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Compatiblization of Polymers via Coalescence from Their Common Cyclodextrin Inclusion Compounds

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ABSTRACT: We have found, when inherently immiscible polymers are included as guests in the narrow channels of their common inclusion compounds (ICs) formed with host cyclodextrins (CDs) and then these polymer-1/polymer-2-CD-IC crystals are washed with hot water to remove the host CD lattice and coalesce the guest polymers, that intimately mixed blends of the polymers are obtained. This behavior had been observed previously by us for the crystallizable poly(ϵ-caprolactone) (PCL)/poly(L-lactic acid) (PLLA) pair, where in the coaelsced blend PCL and PLLA crystallinity was completely and nearly completely suppressed, respectively. Here we report similar observations made on the polycarbonate (PC)/poly(methyl methacrylate) (PMMA) pair, which are respectively difficult to crystallize and amorphous. PC/PMMA blends coalesced from their common γ-CD-ICs are amorphous and generally exhibit single glass transitions at temperatures (T_g) between those of pure PC and PMMA. Interestingly, a 1:4 molar PC:PMMA blend coalesced from its common γ-CD-IC is characterized by a T_g lower than that of pure PMMA. FTIR spectroscopy suggests an intimate mixing of and possible specific interactions between PC and PMMA chains in the coalesced blends as reflected by substantial shifts in the frequencies of the PMMA and PC C═O vibrations. In addition, repeated DSC scanning or annealing of the coalesced PC/PMMA blends for up to 2 h at $T \geq 200$ °C did not lead to phase separation as judged from the constancy of the single T_g's observed by DSC. Though not described in detail here, very similar results were also obtained for the PC/polystyrene (PS) pair, including a T_g for a PS-rich blend that is below the T_g for pure PS. We are currently studying the molecular-level mixing in and thermal stabilities of these blends.

Introduction

Recently, we reported[1] an attempt to blend polymers by first forming their common inclusion compound (IC) with cyclodextrin (CD) as the host and then coalescing the guest polymers from their CD-IC crystals by washing them with hot water. This procedure was used in the hope of obtaining an intimately mixed, compatible blend of the poly(ϵ-caprolactone) (PCL)/poly(L-lactic acid) (PLLA) pair, which are normally incompatible. In the PCL/PLLA-α-CD-IC crystals neighboring PCL and PLLA chains residing in the narrow channels provided by the host α-CD lattice are likely in close proximity. When the PCL/PLLA-α-CD-IC crystals are washed with hot water, which does not dissolve either of the guest polymers, the α-CD host is removed and the PCL and PLLA chains coalesce into a blend. Because they are proximal in their common α-CD-IC crystals, we anticipated that the PCL/PLLA blend coalesced from them might be compatible, with an intimate mixing of PCL and PLLA chains.

We observed the coalesced PCL/PLLA blend to no longer evidence crystallinity for the PCL chains, and only a very small fraction (∼5%) of the PLLA chains were crystalline. By contrast, when the PCL/PLLA blend is formed by casting from tetrahydrofuran (THF), ∼45% of both the PCL and PLLA chains crystallize, and large and small PCL and PLLA spherulites were observed in the photomicrograph of the phase-separated, solution-cast blend. A photomicrograph of the coalesced PCL/PLLA blend, on the other hand, appeared to show an amorphous matrix embedded with a few small PLLA spherulites.

Annealing the PCL/PLLA blend coalesced from their common α-CD-IC crystals for 24 h at 200 °C, which exceeds the melting temperatures of both PCL and PLLA, did not appear to alter the as-coalesced, intimate morphology, as evidenced by DSC and microscopic observations. In addition, we have not been able to redissolve the coalesced PCL/PLLA blend, even in THF, which is commonly used to cast their blended films.

These intriguing observations have led us to attempt the formation of similar blends with amorphous polymer pairs, such as polycarbonate (PC)/poly(methyl methacrylate) (PMMA) and PC/polystyrene (PS). Here we describe our initial efforts to obtain intimately mixed, compatible blends of the inherently immiscible polymer pairs PC/PMMA and PC/PS by formation of their common γ-CD-ICs, followed by coalescence of the guest polymer pairs from their γ-CD-IC host crystalline lattices.

The miscibility of binary blends of bisphenol A−polycarbonate (PC) with PMMA and their equilibrium phase phenomena have been widely investigated.[2−10] However, the precise phase behavior of the blends remains controversial. A number of papers reported methods to prepare homogeneous blends of the two polymers, but most of the mixtures were found to phase separate after heating to relatively low temperatures (∼160 °C). These results were explained by the existence of a lower critical solution temperature (LCST) for the system. Cloud point estimates further suggested that the temperature range between the LCST and T_g of PC (∼150 °C) is too narrow for industrial processing or use. This shortcoming might be surmountable, if specific molecular interactions between the two different polymer chains could be induced. If the two polymers can be well or intimately blended, i.e., at the molecular level, specific interactions between the polymers might be enhanced and result in stable, intimate PC/PMMA blends which can withstand the heating process.

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Since we have found, when inherently immiscible polymers are simultaneously included as guests in the narrow channels of their common inclusion compounds (ICs) formed with host cyclodextrins (CDs) and then these polymer-1/polymer-2-CD-IC crystals are washed with hot water to remove the host CD lattice and coalesce the guest polymers, that an intimately mixed blend of the polymers are obtained, here we extend this procedure to the CD-IC fabrication of PC/PMMA blends.

Experimental Section

Materials. Polycarbonate (PC) of bisphenol A [poly(oxacarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene) with average molecular weight $M_w = 28\,800$ and $M_n = 17\,300$ was obtained from Aldrich Chemical Co. Inc. Poly(methyl methacrylate) (PMMA) with average molecular weight $M_w = 350\,000$ was also obtained from Aldrich Chemical Co. Inc. γ-Cyclodextrin was purchased from Cerestar Co. Tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) were analytical grade and obtained from Fisher.

Preparation of Samples. γ-CD was dissolved in DMSO and heated to 60 °C. PC and PMMA with different molar blend ratios (4:1, 1:1, 1:4) were dissolved in THF, and the solutions were heated to 50 °C. The THF solution of PC/PMMA was slowly added to the saturated γ-CD/DMSO solution while stirring and heating. Heating and stirring at 60 °C was continued for 3 h to keep the combined solution homogeneous. The mixture was slowly cooled to 20 °C, and stirring was continued overnight. The resulting precipitate was filtered out and dried in a vacuum oven at 60 °C for 24 h.

The physical blends of the two polymers were made by dissolving both polymers in THF and then drying the solutions in a vacuum oven at 60 °C for 24 h.

Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectral studies of PC, PMMA, γ-CD, PC/PMMA physical blend, PC/PMMA-γ-CD-ICs, and the IC samples after washing with hot water or THF were carried out in a Nicolet 510P FTIR spectrometer in the range between 4000 and 400 cm^{-1}, with a resolution of 2 cm^{-1}.

Differential Scanning Calorimetric (DSC) Analysis. The thermal scans of the individual polymers, polymer blends, and the IC samples before and after coalescence by washing with hot water were performed with a Perkin-Elmer DSC-7 differential scanning calorimeter. The measurements were run in the range of 30−260 °C at a heating rate of 10 °C /min.

Thermogravimetric Analysis (TGA). TGA scans of 5−10 mg samples were obtained by using a Perkin-Elmer Pyris 1 thermogravimetric analyzer (TGA). The samples were put into platinum pans which were hung in the heating furnace. The weight percentage of material remaining in the pan was recorded while heating from 25 to 800 °C at a heating rate of 20 °C/min. Nitrogen was used as the purge gas.

X-ray Diffraction. The X-ray diffraction scans of PC, PMMA, γ-CD, and PC/PMMA-γ-CD ICs were carried out with a Seimens type-F X-ray diffractometer. The X-ray source was Ni-filtered Cu Kα radiation (30 kV, 20 mA). The specimens were mounted on aluminum frames and scanned from 5 to 40° = 2θ at a speed of (2θ = 1.2°)/min.

Results and Discussion

FTIR Analysis. Figure 1 shows the FTIR spectra of (a) PC, (b) PMMA, (c) PC/PMMA physical blend, and (d) PC/PMMA-γ-CD IC coalesced (washed with hot water). The FTIR spectrum of PC is characterized by an intensive C=O band at ~1775 cm^{-1}, a phenyl ring structure band at ~1505 cm^{-1}, and a strong C−O band at 1194 cm^{-1}. The absorption peak at 1386 cm^{-1} is contributed by the terminal phenyl groups in the polymer. In pure PMMA, the characteristic C=O peak occurs at ~1731 cm^{-1} and the peaks at 2950 and 2998 cm^{-1} are contributed by the methyl groups. For γ-CD, the peak at 1079 cm^{-1} is contributed by CH$_2$−OH vibrations and the peak at 1158 cm^{-1} is from the −OHs on the cycle. The C−H bond absorption peak at 2925 cm^{-1} also can been seen for γ-CD in its FTIR spectrum. All of the characterized IR absorption peaks of PC, PMMA, and γ-CD are found in the spectrum of PC/PMMA-γ-CD IC in Figure 2b. This means that the experimental sample contains PC, PMMA, and γ-CD. There is very little difference between the FTIR spectrum of the physical blend and the individual FTIR spectra of the pure polymers (see Figure 1a−c). This

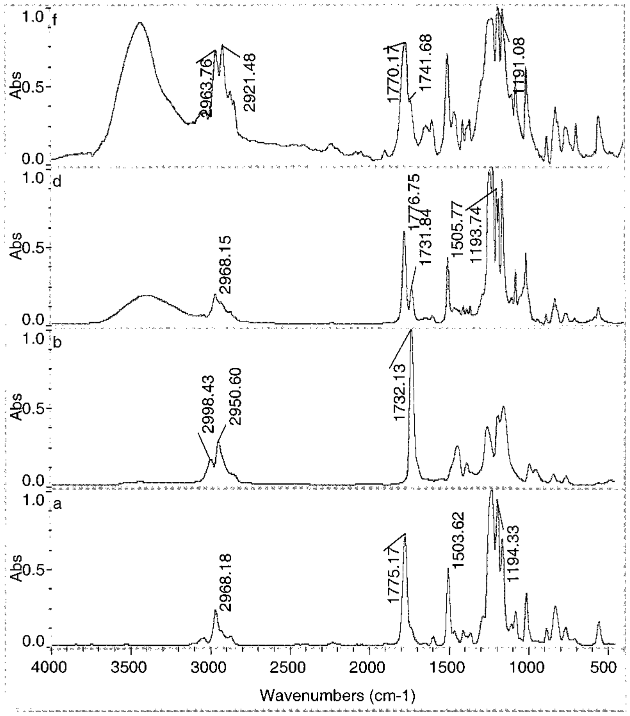

Figure 1. FTIR spectra of (a) PC, (b) PMMA, (c) PC/PMMA physical blend (PC:PM = 1:1 molar ratio), and (d) PC/PMMA-γ-CD IC coalesced (washed with hot water, PC:PMMA = 1:1 molar ratio).

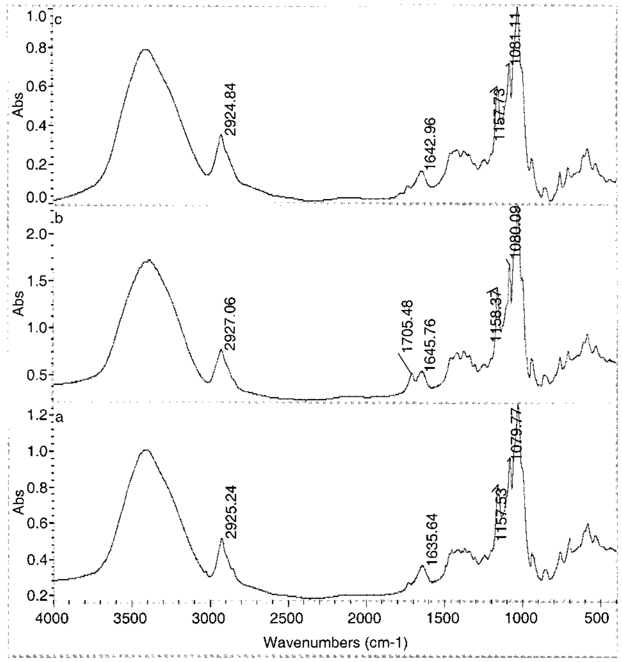

Figure 2. FTIR spectra of (a) γ-CD, (b) 1:1 PC/PMMA-γ-CD IC, and (c) 1:1 PC/PMMA-γ-CD IC washed with THF.

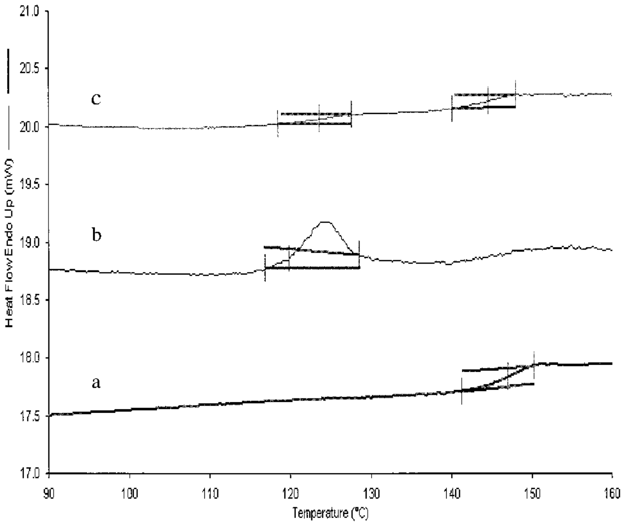

Figure 3. DSC thermograms of (a) PC, (b) PMMA, and (c) 1:1 PC/PMMA physical blend.

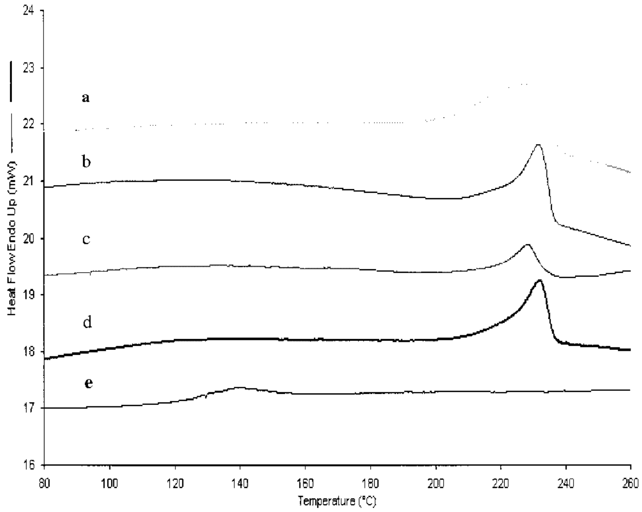

Figure 4. First DSC scans for the (a) PC-γ-CD IC, (b)PC/PMMA-γ-CD IC (PC:PMMA = 4:1 molar ratio), (c) PC/PMMA-γ-CD IC (PC:PMMA = 1:1 molar ratio), (d) PC/PMMA-γ-CD IC (PC:PMMA = 1:4 molar ratio), and (e) PMMA-γ-CD IC, all after washing with hot water.

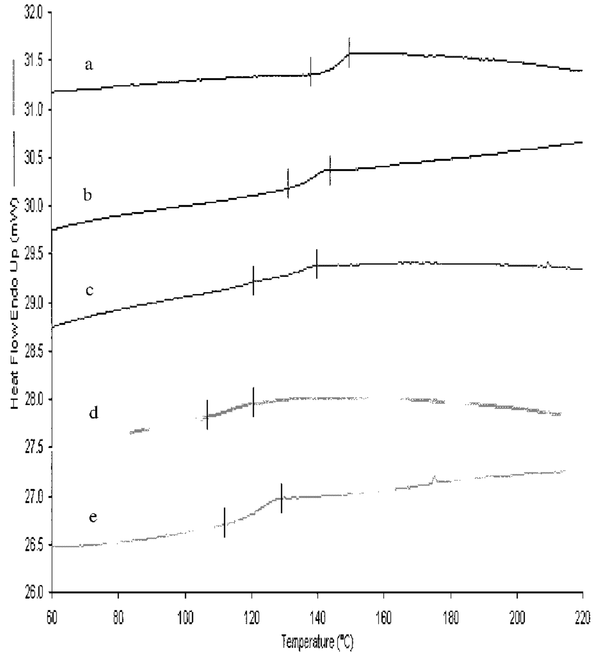

Figure 5. Second heating DSC scans for the (a) PC-γ-CD IC, (b) PC/PMMA-γ-CD IC (PC:PMMA = 4:1 molar ratio), (c) PC/PMMA-γ-CD IC (PC:PMMA = 1:1 molar ratio), (d) PC/PMMA-γ-CD IC (PC:PMMA = 1:4 molar ratio), and (e) PMMA-γ-CD IC, all after washing with hot water.

means that there is no significant interaction between the two components in the physical blend, although some reports[11] suggest that there might be some weak interactions between PC and PMMA.

However, in the spectrum of the PC/PMMA-γ-CD-IC sample coalesced by washing with hot water (Figure 1d) the PMMA C=O absorption peak at 1732 cm^{-1} has shifted to 1741 cm^{-1} and is partly overlapped by the PC C=O, which shifted to 1770 cm^{-1}. Moreover, the peak characteristic for the methyl groups on PMMA also shifted from 2950 to 2921 cm^{-1}. These vibrational shifts may result from interactions occurring between the carbonyl and methyl groups of PMMA with the carbonate groups and phenyl rings of PC,[12] which may be facilitated when the chains of the two polymers are close enough, as in the intimately mixed, γ-CD-IC coalesced PC/PMMA blends. In an effort to develop a detailed understanding of the intimacy and interactions between PC and PMMA chains in the blends coalesced from their common γ-CD-ICs, we are beginning to study them by means of various solid-state NMR techniques.

In Figure 2b we observe that both the PC and the PMMA C=O vibrations shift to a single band at 1705 cm^{-1} for the PC/PMMA-γ-CD-IC, which is characteristic of hydrogen-bonded carbonyls[13] and likely results from hydrogen bonds formed with the −OH groups of the γ-CD host. Note that the FTIR spectra of (a) pure γ-CD and (c) PC/PMMA-γ-CD-IC washed with THF in Figure 2 are virtually identical. Apparently, the THF wash completely disrupts the γ-CD-IC crystals and dissolves and removes the included PC/PMMA.

Thermal Behavior. Figure 3 is the DSC thermogram of the solution-cast physical blend of PC/PMMA observed in the second scan after melting of the PC crystals. It indicates that the T_g's of PC and PMMA are unchanged in the physical blend. This means that the two polymers are not miscible when blended in the normal way. For pure γ-CD, there is no thermal transition in the measured range 30−260 °C. In Figure 4, the first DSC scanning results for PC/PMMA blends with different PC/PMMA compositions (molar ratios), which were obtained after washing their common γ-CD-ICs with hot water, are shown. Melting peaks for crystalline PC are clearly observed in Figure 4 (also see the X-ray results below). As we might expect, these PC crystals are not reversibly stable and so disappear after melting and are not re-formed during the second DSC heating. Figure 5 shows the second scans of the washed IC samples. In this figure, we can see that there is only one T_g for each washed IC sample with different blend ratios. These single T_g's decrease with an increase of PMMA content in the CD-IC blend samples. This phenomenon is in agreement with the description of miscible polymers by Olabisi et al.[14] The most interesting observation is that for the 1:4 IC blend of PC:PMMA the single T_g of the sample, which is 110 °C, is lower than the T_g of pure PMMA (118 °C). One explanation maybe that the PC chains act as a plastizer in the homogeneous system, because the PC we used has a relatively low molecular weight and correspondingly short chains. Remember that DSC scans of PC, PMMA,

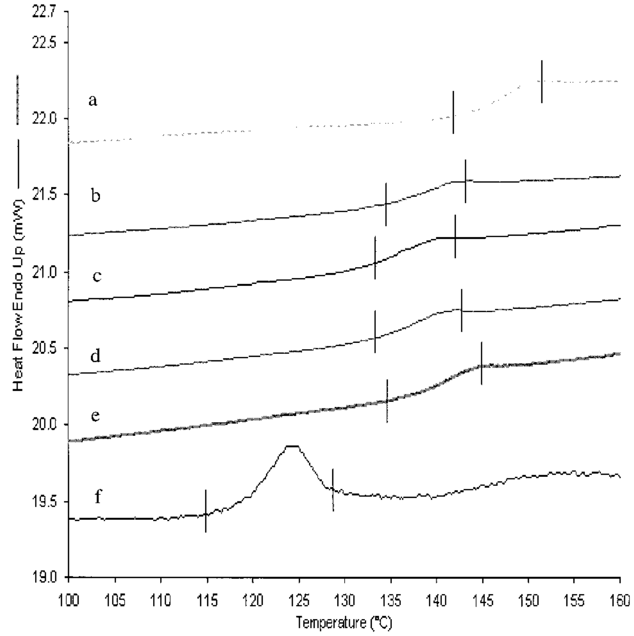

Figure 6. DSC heating scans of (a) PC, (b) run II of coalesced PC/PMMA-γ-CD IC (PC:PMMA = 4:1 molar ratio), (c) run III of coalesced PC/PMMA-γ-CD IC (PC:PMMA = 4:1 molar ratio), (d) run IV of coalesced PC/PMMA-γ-CD IC (PC:PMMA = 4:1 molar ratio), (e) coalesced PC/PMMA-γ-CD IC (PC:PMMA = 4:1 molar ratio) after annealing for 2 h at 200 °C, and (f) PMMA.

and a solution-cast blend (1:1 mole ratio) (see Figure 3) show that initially pure PC and PMMA are amorphous polymers and only exhibit glass transition temperatures at 145 and 118 °C, respectively.

To examine the thermal stability of the intimate blends, repeated heating scans and a scan taken after annealing for 2 h at 200 °C were performed on the coalesced PC/PMMA-γ-CD-IC samples. Figure 6 presents the DSC scans of runs II, III, and IV and the sample annealed at 200 °C for 2 h, which were observed for the coalesced PC/PMMA-γ-CD-IC (PC:PMMA = 4:1 molar ratio). As evidenced by the repeated observation of a single T_g between the T_g's of pure PC and PMMA, no phase separation is found to take place after repeatedly heating to 260 °C or annealing at 200 °C for 2 h.

Since the CD-IC coalesced blends appear to be homogeneous from both FTIR and DSC observations, the two intimately mixed polymers might be expected to have some effect on each other's decomposition when they are heated to degradation. Figure 7 shows the degradation of a CD-IC coalesced blend compared with the pure polymers and their physical blend. Bisphenol A–polycarbonate exhibits outstanding thermal stability and has a T_d at ~ 510 °C, while PMMA has a lower T_d of 290 °C. Two significant changes in the slopes of the degradation curves can be observed in the physical blend although they are different from the T_d's of the pure polymers. The two transitions disappeared in the CD-IC blended samples, and only a nearly straight line is seen between the decomposition ranges of the two pure polymers. In the blends coalesced from their γ-CD-ICs the two polymers apparently co-degrade together at a molecular level. These results demonstrate that there is likely some interaction between the two polymers and that they form a homogeneous phase.

X-ray Diffraction. The X-ray diffraction patterns of the two polymers, their physical blend, γ-CD, PC/PMMA-γ-CD-ICs, and PC/PMMA-γ-CD-ICs washed with hot water are shown in Figures 8 and 9. As is well-known,[15] the peak at $2\theta \sim 7.8°$ in the wide-angle X-ray scattering is characteristic for the channel structured crystals of γ-cyclodextrin-ICs. This structure is only formed when there are certain guest molecules, such as polymers included. Since both THF and DMSO do not form the channel structure with γ-CD, the two polymers must be the only included guests. The X-ray patterns of PC/PMMA-γ-CD-ICs show no peak for pure PC crystals. This indicates that PC is included in the channel structure of γ-CD, with individual isolated chains occupying the channels and so are not able to form macromolecular crystals. However, when the polymer ICs are washed with hot water, the CD that

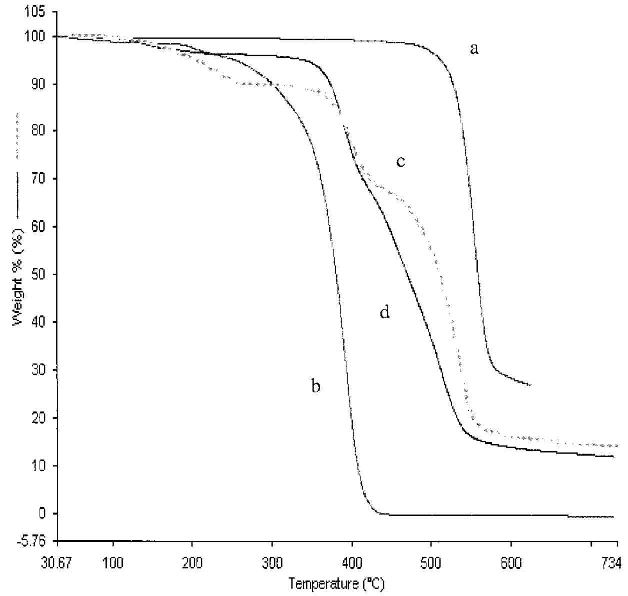

Figure 7. Thermal degradation of (a) PC, (b) PMMA, (c) PC/PMMA physical blend (PC:PMMA = 1:1 molar ratio), and (d) coalesced PC/PMMA-γ-CD-IC (PC:PMMA = 1:1 molar ratio).

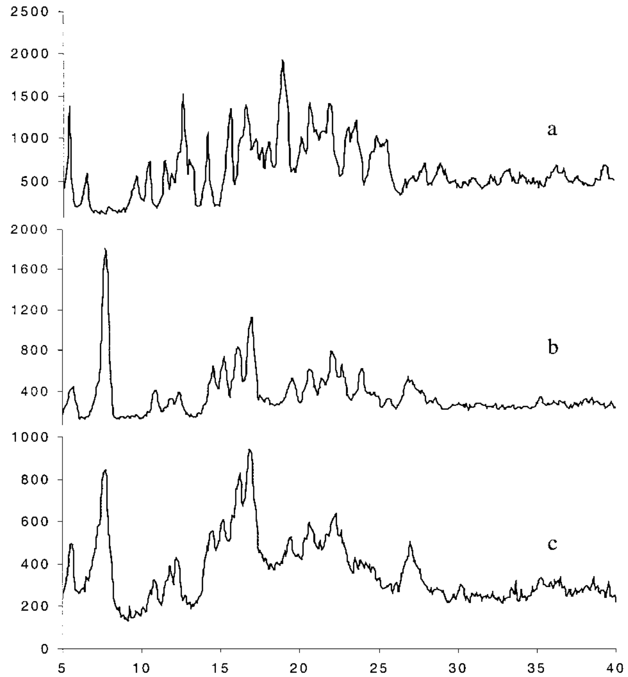

Figure 8. Wide-angle X-ray Diffraction of (a) γ-CD (cage structure), (b) 1-propanol-γ-CD-IC (channel structure[15]), and (c) PC/PMMA-γ-CD-IC.

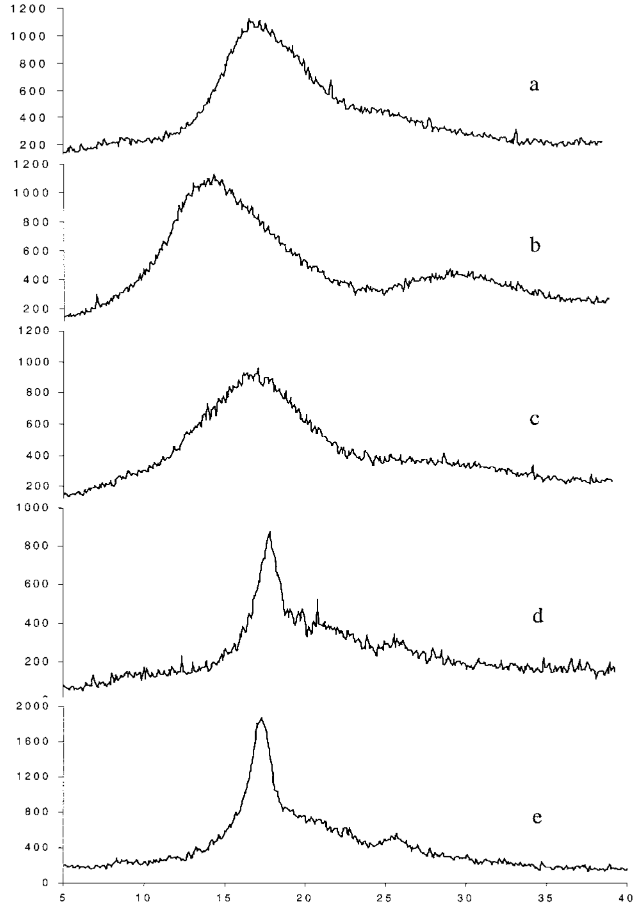

Figure 9. Wide-angle X-ray diffraction of (a) PC, (b) PMMA, (c) PC/PMMA physical blend, (d) PC/PMMA-γ-CD coalesced, 1:1 blend, and (e) crystalline PC.

holds the polymers will separate from the guest polymers, and the guest polymers will come together again. The process is called "coalescence" and produces the polymer blend. Since there is no difference between the outside surfaces of the IC crystals, PC-IC, PMMA-IC, or PC/PMMA-IC crystals might be evenly distributed in the sample. Coalescence takes place so rapidly that the polymers have insufficient time to form a separate continuous phase for each polymer component of the blend. Instead, a single phase, miscible polymer blend is obtained in this manner.

Note in Figure 9e the prominent peak at $2\theta = 18°$ attributable to some PC crystals formed during the coalescence of the PC/PMMA blend. When the coalesced blend is heated above the melting temperature of PC, cooled to room temperature, and observed again by X-ray diffraction, the $2\theta = 18°$ peak due to PC crystals disappears, confirming the DSC observations made on the coalesced PC/PMMA blends.

Conclusions

By simultaneously forming their common inclusion compounds with γ-CD, followed by washing these CD-IC crystals with hot water to coalesce the guest polymers, miscible polycarbonate/poly(methyl methacrylate) blends were obtained. The characteristics of the samples coalesced from their γ-CD-ICs were examined with FTIR, DSC, TGA, and WAXD. WAXD results indicated that PC/PMMA can form a channel structured inclusion compound with γ-CD. PC/PMMA blends coalesced from their common γ-CD-ICs are amorphous and generally exhibit single glass transitions at temperatures (T_g) between the T_g's of pure PC and PMMA. Interestingly, a 1:4 PC:PMMA blend coalesced from its γ-CD-IC is characterized by a T_g lower than that of pure PMMA. In addition, the coalesced PC/PMMA were observed by DSC to be stable to repeated heating and annealing at $T \geq 200$ °C without phase separation. Though not presented here, very similar results were also obtained from the PC/polystyrene (PS) pair, including a T_g for a PS-rich blend that is below the T_g for pure PS.

The simultaneous, cothermal degradation of PC/PMMA also demonstrated that polymer blends obtained by coalescence from their common γ-CD-ICs are well-mixed with intimate contact between the component polymers in the sample. In fact, in the PC/PMMA blends coalesced from their γ-CD-ICs, the C=O stretching bands observed at ~1730 cm^{-1} in pure PMMA and at ~1776 cm^{-1} in pure PC shift to ~1740 and ~1770 cm^{-1}, respectively, where they partially overlap. This serves as a strong indication of specific interactions between the PMMA and PC chains and is a further testament to the intimate mixing of PC and PMMA chains in the blends coalesced from their common γ-CD-IC crystals.

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