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Thermal degradation of polycarbonate, poly(vinyl acetate) and their blends

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Abstract

We have recently developed a novel approach for intimately mixing thermodynamically incompatible polymers, which utilizes the formation of inclusion compounds (ICs) formed with host cyclodextrins (CDs), followed by removal of CD and coalescence of the common guest polymers into a blend. In this paper direct insertion probe pyrolysis mass spectrometry (DIP-MS) analyses of polycarbonate (PC), poly(vinyl acetate) (PVAc) and PC/PVAc blends, obtained by coalescence from their inclusion compounds formed with host γ-CD (coalesced blend) and by co-precipitation (physical blend), have been performed. Variations in the thermal stabilities of the coalesced polymers were recorded both by TGA and DIP-MS and compared to the corresponding as-received polymers. It has been determined that for both coalesced and physical blends of PC/PVAc, CH_3COOH formed by deacetylation of PVAc above 300 °C, reacts with PC chains decreasing their thermal stability. This process was more effective for the physical blend, most likely due to enhanced diffusion of CH_3COOH, produced by deacetylation of PVAc, into the PC domains, where it can further react producing low molecular weight PC fragments bearing methyl carbonate chain ends.

Keywords: Polycarbonate; Poly(vinyl acetate); Blend; Cyclodextrin; Inclusion compound; Pyrolysis mass spectrometry

1. Introductıon

Interest in studying polymer blends has considerably increased due to their significant industrial applications. Materials with improved characteristics are produced by blending two or more polymers in order to combine their properties for certain purposes. The conventional methods for producing polymer blends are melt blending, co-precipitation, and solvent casting [1]. When two or more polymer components are blended together, it is usual to obtain phase-separated materials, due to a small entropy and the generally unfavorable enthalpy of mixing when there are no specific interactions (hydrogen bonds, van der Waals and/or polar interactions, etc.) between the polymer components. In the case of poor mixing, the blends exhibit properties inferior to their component polymers due to the poor degree of interfacial adhesion between the phase-separated components, which create a multiplicity of defects in the system [2]. In addition to the properties of each polymer component and their compositions, the eventual characteristics of a polymer blend depend most importantly on the miscibility of the component polymers in the blend [1–3]. The preparation of miscible polymer blends depends on many factors, such as solvent, temperature, weight/molar ratio of the components, molecular weight, and specific interactions [3].

Cyclodextrins (CDs), cyclic starch oligomers, are truncated molecular cones consisting of 6, 7, and 8 glucose units, and are named alpha (α-), beta (β-) and gamma (γ-) cyclodextrins (CDs), respectively (see Fig. 1). Although the depth of the cavities for the three CDs is the same (∼7.9 Å), their cavity diameters are ∼6, 8, and 10 Å, respectively [4]. Because of their unusual structure, CDs may host both polar and nonpolar guests, including small molecules as well as polymers [5–11].

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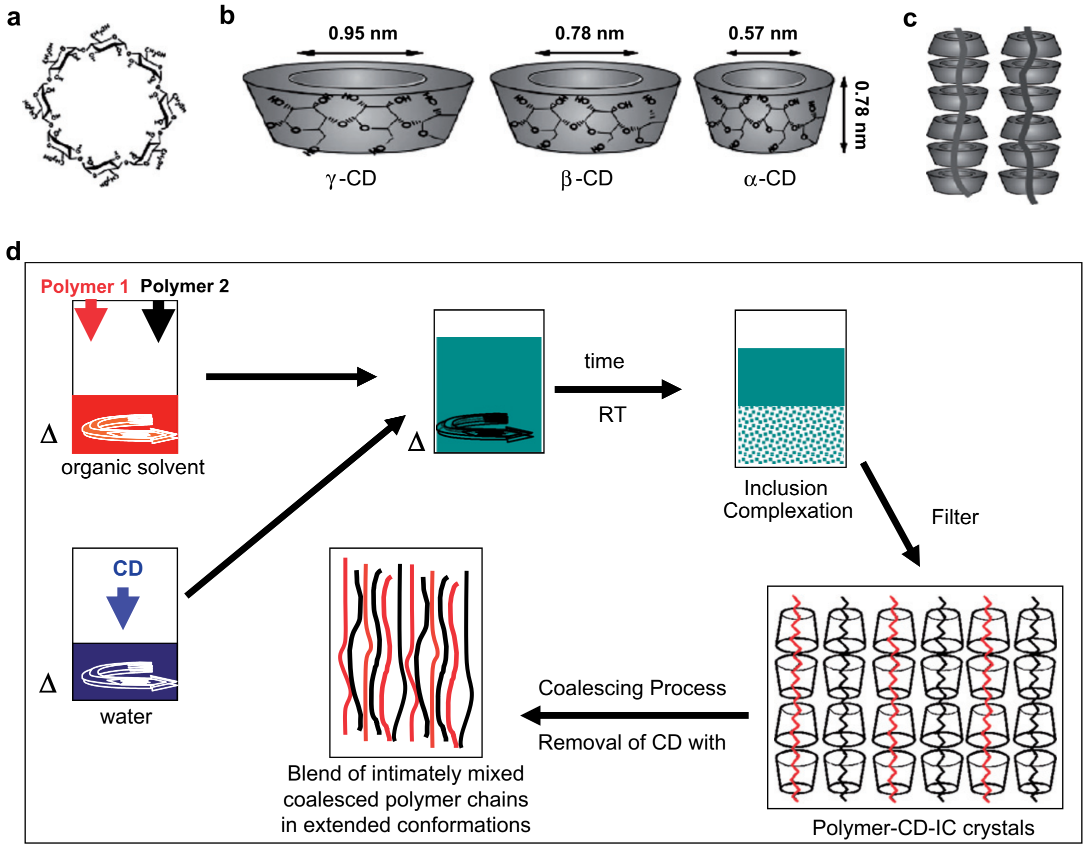

Fig. 1. (a) γ-CD chemical structure; (b) approximate dimensions of α-, β- and γ-CDs; schematic representation of (c) polymer–cyclodextrin–inclusion compound (polymer–CD–IC); (d) polymer–CD–IC formation, the coalescence process, and the coalesced polymer blend.

Our own research studies have shown that CDs may act as hosts in the formation of inclusion compounds (ICs) with various guest polymers [7–19]. Polymer–CD–ICs represent crystalline compounds obtained by threading of the CD molecules onto the guest polymer chains. The included polymers are confined to the narrow, continuous CD channels, and so are necessarily highly extended and segregated from neighboring polymer chains by the walls of the CD stacks (see Fig. 1c). We have shown that coalescence of guest polymers from their CD–IC crystals can result in a significant improvement in their bulk physical properties caused by modification of their structures, morphologies and even conformations compared to those observed in their normally produced bulk samples.

Recently, we have developed a novel approach for mixing thermodynamically incompatible polymers by first obtaining a common polymer–CD–IC. Subsequently, the guest polymers are coalesced from their common CD–IC crystals by removal of the CD host [15–19]. This method has successfully produced intimate blends of poly(ε-caprolactone) (PCL)/poly(L-lactic acid) (PLLA) [15], poly(ethylene terephthalate) (PET)/poly(ethylene 2,6-naphthalate) (PEN) [16], polycarbonate (PC)/poly(methyl methacrylate) (PMMA) [17,18], (PC)/poly(vinyl acetate) (PVAc) [18], PMMA/PVAc [18] and the ternary blend PC/PMMA/PVAc [19].

These well-mixed binary blends achieved by coalescence from their common γ-CD–ICs exhibited thermal stabilities and thermal degradation mechanisms that were distinct from those of the pure component polymers and their binary blends obtained by both solvent-casting and co-precipitation methods. The details of thermal degradation characteristics of coalesced and physical blends of PMMA/PVAc, and PC/PMMA have been studied by direct pyrolysis mass spectrometry and discussed in our recent publications [18,20,21].

In the literature, studies on the PC/PVAc blend system are limited. Sato et al. reported that PC forms partially miscible blends with poly(vinyl alcohol) (PVA) and partially saponified PVAc due to the existence of side-chain hydroxyl groups, which improves their miscibility by intermolecular hydrogen bonding, but PVAc was found to be immiscible with PC [22]. We have recently shown that thermally stable and intimately mixed blends of PC/PVAc can be obtained by formation of and coalescence from their common IC with γ-CD [18].

In this paper, the details of direct pyrolysis mass spectrometry analyses of PVAc, PC, and the binary PVAc/PC blend when coalesced (c-) from their γ-CD–ICs are investigated and their thermal behaviors and degradation mechanisms are reported. The thermal characteristics of c-PVAc, c-PC and the c-PVAc/PC blend were characterized by comparing their direct pyrolysis mass spectrometry results with those for γ-CD, as-received PVAc and PC, PVAc/PC physical mixture, and their inclusion compounds.