Crystal–Amorphous Interphases in Binary Polymer Blends

The role of a crystal–amorphous interphase in semicrystalline homopolymers was first proposed by Flory in 1962[1] as a transition region where the order inherent in the stems issuing from the crystal was dissipated, so that chains assumed their isotropic orientations in the amorphous phase. Although there is reasonably good understanding of the characteristics of the interphase in homopolymers, the corresponding interphase in a melt miscible binary polymer blend, consisting of one semicrystalline component, is not well understood. Kumar and Yoon[2] have proposed a lattice model to model this situation and show the existence of an order–disorder interphase for the segments of the crystalline component of thickness ca. 1.5–3.0 nm, whose characteristics are largely independent of the nature of the amorphous polymer.

There has been much experimental work focused on two model systems, poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA)[3–7] and poly(ethylene oxide) (PEO)/PMMA,[8–11] and it is well established that both of these blends are miscible in the melt state.[3,8] The PVDF/PMMA system has been studied through the use of dynamical-mechanical measurements (DMA)[4,5] and dielectric spectroscopy.[6,7] In both cases, the existence of a transition in the same location as pure PVDF (i.e., ca. 273 K at 100 kHz) for all blends containing more than 50% of the PVDF was found. On the basis of these results, the existence of a crystal–amorphous interphase comprised purely of PVDF was established. Russell[12] has also examined melt-crystallized blends of PVDF/poly(vinylpyrrolidone) (PVP) and found qualitatively similar results.

Experimental work to delineate the behavior of the PEO/PMMA blends includes some rigorous SAXS and SANS measurements by Russell et al.,[9] who have illustrated the existence of a ca. 2.0-nm region (interphase) comprised of pure, disordered PEO in the vicinity of the crystals. The results obtained in the case of the PVDF/PMMA and PEO/PMMA blends are therefore in agreement since they suggest the existence of a pure crystalline polymer interphase, which behaves as though it were amorphous but completely pure.[2]

To probe this problem in more detail, we examined several melt miscible polymer blends with the aid of dielectric spectroscopy and differential scanning calorimetry (DSC). These included PEO/PMMA, poly(ϵ-caprolactone) (PCL)/poly(vinyl chloride) (PVC), and poly(butylene terephthalate) (PBT)/polyarylate (PAr). It was the goal of this research to understand if the characteristics of the interphase in all cases examined here were similar to those found for the PVDF/PMMA system.

Measurement of the heats of fusion was accomplished with a Perkin-Elmer DSC-7 at a heating rate of 20 K/min. Weight percent crystallinities were calculated by using perfect crystal heats of fusion of 49, 32, and 34 cal/g for PEO,[13] PCL,[14] and PBT,[15] respectively. Dielectric measurements were conducted on a Hewlett-Packard (4274A) multifrequency LCR meter in the frequency range 2–100 kHz and over a temperature range of ca. 120–450 K.

PEO Blends. Melt-crystallized blends of PEO/PMMA with more than ca. 50% by weight of the PEO were prepared from commercially available PEO (Polysciences; $M_w \approx 247\,000$) and PMMA (Aldrich Chemical; $M_w \approx 64\,000$) by casting from a 2% chloroform solution, vacuum drying at 393 K for 6 h, and then melt pressing at ca. 373 K for 1 min. Representative dielectric results plotted as tan δ vs T at 40 kHz for blends having more than 80% PEO are shown in Figure 1. PEO exhibits two relaxations in this temperature range of interest, which are termed β and γ. The higher temperature relaxation (at ca. 230 K at 40 kHz) is associated with T_g-like motion.[16] It is speculated that PEO being a flexible polymer has a small interphase composed of relatively tight folds, which are unaffected by the presence of the PMMA, thus leading to a transition that is apparently constant. This statement is based on the following factors:

(i) The peak shapes for this relaxation are similar for PEO and the blends of interest.

(ii) The amount of interphase formed, as determined from peak intensities, was found to scale linearly with the amount of crystallinity in the samples. DSC measurements have established that the percent crystallinity of the PEO (per gram of PEO and not of the blend) remains relatively constant around 70% for all the compositions that are illustrated in Figure 1.

The relaxation observed at 230 K for this mixed blend, which is surmised to be the interphase, is deduced to be a pure, amorphous PEO phase, since it has the same characteristics as the T_g-like relaxation in the pure crystalline component. These results are also in agreement with the conclusions obtained on PVDF blends,[4–7] as well as the SAXS and SANS measurements of Russell and co-workers.[9]

PCL/PVC Blends. The PCL/PVC blend is apparently very similar to the PEO/PMMA blend in that the glass transition temperatures of PEO and PCL are very similar, as are those for PVC and PMMA. Blends of PCL (Union Carbide; $M_w \approx 40\,000$) and PVC (Aldrich; nominal molecular weight $\approx 110\,000$) were cast as films from THF solution and dried under vacuum for ca. 6–12 h. Subsequently, the films were hot pressed at 400 K for 3–5 min and quenched. The pure PCL and PVC were pressed at 340 and 440 K, respectively.

When dielectric measurements were performed on this system, however, the results obtained (shown in Figure 2) are surprisingly different from those observed for the PEO/PMMA system. Pure PCL exhibits a β-transition at approximately 220 K. When one adds small quantities of the PVC, as in the case of a 10% blend of PVC, two distinct amorphous phase relaxations are observed. The lower temperature relaxation is presumably associated with an interphase while the higher temperature relaxation is presumed to be associated with a mixed PVC/PCL amorphous phase. As one proceeds to higher concentrations (i.e., for PVC compositions greater than ca. 15 wt %), it is clear that the interphase peak disappears completely, and one observes the presence of only a single transition, which apparently corresponds to a T_β for the mixed amorphous phase.

The lack of constancy for the location of the interphase peak, as well as its disappearance for PVC compositions larger than 15 wt %, is surprising in light of the results obtained on the PVDF/PMMA and PEO/PMMA systems. SAXS measurements on this system have suggested that it has an interphase, whose size of ca. 1.5 nm is apparently independent of the composition of the blend.[17] The dielectric and SAXS measurements therefore suggest that some other factor has to be considered to reconcile these results. One possibility stems from the fact that PCL is a stiffer polymer than PEO or PVDF, as quantified by the work of chain folding, q.[18] Numerical values quoted for PEO and PVDF are ca. 2 and 3 kcal/mol, respectively, while that for PCL is ca. 5 kcal/mol.[18–21] We speculate that PCL, being a stiffer polymer, would require a larger

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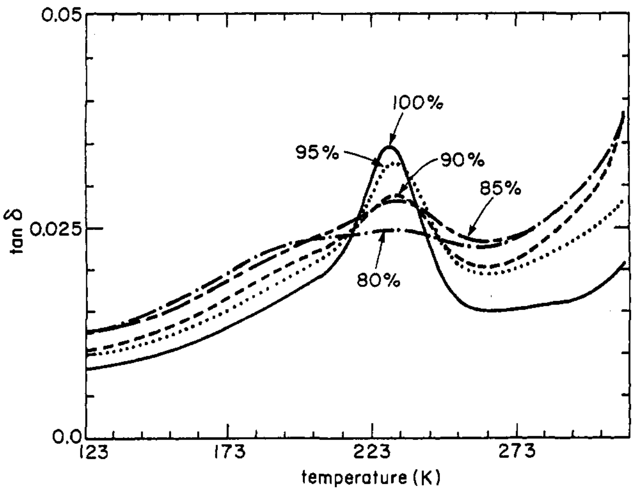

Figure 1. Dielectric tan δ vs T for PEO and four melt-crystallized PEO/PMMA blends (T_c = 298 K) at 40 kHz.

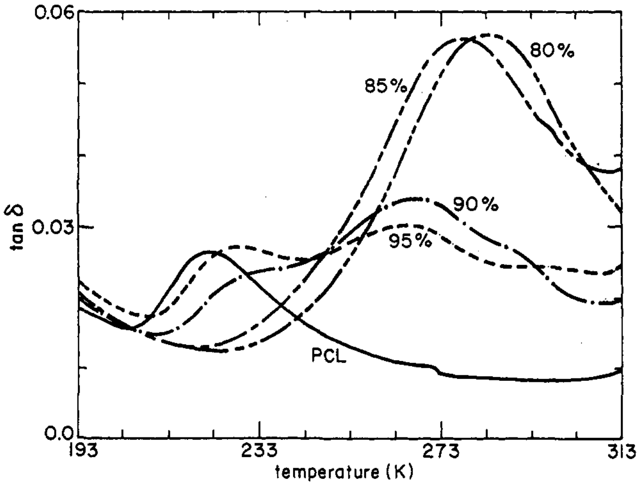

Figure 2. Dielectric tan δ vs T for PCL and four melt-crystallized PCL/PVC blends (T_c = 298 K) at 2 kHz.

order–disorder interphase as dictated by the theory of Kumar and Yoon.[2,22] A larger interphase would significantly alter the transition temperature of this "constrained" amorphous phase. Another factor to consider is that increased interactions may occur between the two polymers, due to a more negative Flory–Huggins interaction parameter. Such interactions are predicted by theory[22] to lead to more penetration of the amorphous polymer into the order–disorder interphase for the crystalline polymer.

PBT/PAr Blends. The final blend system examined in this work is a mixture of PBT (Hoechst Celanese; $M_w \approx 83\,000$) with a polyarylate, which was synthesized from Bisphenol A and isophthalic (75 mol %) and terphthalic acids ($M_n \approx 36\,000$).[23] The blends were coprecipitated into methanol, from a 2% 1,1,2,2-tetrachloroethane/phenol (40/60 wt %) solution, and refluxed in a Soxhlet extractor with fresh methanol. Films were then pressed at ca. 523 K for 5 min, quenched, and showed no signs of transesterification when examined by ^{1}H NMR. This system was selected since PBT, which has a q value of ca. 9 kcal/mol, is a stiff crystalline polymer.[23] The dielectric spectra of these samples are plotted in Figure 3 in the same form as those in previous figures. It can be seen that the dielectric relaxation spectra for these blends are different from the case of those of PEO/PMMA and are similar to those observed for the PCL/PVC blend. These results add further support to our proposed relationship between chain stiffness and interphase purity described above.

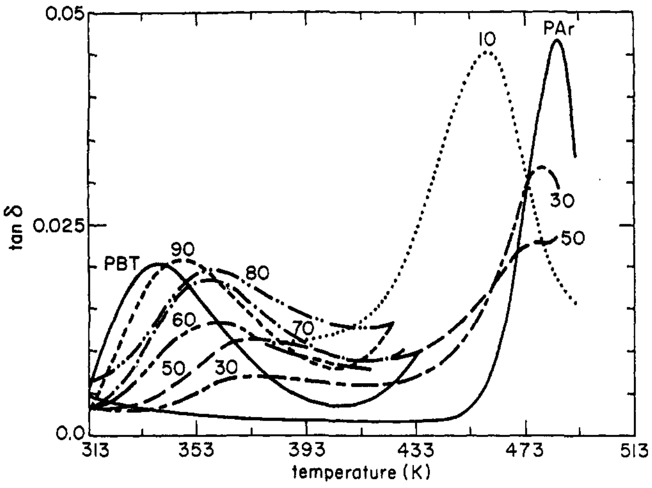

Figure 3. Dielectric tan δ vs T for PBT, PAr, and several melt-crystallized PBT/PAr blends at 2 kHz.

We have performed SAXS measurements on these blends, and the results indicate that PAr is present in the interlamellar regions.[25] No estimate for the interphase thickness is available, however. DSC measurements indicate that PBT and blends containing up to 50% PAr have crystallinities of 45–50% (based on the weight of the PBT in the blend). The 30% PBT blend has a degree of crystallinity of 35–40%, while the 10% blend is amorphous. PBT and PAr exhibit T_g-like transitions in the temperature range of interest (see Figure 3). Like the PVC/PCL blend the lower temperature transition, presumably associated with the interphase, is seen to move to higher temperatures and to reduce in intensity as the concentration of the PBT in the blend is reduced. Further, a mixed-phase transition close to the T_α of the pure PAr is also observed in some cases, and its intensity increases, as expected, with decreasing PBT concentration. It is therefore suggested that the unusual spectra obtained for the PCL/PVC blend do not constitute an isolated example and suggest strongly that the fundamental physics underlying the crystal–amorphous interphase in miscible blends is more complicated than thought before.

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CORRECTIONS

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The ordinate and abscissa of Figure 3 were incorrectly labeled. The correctly labeled version of Figure 3 appears below. The formulas for x and y in the text and in the legend to Figure 3 are actually for $-x$ and $-y$.