

Phase Behavior, Crystallization, and Curie transition in Blends of Poly(Vinylidene Fluoride-co-Trifluoroethylene) and Poly(1,4-butylene adipate)

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INTRODUCTION

Recently, Manley's group published several papers on the blend of PVDF and poly(1,4-butylene adipate) (PBA) chosen as a model system of semicrystalline/semicrystalline polymer blend.[1-4] This blend system has several advantages over the other PVDF/semicrystalline polymer blends. Their melting points(ca. 60°C for PBA and ca. 160°C for PVDF) lie within an experimentally accessible temperature range and are about 100°C apart, so the melting behavior and crystallization occurring in both PVDF and PBA phases could be studied separately. And the liquid-liquid phase separation behavior could also be observed from the presence of a typical thermally reversible LCST behavior at ~60°C above the melting temperature. In addition to crystallization and melting transitions, the random copolymers of VDF and TrFE [P(VDF/TrFE)] have a Curie transition at which ferroelectricity is lost through a solid-state phase transition and they become paraelectric. Even though there have been many reports on the Curie transition behavior of the VDF copolymer, only one paper refers to the Curie transition behavior of the P(VDF/TrFE) and amorphous PMMA blend.[5]. To date, no one has reported the blend of P(VDF/TrFE) and crystalline polymer. PVDF has shown to be miscible with PBA,[1-4] and P(VDF/TrFE) is therefore expected to form miscible blends with PBA. In the P(VDF/TrFE)/PBA blend, the phase behavior will be more complex than in the PVDF/PBA blend due to the presence of Curie transition. In this study, our attentions are focused on the phase behavior, miscibility, crystallization, and Curie transition of the P(VDF/TrFE)/PBA system using FTIR, DSC, and cloud point measurements and the comparison with the PVDF/PBA system.

EXPERIMENTAL

The sample of P(VDF/TrFE) with a molar ratio of 75/25 was supplied as in the chip state from Atochem and was used as received. Its molecular weight is unknown. The PBA sample was purchased from Scientific Polymer Products, Inc. and used without further purification. Its molecular weight is 12,000. Film samples of P(VDF/TrFE) and PBA blend were cast from the mixture. Blend samples were prepared in various compositions ranging from 90/10 to 10/90 in the ratio of weight percent by casting from the mixture solution. The IR absorbance spectra of blends were recorded as a function of temperature in the region from 4200 to 450cm⁻¹ using a Perkin-Elmer Model 16PC FTIR spectrometer with a resolution of 2 cm⁻¹ and 32 scans. Non-isothermal crystallization, melting, Curie transition, and glass transition of the blends were measured using a Perkin-Elmer DSC-7. Isothermal crystallization at small undercoolings was performed on a Nikon polarizing microscope(Model : Optiphot Pol) equipped with a Mettler FP82HT hot stage and a photomonitor under the crossed polarization. Cloud point was determined from the abrupt increase in the scattered laser light intensity at $\theta=10^\circ$ with the heating rate of 0.5°C/min.

RESULTS AND DISCUSSION

The overall phase diagram of the P(VDF/TrFE)/PBA blend system is shown in *Figure 1*. The pure PBA undergoes only two phase transitions, a glass transition(T_g) and melting(T_m), whereas the pure P(VDF/TrFE) exhibits four phase transitions, a glass transition, melting, and two Curie transitions[paraelectric-to-ferroelectric phase transition($T_{P\Rightarrow F}$) and ferroelectric-to-paraelectric phase

transition ($T_{F \rightarrow P}$)]. Their mixtures, in the central range of compositions, undergo more complex phase transitions, that is, a single glass transition, two melting transitions, two Curie transitions, and liquid-liquid phase separation above a lower critical solution temperature (LCST). P(VDF/TrFE) and PBA are miscible in the melt and their mixture forms a single phase (region II) between the melting curve of P(VDF/TrFE) and the cloud point. Raising the temperature from region II will eventually lead to liquid-liquid separated phase (region I). This LCST behavior is associated with the negative Flory-Huggins interaction parameter ($\chi_{12} < 0$). Lowering the temperature from region II to $T_{P \rightarrow F} < T < T_{m, P(VDF/TrFE)}$ will cause the P(VDF/TrFE) component to crystallize into a paraelectric crystalline phase and thus induce phase separation from the single phase forming an amorphous/paraelectric crystalline phase (region III). Further cooling to $T_{m, PBA} < T < T_{P \rightarrow F}$ will transform the paraelectric crystalline phase into the ferroelectric crystalline phase (region IV). Since, through this crystalline phase transition, only the paraelectric crystalline phase is subdivided and transformed into the small ferroelectric crystalline phase, [6] further phase separation from the mixture is not expected. Further lowering of the temperature to $T < T_{m, PBA}$ will also cause the crystallization of PBA in the amorphous phase, leading to a three-phase morphology in which two distinct crystalline phases coexist with a mixed amorphous phase.

Analysis of non-equilibrium melting points of P(VDF/TrFE) as a function of PBA concentration considering the paraelectric crystalline morphology yields a large negative value of $\chi_{12} = -0.592$ at 160°C. Liquid-liquid phase separation is observed above LCST curve located at more 50°C higher temperature than the melting point. The interaction parameter value calculated from the melting point depression of PBA is close to zero ($\chi_{12} = -0.071$ at 61°C), which can make the miscibility of this polymer pair much poorer in the temperature range well below the melting temperature of P(VDF/TrFE). It is very consistent with the glass transition behavior of the PBA-rich blends.

The fact that the interaction χ_{12} parameter calculated from the melting point depression of P(VDF/TrFE) has a large negative value indicates that there is a specific interaction between PBA and P(VDF/TrFE) such as hydrogen bonding and/or dipole-dipole interaction. The degree of frequency shift of the C=O stretching band of PBA to lower frequencies is proportional to the number fraction of the C=O groups participating the specific interaction with CF₂ or CH₂ group of P(VDF/TrFE). We could evaluate the level of specific interaction in the blend with changes in the peak position and line shape of the C=O stretching band of PBA at various blend compositions. *Figure 1* depicts changes in peak position of $\nu_{C=O}$ as a function of temperature for the P(VDF/TrFE)/PBA blends. In the whole temperature range, the peak position is lower with the addition of P(VDF/TrFE) due to the increasing number of the C=O groups of PBA interacting with the C-F and/or CH₂ of P(VDF/TrFE). The steep peak shift to higher frequencies in the range of 50-60°C is associated with the melting of PBA. After that the peak position of pure PBA increases keeping a nearly same slope, whereas the increasing slope of the blend with more than 50% P(VDF/TrFE) is much less up to 90°C. This is attributed to the increasing fraction of PBA molecularly mixed with the amorphous P(VDF/TrFE) after the melting of PBA in the blend. However, the slope becomes extremely high in the range of 90 to 120°C. This implies that the amorphous P(VDF/TrFE) in the as-cast blend sample is crystallized into the paraelectric phase and phase separation is induced. This crystallization-induced phase separation reduces the number of carbonyl groups of PBA interacting with the amorphous P(VDF/TrFE) part. After that the slope has a considerably large negative value up to 130-145°C depending on the blend composition. This is caused by the increasing number of C=O groups intermixed with P(VDF/TrFE) due to the melting of the paraelectric crystalline P(VDF/TrFE). After that temperature, the C=O peak position of the blend is increased as a function of temperature with a little higher slope compared with the slope of the pure PBA. This is associated with the reduction of the dipole-dipole interaction and/or hydrogen bonding strength caused by the increasing distance between the C=O and C-F groups due to the increasing thermal energy. Since the blend with a single phase is separated into

two phases, i.e., a P(VDF/TrFE)-rich phase and a PBA-rich phase, above LCST shown in *Figure 1*, the number of the C=O groups interacting with the P(VDF/TrFE) is expected to be extremely reduced. This may yield a sudden shift of the C=O peak position. In the practical observation, even though that transition position is not clearly observed, the peak position of the blend become closer to that of the pure PBA above LCST.

From the sophisticated application of factor analysis, one can extract each spectrum of the independent pure components and its concentration without knowing the spectral information of each pure component. However, it is not easy to analyze quantitatively in the case of large number of factors, especially when new factors are created by the mutual specific interactions. In this situation, least-squares curve-fitting (LSQ) can be used to evaluate the concentration of new factors in the mixture indirectly. For instance, we consider that, when any information about the interaction spectrum is not available in the miscible binary mixture having specific interaction, the concentration of the two pure components is calculated via LSQ method in a series of binary mixture using only the two pure component spectra. The calculated blend composition will have the biggest difference from the real composition in the binary mixture having the greatest amount of newly formed interaction species. As seen in the *Figure 3*, the blends having around the 70/30 ratio have the greatest value of difference between the nominal and calculated compositions. This implies that the concentration of newly formed interaction factors is greatest around 70/30 composition.

Most of miscible blend systems show a single glass transition behavior. When the above discussion about the results obtained from the melting point depression and IR spectroscopic analysis are taken into consideration, there will be no doubt about the prediction of a single glass transition behavior. In the case of the P(VDF/TrFE)-rich blends, it is impossible to measure T_g of the P(VDF/TrFE) phase due to the interference of the onset temperature range of the PBA melting, even if the separated P(VDF/TrFE) phase can exist. As shown in *Figure 1b*, even though a single T_g seems to be observed, the glass transition of the blends is dominated in the whole range by the T_g of PBA phase. This seems that the miscibility is not as good as expected from the melting point depression of P(VDF/TrFE). Even if the origin of poor miscibility in the very low temperature region is not identified yet, this poor miscibility may cause partial phase separation in the low temperature range, that is, the upper critical solution temperature (UCST) type phase separation is possible.

The effect of PBA on the crystallization behavior of P(VDF/TrFE) and the effect of P(VDF/TrFE) on the crystallization of PBA were also analyzed from the isothermal and non-isothermal crystallization of the blends. And the Curie transition behavior was related to the crystallization behavior. The addition of PBA increases the Curie transition enthalpy as well as the Curie transition temperature up to 70 wt.% of PBA. The possibility that some of ferroelectric phases can be formed directly from the melt without the prior formation of paraelectric phase is suggested for the blends with high PBA concentration.

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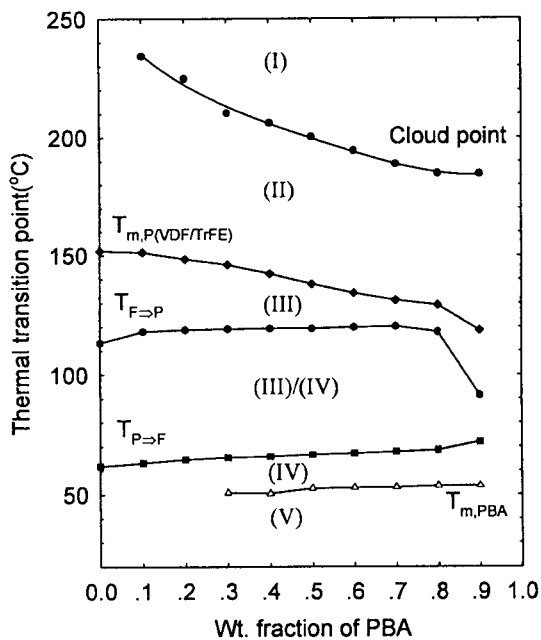


Figure 1a: Phase diagram of P(VDF/TrFE)/PBA blends.

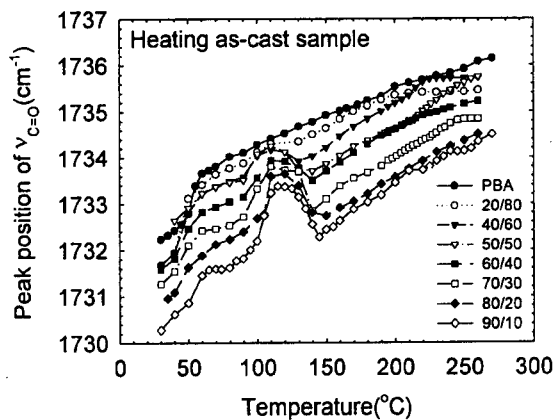


Figure 2. Plots of peak position of versus temperature for the P(VDF/TrFE)/PBA blends.

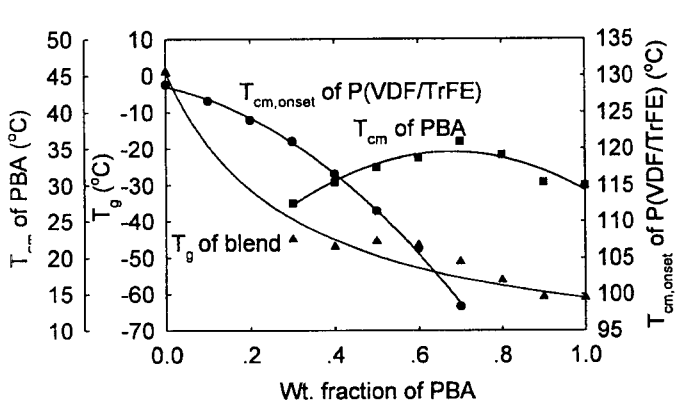


Figure 1b. Melt crystallization behaviors of P(VDF/TrFE) and PBA in P(VDF/TrFE)/PBA blends and glass transition behavior of P(VDF/TrFE)/PBA blends.

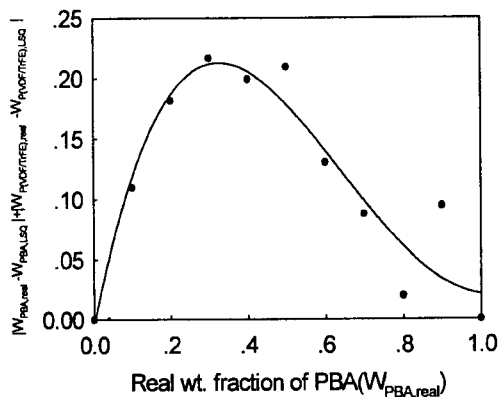


Figure 3. The plot of the difference value between the nominal and calculated compositions versus the blend compositions