of the 980 cm^{-1}, CH_2 deformation, band was normalized to the intensity of the C═O stretching vibration. When correlated to samples of known crystallinity (Table 1), the degree of crystallinity of PHMS/PPG blends can then be measured (Figure 6). Similar to the PHMA/PPG blends, different Δ*T*'s were used. At Δ*T* = 23 °C, PHMS in the blend crystallizes rapidly at a crystallization rate comparable with that of PHMA/PPG blends. Crystallinity develops more slowly with decreasing Δ*T* from 23 to 13 °C. The ultimate degree of crystallinity achieved is also lower and is far from theoretical levels based on pure PHMS (1/2 to 1/3). This indicates that the crystallization of PHMS in miscible blends changes noticeably with small differences in Δ*T*, in contrast to the crystallization behavior observed for immiscible PHMA/PPG blends.

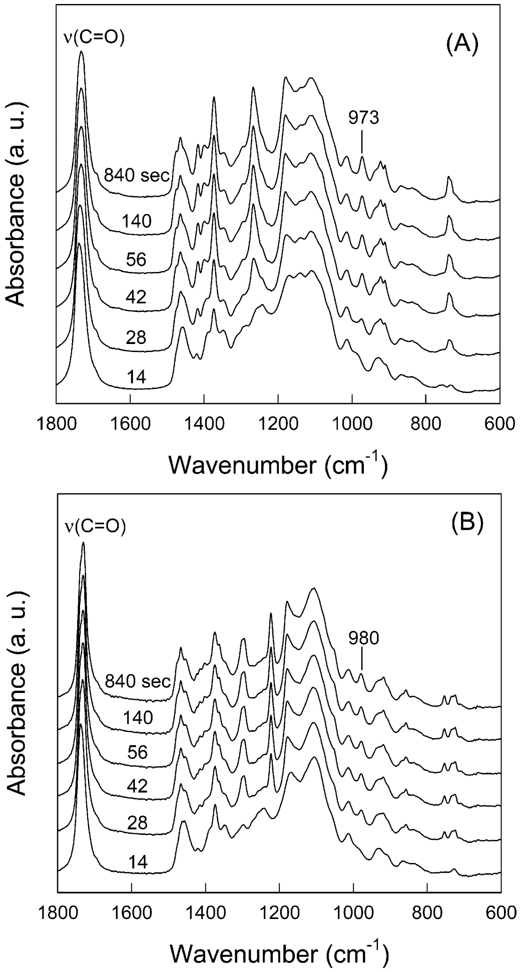

Figure 4. Time-dependent infrared spectra of (A) PHMA/PPG (1/1) and (B) PHMS/PPG (1/1) blends crystallized at Δ*T* = 23 °C.

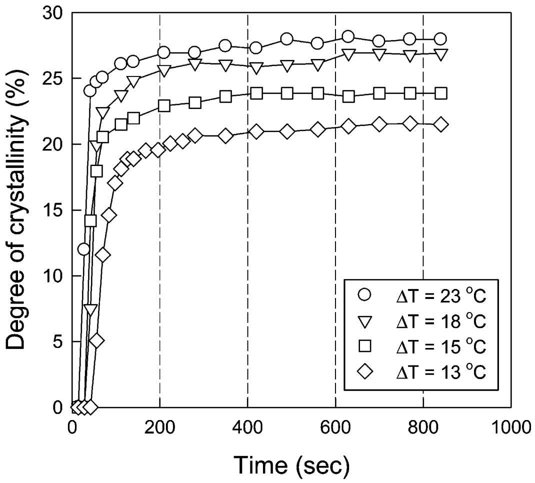

Figure 5. Changes of the degree of crystallinity for the PHMA/PPG (1/1) binary blend crystallized at various Δ*T*'s of 13−23 °C.

The crystallization process is generally described in terms of nucleation and crystal growth via molecular diffusion. Nucleation behavior in a polymer−diluent system was previously investigated.[15,16] The critical free energy for nucleation in polymer−diluent mixtures is considered in terms of the

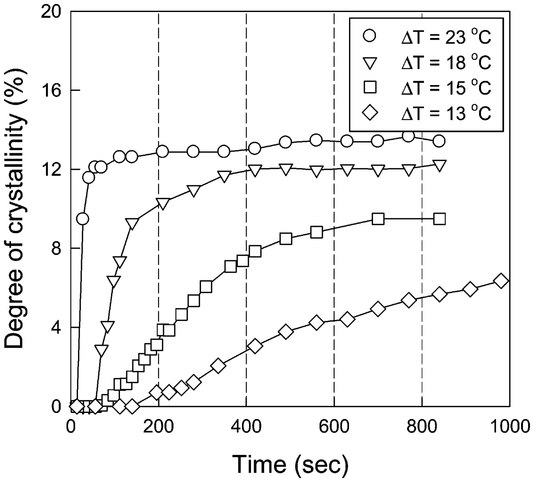

Figure 6. Changes of the degree of crystallinity for the PHMS/PPG (1/1) binary blend crystallized at various ΔT's of 13−23 °C.

depressed melting temperature (T_m). Here T_m in the critical free energy reflects the effects of the noncrystallizable component on the nucleation mechanism, which is influenced by both dilution (blend composition) and interaction parameter.[17] Therefore, it is not surprising that miscibility in polymer blends significantly affects crystallization kinetics at different ΔT's. The melting temperature depression in polymer blends is expressed as[17]

$$\frac{1}{T_m} - \frac{1}{T_m^o} = \frac{-\chi_{12} R V_{2u}}{\Delta H_{2u} V_{1u}} \phi_1^{\ 2} \qquad (1)$$

where the subscripts 1 and 2 refer to the noncrystallizable and crystallizable polymer, respectively. T_m and T_m^o are the melting temperatures of the blend and of the pure crystallizable polymer, respectively. V_u is the molar volume per repeat unit of polymer, ΔH_u the enthalpy of fusion of 100% crystalline polymer, χ_{12} the interaction parameter, ϕ the volume fraction of the component in the blend, and R the gas constant. In our previous study,[5] the melting temperatures of PHMS/PPG blends with various blend composition were measured. The interaction parameter was found to be $\chi_{12} = -0.0325$ using eq 1. The melting temperature of the PHMS/PPG (1/1) blend was found to be lowered only by <2 °C from the value of PHMS homopolymer. PHMA did not exhibit any reduction in melting temperature. Therefore, the reduction in melting temperature in various blends was not considered.

The crystal growth rates of miscible blends are also retarded by the need to transport crystallizable materials to the crystal growth front and push the noncrystallizable material away from the growth front.[18,19] This leads to reduction in crystal growth rates and final degree of crystallinity. An enrichment of the noncrystallizable materials at interlamellar, interfibrillar, and interspherulitic regions can occur.[18−24] Therefore, crystallization kinetics, including both nucleation and crystal growth, of the miscible PPG/PHMS blend is extremely sensitive to supercooling, in contrast to the immiscible PPG/PHMA blend. Although the details of individual crystallization mechanisms differ, there is little doubt that crystallization kinetics are slower in miscible blends as we have found.

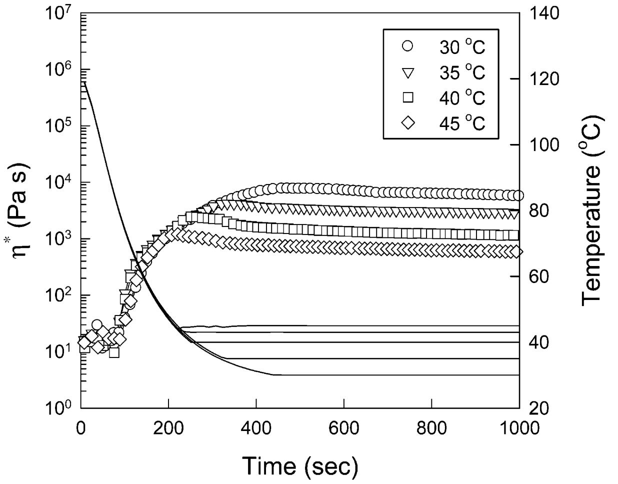

Figure 7. Time-dependent viscosity changes of the PPG/P(MMA-*co*-*n*BMA) (2/1) binary blend under the cooling process from 120 °C to various ΔT's of 13−23 °C.

As noted above, the viscosity of the immiscible PHMA/PPG blend crystallized at all ΔT's reached the saturated maximum value (Figure 2). The crystallinity achieved ranges from 20 to 28% (Figure 5). The viscosity change for the miscible PHMS/PPG blends has a broad range depending on the degree of crystallinity. The transformation from liquid to viscoelastic phase is not well characterized. A previous study on physical gelation reported that the critical crystallinity to form a three-dimensional network can be very low such as 2%.[25] Overall, viscosity changes of both PHMA/PPG and PHMS/PPG binary blends at various ΔT's are quite consistent with crystallization kinetics. Therefore, it is valid to conclude that the viscosity changes in binary blends during the cooling process are dominantly contributed by crystallization of crystallizable polyesters. The shear stress has been reported to influence mixing, demixing, and crystallization.[26−30] As the viscosity development matches well with crystallization kinetics, we assume the shear effects on phase separation and crystallization to be negligibly small.

Viscosity changes of ternary blends containing both crystallizable polyesters and a high-T_g acrylate component are expected to be more complicated. As noted above, the inclusion of the high-T_g acrylate into the blends reduces molecular mobility and changes phase behavior and therefore crystallization kinetics. To examine the influence of the high-T_g acrylate on blend viscosity, PPG/P(MMA-*co*-*n*BMA) (2/1) binary blends without crystallizable polyesters were prepared, and viscosity changes during cooling from 120 °C to various temperatures were investigated (Figure 7). Clearly, the viscosity increases during the cooling process reaches a constant value. In this case, the viscosity increase originates from the reduced segmental mobility of the high-T_g acrylate. Because of their low T_g values ($T_g \sim -60$ °C), reduction in segmental mobility of polyester or polyether is not observed.

The viscosity changes of the PHMA/PPG/P(MMA-*co*-*n*BMA) (1/1/1) ternary blend when cooled from 120 °C to various ΔT's are shown in Figure 8. The viscosity of this ternary blend was observed to develop in two steps in comparison to the single-step viscosity development of all observed binary blends. In this ternary blend, the viscosity increases during cooling from 120 °C to each ΔT temperature and reaches a certain plateau value dependent on ΔT. At those ΔT temperatures, there is change in the viscosity development, also dependent on ΔT. We assigned the initial change in viscosity during cooling as due to the reduced segmental mobility of the high-T_g acrylate component. The subsequent increase originates from the crystallization of the PHMA component.

Figure 9 presents the crystallization kinetics of the PHMA/PPG/P(MMA-*co*-*n*BMA) (1/1/1) ternary blend at various ΔT's. As mentioned above, the normalized intensity of the PHMA

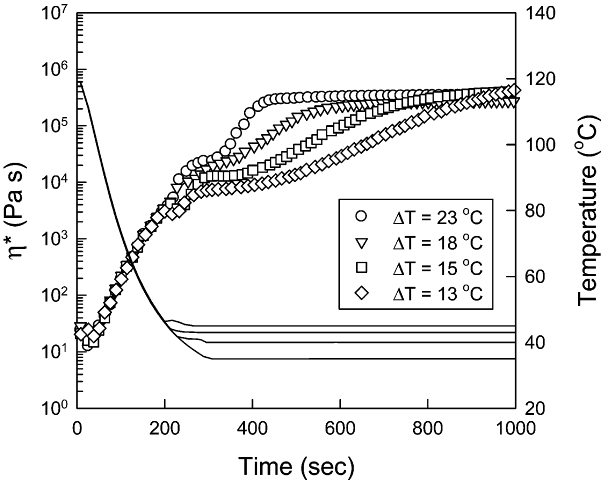

Figure 8. Time-dependent viscosity changes of the PHMA/PPG/P(MMA-*co*-*n*BMA) (1/1/1) ternary blend under the cooling process from 120 °C to various Δ*T*'s of 13−23 °C.

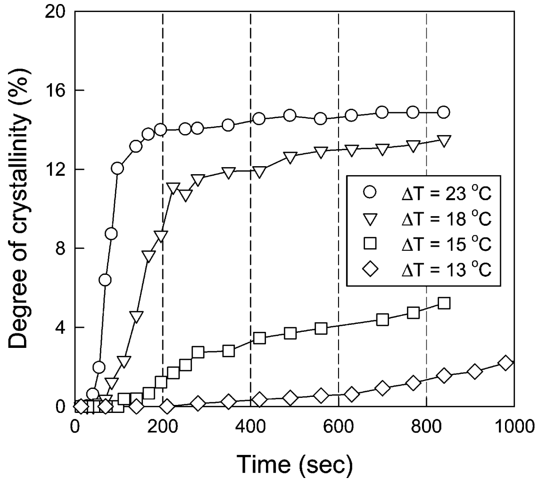

Figure 9. Changes of the degree of crystallinity for the PHMA/PPG/P(MMA-*co*-*n*BMA) (1/1/1) ternary blend crystallized at various Δ*T*'s of 13−23 °C.

crystalline band at 973 cm^{-1} was calibrated to the degree of crystallinity of ternary blends using the relationship in Table 1. Unlike the crystallization behavior of the immiscible PHMA/PPG (1/1) blend in Figure 5, the crystallization of the ternary blend is extremely sensitive to the degree of supercooling. The crystallinity development of the ternary blend is significantly slower with decreasing Δ*T* from 23 to 13 °C. The ultimate degree of crystallinity obtained is noticeably lower in the time period examined. The large reduction in the crystallization rate and degree of crystallinity at small Δ*T* is believed to be correlated to the presence of an immobile acrylate component. Previous studies indicated that the high-T_g acrylate appreciably affects miscibility of the ternary blends as well as segmental mobility in the crystallization process.[7] It therefore suffices to conclude that, due to the presence of the high-T_g acrylate component, the segmental mobility of ternary blends decreases with increasing Δ*T* and eventually leads to slower crystallization kinetics.

It should be noted that the viscosity of the PHMA/PPG/P(MMA-*co*-*n*BMA) (1/1/1) blend reaches a certain plateau value, irrespective of Δ*T* (Figure 8). The ultimate degree of crystallinity for various samples is noticeably different depending on Δ*T* (Figure 9). The difference in the size of phase-separated domains (PHMA-rich phase) was observed to be negligibly small for all blends cooled to different Δ*T*'s of 13−23 °C. Preliminary results indicate that the "effective" percolation limit is an important consideration. This study will be reported shortly.

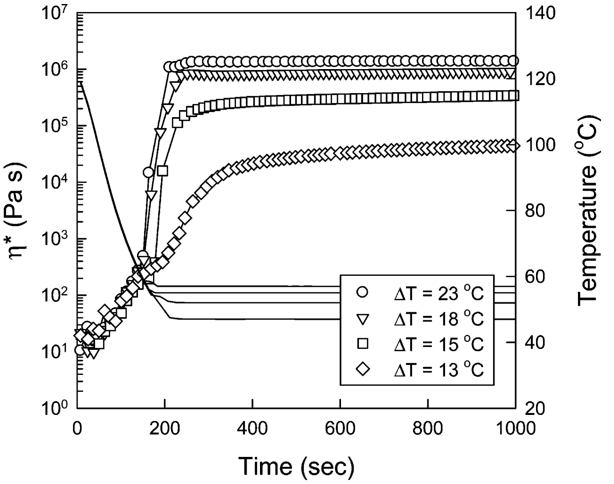

Figure 10. Time-dependent viscosity changes of the PHMS/PPG/P(MMA-*co*-*n*BMA) (1/1/1) ternary blend under the cooling process from 120 °C to various Δ*T*'s of 13−23 °C.

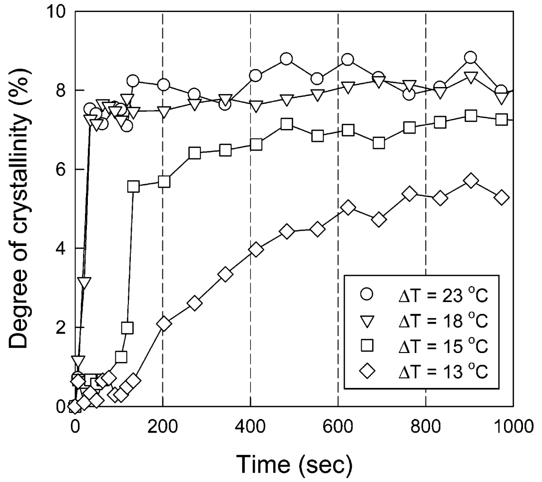

Figure 11. Changes of the degree of crystallinity for the PHMS/PPG/P(MMA-*co*-*n*BMA) (1/1/1) ternary blend crystallized at various Δ*T*'s of 13−23 °C.

The viscosity development of the PHMS/PPG/P(MMA-*co*-*n*BMA) (1/1/1) ternary blend at various Δ*T*'s is shown in Figure 10. Similar to the PHMA/PPG/P(MMA-*co*-*n*BMA) (1/1/1) ternary blend, there are two-step viscosity changes due to the vitrification behavior of the acrylate component during cooling from 120 °C to each Δ*T* temperature and the crystallization of PHMS. In comparison to the PHMS/PPG (1/1) binary blend, the viscosity development of the ternary blend is somewhat faster because ternary blends have a high-T_g acrylate in spite of less PHMS content. In the previous study, we found that the PHMS/PPG/P(MMA-*co*-*n*BMA) (1/1/1) ternary blend becomes immiscible by adding an acrylate component into miscible PHMS/PPG blends.[5] One can therefore conclude that the faster viscosity development during the second step of the ternary blends is due to the increased crystallization rate in the immiscible ternary blends, as seen in Figure 11. In this figure, the crystallization behavior of the PHMS/PPG/P(MMA-*co*-*n*BMA) (1/1/1) ternary blend is clearly illustrated. From Figures 6 and 11 the crystallization rate of the immiscible PHMS/PPG/P(MMA-*co*-*n*BMA) (1/1/1) ternary blend has been shown to be even faster than that of the miscible PHMS/PPG (1/1) blend, although the crystallinity of the ternary blend is somewhat lower

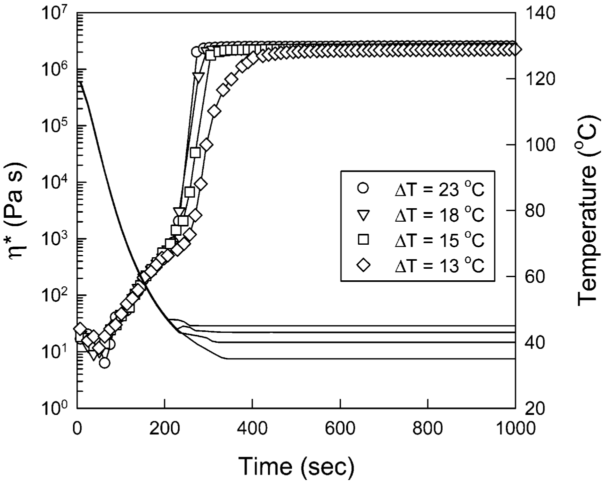

Figure 12. Time-dependent viscosity changes of the PHMA/PPG/P(MMA-*co*-*n*BMA) (3/1/1) ternary blend under the cooling process from 120 °C to various Δ*T*'s of 13−23 °C.

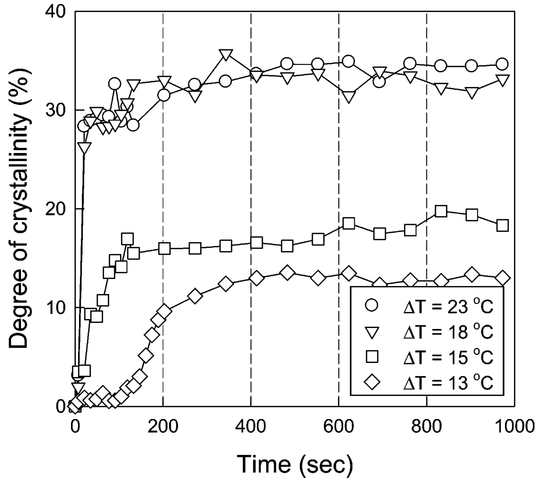

Figure 13. Changes of the degree of crystallinity for the PHMA/PPG/P(MMA-*co*-*n*BMA) (3/1/1) ternary blend crystallized at various Δ*T*'s of 13−23 °C.

than that of the binary blend and still 1/2 to 1/3 of theoretical values based on pure PHMS.

The viscosity and crystallinity development of PHMA/PPG/P(MMA-*co*-*n*BMA) ternary blends with different compositions of (3/1/1), (1/1/1), and (1/3/1) have also been investigated. It should be noted that all ternary blends prepared in this study are immiscible, leading to phase-separated structures.[5] We therefore focused on ternary blends involving PHMA. In the PHMA/PPG/P(MMA-*co*-*n*BMA) (1/3/1) blend, the phase-separated domains are the PHMA-rich phase and the continuous matrix is the PHMA-poor phase, similar to the (1/1/1) ternary blend. However, the phase-separated domain (PHMA-rich phase) size is much smaller than the (1/1/1) ternary blend. For the PHMA/PPG/P(MMA-*co*-*n*BMA) (3/1/1) blend, there is a phase inversion, indicating that the phase-separated domains are the PHMA-poor phase and the connected matrix is the PHMA-rich phase, unlike the (1/1/1) and (1/3/1) ternary blends.

The viscosity development of the PHMA/PPG/P(MMA-*co*-*n*BMA) (3/1/1) blend in the cooling process from 120 °C to various Δ*T*'s is represented in Figure 12. This ternary blend also shows a two-step viscosity development, regardless of Δ*T*. The initial viscosity increase during cooling is affected by the acrylate and the later by crystallization. Figure 13 shows crystallinity development as a function of time at various Δ*T*'s, which is in good agreement with the viscosity development by crystallization. Since this ternary blend has a higher content of PHMA as well as the inverted phase-separated structure, in comparison to the (1/1/1) ternary blend noted above, its viscosity developed rapidly at all Δ*T*'s to form the solid phase.

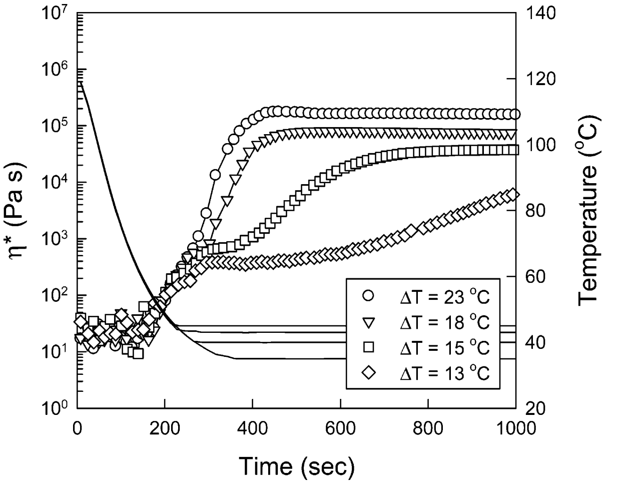

Figure 14. Time-dependent viscosity changes of the PHMA/PPG/P(MMA-*co*-*n*BMA) (1/3/1) ternary blend under the cooling process from 120 °C to various Δ*T*'s of 13−23 °C.

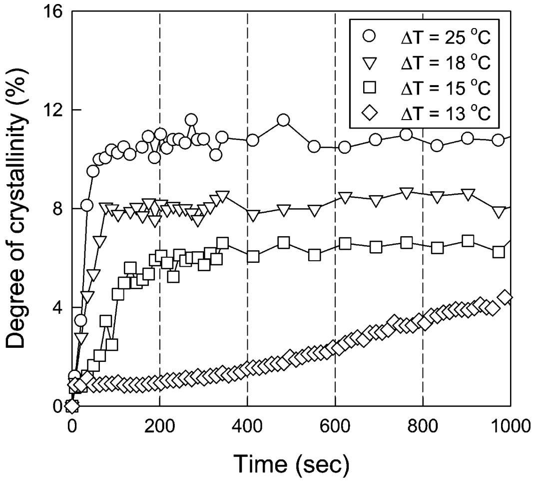

Figure 15. Changes of the degree of crystallinity for the PHMA/PPG/P(MMA-*co*-*n*BMA) (1/3/1) ternary blend crystallized at various Δ*T*'s of 13−23 °C.

The viscosity and crystallinity development of the PHMA/PPG/P(MMA-*co*-*n*BMA) (1/3/1) blend at various Δ*T*'s are shown in Figures 14 and 15. Similar to other ternary blends with different compositions, this ternary blend again shows the two-step viscosity development, correlated to the segmental mobility and crystallization processes. As expected, the viscosity development by crystallization (Figure 14) is consistent with the crystallization rate (Figure 15). Crystallization rates of PHMA/PPG/P(MMA-*co*-*n*BMA) (1/3/1) and (1/1/1) blends are much slower than those of the (3/1/1) ternary blend, as seen in Figures 9, 13, and 15. The first step viscosity development of ternary blends is dependent on acrylate content. The higher acrylate content, the higher viscosity achieved without the crystallization contribution (Figures 8, 12, and 14). In addition, the second step viscosity development by crystallization and the final viscosity achieved at a given Δ*T* temperature are dependent on the PHMA content, phase-separated structure, and miscibility in the ternary blends.

Conclusion

The solidification process in multicomponent crystallizable blends was investigated at various degrees of supercooling ($\Delta T = 23-13$ °C) using viscometry, vibrational spectroscopy, and calorimetric methods. The solidification process of blends was found to correlate well with chain dynamics of the high-T_g acrylate component. In addition, the contribution of the crystallization process can also be measured independently. These measurements have been made for miscible and immiscible binary and ternary blends.

The role of crystallization in the solidification process of binary blends could be studied directly. Although PHMA and PHMS are crystallizable polyesters with similar chemical structures, they have different miscibility with PPG. In the case of the immiscible PHMA/PPG (1/1) binary blend, solidification was not strongly dependent on ΔT since the crystallization process remains the same. The viscosity increased rapidly when the blends reached the crystallization temperature. However, in the case of the miscible PHMS/PPG (1/1) blend, the solidification originating from crystallization was noticeably sensitive to ΔT of 23−13 °C. The viscosity or crystallinity development became appreciably slower with decreasing ΔT from 23 to 13 °C. The ultimate viscosity was considerably lower at low ΔT due to reduced crystallinity, far below theoretical values.

Viscosity and crystallinity development with time for ternary blends including a high-T_g acrylic component, PHMA/PPG/P(MMA-*co*-*n*BMA) and PHMS/PPG/P(MMA-*co*-*n*BMA), was also examined. The viscosity behavior of ternary blends in the cooling process was more complicated due to the presence of both crystallizable and high-T_g components. It was revealed that the viscosity of ternary blends increases in two-step processes when cooled from 120 °C to each temperature. The first step viscosity increase is due to the reduction in segmental mobility of the high-T_g component during cooling. The second increase is due to crystallization of the polyester component in blends. For the PHMA/PPG/P(MMA-*co*-*n*BMA) (1/1/1) ternary blend, the viscosity and crystallinity development was much slower than that of the PHMA/PPG (1/1) binary blend due to the presence of the high-T_g acrylate and enhanced miscibility. In contrast, the viscosity development of the immiscible PHMS/PPG/P(MMA-*co*-*n*BMA) (1/1/1) ternary blend was faster than that of the miscible PHMS/PPG (1/1) blend. By comparing the viscosity and crystallization behavior between PHMA/PPG/P(MMA-*co*-*n*BMA) ternary blends with different compositions of (3/1/1), (1/1/1), and (1/3/1), viscosity development was revealed to be strongly correlated with composition. The higher acrylate and/or PHMA content, the higher viscosity and/or faster viscosity development. In summary, the phase miscibility, chain dynamics, and crystallization contribute to viscosity changes in ternary blends, individually or collectively.

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