Thermal degradation processes of poly(carbonate) and poly(methyl methacrylate) in blends coalesced either from their common inclusion compound formed with γ-cyclodextrin or precipitated from their common solution

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Abstract

Direct insertion probe pyrolysis mass spectrometry (DIP-MS) analyses of a PC/PMMA blend, coalesced from their common inclusion compound (ICs) formed with host γ-cyclodextrin (γ-CD) through removal of the γ-CD host, and a physical PC/PMMA blend, precipitated from their common solution, have been performed and compared with those of the coalesced and as-received homopolymers. A slight increase in the thermal stability of the PMMA component in the presence of PC was recorded both by TGA and DIP-MS compared to the corresponding homopolymers. The DIP-MS observations pointed out that the thermal stability and degradation products of these polymers are affected once they are included inside the IC channels created by the stacked host CDs. DIP-MS observations suggested that for both coalesced and physical PC/PMMA blends, an exchange reaction occurs between carbonates of PC and MMA, formed by depolymerization of PMMA above 300 °C, most likely due to diffusion of MMA monomer at the interface or even into the PC domains, where it can react producing low molecular weight PC bearing methyl carbonate and methacrylate chain ends. The results also indicated an ester–ester interchange reaction between PC and PMMA yielding a graft copolymer and low molecular weight PC chains bearing methyl carbonate end groups in the case of the coalesced blend. This can be attributed to the presence of specific molecular interactions between the intimately mixed PMMA and PC chains in the coalesced PC/PMMA blend.

Keywords: Cyclodextrin; Inclusion compound; Poly(methyl methacrylate); Polycarbonate; Blend; Thermal degradation

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of 6, 7, and 8 α,1,4-linked glucopyranose units and are named alpha (α), beta (β), and gamma (γ)-CDs, respectively (Fig. 1). Due to the unique chemical structure of the CD molecules, their cavities are hydrophobic relative to their outer surface. The hydrophobic nature of the CD cavities facilitates the ability of CDs to act as a host clathrate for both nonpolar and polar guests to form inclusion compounds (ICs) [1]. Though limited by the sizes of the host CD cavities and the cross sections of included guests, CDs can include small molecules, as well as polymers, to form guest–host CD-ICs [2–7]. The guest polymer chains included inside the IC channels created by the stacked CDs are segregated from neighboring polymers chains by the walls of the CD crystalline lattice and are forced to adopt highly extended conformations by the narrow host CD channels (diameters ~0.5–1.0 nm). It has been shown that modification of the microstructures, morphologies, and even conformations can result from the coalescence of guest polymers from their CD-IC crystals, through removal of host CD [8–15], which in turn yields significant improvements in
their physical properties. Our research group has also developed a novel approach for forming intimately mixed polymer blends by coalescence of polymer pairs from their common cyclodextrin inclusion compounds [15].

Polymer blends involving two or more polymers may have better properties than the pure components. The properties depend not only on the properties of the components but also on their composition and most importantly on their miscibility. Miscibility is directly connected to the method of preparation (melt blending, co-precipitation and solvent-casting), solvent, temperature, weight/molar ratio of the components, molecular weight, etc. [16–18]. Blends of polycarbonate (PC) and poly(methyl methacrylate) (PMMA) and their thermal behavior have been of considerable interest for the last 20 years [19–26]. Various chemical reactions between the two polymers have been hypothesized to explain the formation of homogeneous PC/PMMA blends at temperatures higher than 220 °C. Yet, contradictory data/results concerning the nature or the existence of thermally induced chemical reactions between the two polymers appear in the literature. Rabeony et al. suggested an ester-exchange reaction leading to the formation of graft copolymers [23]. Debier et al. proposed a reaction mechanism for the grafting of PC chains onto PMMA chains heated around 300 °C that only took place in air [24]. Montaudo et al. suggested that the exchange reaction takes place between the methyl methacrylate monomer (MMA) generated by thermal depolymerization of PMMA and the carbonate groups of PC [25]. On the other hand, more recently, nuclear reaction analysis showed no evidence of a thermally induced chemical reaction between PC and PMMA [26].

We have recently demonstrated that thermally stable and intimately mixed blends of PC/PMMA, PC/PVAc and PMMA/PVAc can be obtained by the formation of and coalescence from their common inclusion compounds with γ-CD [27,28]. Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), solid-state 1H nuclear magnetic resonance (NMR) spectroscopy, thermogravimetric analysis (TGA) and direct insertion probe pyrolysis mass spectrometry (DIP-MS) data indicated that these binary polymer blends were homogeneously mixed when they were coalesced from their ICs. Additionally, 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 mixtures obtained by both solvent-casting and co-precipitation methods. As a consequence, both the phase structures and the properties of polymer blends can be modified by processing with CDs.

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

2. Experimental

2.1. Materials

Poly(methyl methacrylate) (PMMA) (\(M_w = 15,000\) g/mol), and polycarbonate (PC) (\(M_w = 28,800\) g/mol) were purchased from Aldrich Co., and used as-received. Tetrahydrofuran (THF) (Aldrich, 99+ %) and dioxane (Aldrich, 99+ %) were used without any purification. γ-cyclodextrin (γ-CD) was obtained from Cerestar (Hammond, IN). The water used in this study was deionized (DI-H\(_2\)O).

2.2. Formation of polymer—cyclodextrin inclusion compounds and coalescence

The formation CD-ICs of PMMA, PC, their coalescence were discussed in detail in our previous publications [27,29]. In summary, a quantity of 0.208 g (0.82 mmol, repeating unit) of PC and 0.490 g (4.9 mmol, repeating unit) of PMMA were dissolved together in 100 ml of a common solvent (dioxane) at 50 °C. An aqueous saturated solution of γ-CD (3.712 g (2.86 mmol) in 10 ml DI-H\(_2\)O at 50 °C) was added drop-wise to the binary polymer solution, while the stirring rate was kept maximum at a temperature of 50 °C. A white, turbid solution was observed once the γ-CD aqueous solution was added to the binary polymer solution (Fig. 1). Subsequent to continuous stirring for 3 h at 50 °C, the white suspension was cooled down to room temperature, while the stirring rate was adjusted to a moderate level for another three days. The resulting suspension was then vacuum filtered and the collected white powder was vacuum dried at 45 °C for 24 h. For the formation of individual γ-CD-ICs of PC and PMMA, the same procedure was applied as mentioned above where a quantity of 0.480 g (1.88 mmol, repeating unit) of PC or 0.858 g (8.58 mmol, repeating unit) of PMMA was dissolved in 100 ml of dioxane at 50 °C.

The host γ-CD was removed from the inclusion compounds, PC-γ-CD-IC, PMMA-γ-CD-IC and PC/PMMA-γ-CD-IC, by washing the white crystals with deionized water overnight at 50 °C. The coalesced polymers were then filtered and rinsed several times with water until the presence of γ-CD could not be detected by FT-IR and finally vacuum dried at 30–40 °C for two days. The molar composition of coalesced binary blend, abbreviated as coalesced PC/PMMA, was identified by solution \(^1\)H NMR spectroscopy as 2.8:1. To serve as a control sample, a binary physical blend of PC/PMMA (same 2.8:1 molar composition as in the coalesced blend) was prepared by a co-precipitation method [27]. PC and PMMA were dissolved in THF and precipitated into deionized water. The precipitate was collected by vacuum filtering through the ceramic frit in a Büchner funnel and was vacuum dried for two days.

2.3. Pyrolysis mass spectrometry

The direct insertion probe pyrolysis mass spectrometry (DP-MS) system used for the thermal analyses consists of a 5973 HP quadruple mass spectrometer coupled to a JHP SIS direct insertion probe pyrolysis system. Samples (0.01 mg) were pyrolyzed in flared glass sample vials. The temperature was increased at a rate of 10 °C/min and the scan rate was 2 scans/s. Pyrolysis experiments were repeated using both 70 and 19 eV ionization energies. Unfortunately, the low energy spectra were not reproducible and, therefore, not applicable.

3. Results and discussion

The thermal degradation of both PC and PMMA has received significant attention [30–34]. It is known that PMMA degradation starts at low temperatures with weight losses due to evolution of dimer, low molecular weight oligomers, scission of head-to-head linkages, and loss of unsaturated end groups. However, at elevated temperatures (380–420 °C), initiation of weight loss was thought to be a mixture of chain end and chain scission processes, followed by depolymerization to the end of the polymer chain [30,31]. Thus, the pyrolysis mass spectrum of PMMA is quite similar to the mass spectrum of MMA monomer, showing a molecular ion peak at \(m/z = 100\) Da and intense peaks due to \(\text{CH}_2\equiv\text{CH}_2\equiv\text{CH}_3\) (\(m/z = 41\) Da) and \(\text{CH}_2\equiv\text{CH}_2\equiv\text{CO}(m/z = 69\) Da) due to the dissociation of MMA inside the mass spectrometer.

Unlike PMMA, the thermal degradation of PC takes place by several thermal degradation pathways [32–34]. In the initial stage of pyrolysis around 400–500 °C, cyclic oligomers are generated by intramolecular exchange reaction. Hydrolysis reactions producing phenolic end groups and \(\text{CO}_2\) are active in this temperature range. The formation of ether bridges by de-carboxylation of the carbonate groups is also responsible for the evolution of \(\text{CO}_2\). In general, products due to methyl losses are also detected as C–C bond dissociation of the isopropylidene linkage is energetically the easiest [32]. The thermal degradation pathways of PC around 400–500 °C are given in the literature as shown in Scheme 1.

Recently we have studied direct pyrolysis mass spectrometry of as-received and coalesced PMMA and PC samples [29]. The data obtained were in accordance with literature results. We have determined that the broad evolution profiles of the thermal degradation products observed for as-received PMMA are noticeably narrower when produced during the thermal degradation of the coalesced sample indicating that the separation/purification of PMMA from its low molecular weight oligomers has been attained during the inclusion complexation with γ-CD. Yet, no other noticeable difference in the thermal degradation characteristics of coalesced and as-received PMMA samples was detected.

The pyrolysis mass spectra of as-received and coalesced PC samples were both dominated by several peaks, among which the peaks at \(m/z = 508, 405\) and 213 Da were the most intense. The peak at 508 Da corresponds to cyclic dimer produced by...
an intramolecular exchange reaction (Scheme 1a). Loss of CO₂ from cyclic carbonates generates the fragment ion having m/z = 405 Da, whereas hydrolysis reactions play a role in the production of the 213 Da fragment ion (Scheme 1b and c). It has been determined that a small amount of remnant γ-CD on the polymer chains significantly affects the thermal stability of coalesced PC [29].

### 3.1. Coalesced and physical PMMA/PC blends

The decomposition temperatures, Tₙₙ, were recorded at 431 and 542 °C for the coalesced PC/PMMA blend and at 421 and 546 °C for the physical mixture [27]. The first degradation stage of coalesced PC/PMMA is higher than the main degradation stage of coalesced PMMA (423 °C) indicating an increase in thermal stability of the PMMA component [29]. A similar behavior was also noted for the physical mixture compared to as-received PMMA (410 °C). However, the second Tₙₙ detected for coalesced and physical blends of PC/PMMA is lower than the Tₙₙ of as-received and coalesced PC samples, at 549 and 554 °C, respectively. The total ion current (the variation of total ion yield as a function of temperature) (TIC) curves of physical and coalesced PC/PMMA blends are shown together with those of as-received and coalesced PC and PMMA in Fig. 2. The maxima at 430 and 435 °C in the TIC curves of physical and coalesced PC/PMMA blends, respectively, are more than 20 °C higher than the TIC maximum recorded for coalesced PMMA, in accordance with TGA data. The second decomposition temperature could not be determined by our present system (maximum attainable temperature is 450 °C). Peaks due to the characteristic degradation products of PMMA and PC were both present in the pyrolysis mass spectra of the blends. The mass spectra recorded at the TIC maximum are also given in Fig. 2. The diagnostic peaks of γ-CD were also detected in the pyrolysis mass spectra of the coalesced blend around 340 °C, as in the cases of the coalesced homopolymers, due to the presence of remnant γ-CD.

The pyrolysis mass spectra of all the samples under investigation were dominated by peaks having the same m/z values, though they were due to different thermal degradation products, causing some additional difficulty in the analyses of PMMA/PC physical and coalesced blends. Thus, to reach reliable conclusions more emphasis was given to the trends in the evolution profiles of their thermal degradation products.

The evolution profiles of cyclic dimer (m/z = 508 Da), the 408 Da fragment due to loss of CO₂ and CH₃ groups, and the 213 Da fragment bearing an OH end group due to the hydrolysis reactions related to thermal degradation of the PC component of coalesced and physical blends are shown together with those of MMA (m/z = 100 Da), CH₂==C(CH₃)CO (m/z = 69 Da) and CH₂==C(CH₃) (m/z = 41 Da) related to the PMMA component in Fig. 3. The evolution profiles of the same products generated during the thermal degradation of coalesced and as-received homopolymers are also included in this figure for comparison. It can be observed that PMMA based products appeared slightly earlier than the PC based products for the physical blend. On the other hand, the evolution profiles of PC based thermal degradation products in the coalesced blend showed two maxima, the first coinciding with those of PMMA based products. This may be an indication of a strong interaction between PMMA and PC chains in the coalesced blend, suggesting either two separate thermal degradation steps or the presence of PC chains with different stabilities.

Another observation that should be noticed is the change in the relative intensities of PMMA based products generated during the thermal degradation of the physical blend. About a threefold decrease in the relative intensity of MMA (m/z = 100 Da) monomer peak and a twofold decrease in the relative intensity of the 41 Da fragment peak with respect to that of the 69 Da peak were detected for this sample. The relative intensities of PMMA based product peaks in the pyrolysis mass spectra of the coalesced blend (41:69:100 = 1.0:0.91:2.0) were almost identical with those recorded for the coalesced PMMA homopolymer (41:69:100 = 1.0:1.0:2.1). As PMMA degrades by depolymerization yielding mainly monomer, CH₂==C(CH₃)CO (m/z = 69 Da) and CH₂==C(CH₃) (m/z = 41 Da) fragments are generated by dissociative ionization of MMA monomer inside the mass spectrometer, the relative intensities of 100, 69,
Fig. 2. TIC curves (left) and pyrolysis mass spectra (right) recorded at the maximum of the peaks in the TIC curves of (a) as-received PMMA, (b) as-received PC, (c) PC/PMMA physical blend, (d) γ-CD, (e) coalesced PMMA, (f) coalesced PC, and (g) coalesced PC/PMMA blend.
and 41 Da peaks should be nearly constant unless degradation pathways of PMMA some how have changed. Thus, the changes in relative intensities of PMMA based products in the case of the physical mixture point out that thermal degradation of PMMA was affected by PC in a different manner than in the coalesced blend.

The relative intensities of the 508, 405 and 213 Da product peaks are nearly identical for all PC containing samples. Yet,
a new peak around 340 °C appeared in the evolution profile of the 213 Da fragment generated during the pyrolysis of the coalesced PC and PC/PMMA blend. This low temperature evolution was also noticed in the single ion pyrograms of \( m/z = 228, 482, \) and 467 Da products as shown in Fig. 4. Furthermore, a three to fourfold increase was also recorded in the relative intensities of 482 and 467 Da peaks with respect to the corresponding ones in the pyrolysis mass spectra of as-received PC and the physical PC/PMMA blend. Fragments (482 and 228 Da) are generated by alcoholysis and hydrolysis reactions taking place during the thermal degradation of PC around 400–500 °C, and their intensities are usually low and depend on the end groups and extent of adsorbed water. The coalesced samples contained some unremoved \( \gamma \)-CD that degrades around 340 °C generating several hydroxy bearing products, such as \( \text{C}_2\text{H}_4\text{O}_2 \) [29]. These hydroxides should readily interact with the carbonate linkages of the PC chains generating oligomers with hydroxyl groups at both ends, such as products with \( m/z = 482 \) and 228 Da shown in Scheme 2 [33]. Loss of a methyl group from these products further produces intense products with \( m/z = 467 \) and 213 Da fragments. This should in turn decrease the thermal stability of coalesced PC samples. Thus, the trends in the evolution profiles of the products bearing OH end groups clearly indicate the hydrolysis of PC around 340 °C by the remnant \( \gamma \)-CD.

Though how, or even whether, PMMA and PC react remains controversial, two different types of chemical reactions occurring in PC/PMMA blends were proposed in the literature [23,25]. Rabeony et al. suggested that ester—ester exchange reactions between PC and PMMA occur at 250 °C leading to in situ formation of a graft copolymer as shown in Scheme 3 [23]. If a graft copolymer is produced, one should expect the thermal decomposition temperatures of PMMA and PC blocks to shift towards a value in between those of the pure

![Fig. 4. Evolution profiles of products bearing OH from (a) as-received PC, (b) physical mixture, (c) coalesced PC/PMMA, and (d) coalesced PC.](image-url)
homopolymers depending on the size of each block. If the chain lengths are sufficiently long, both components of the graft copolymer should decompose through the same degradation pathways depicted for the pure components. Besides generating the graft copolymer, the exchange reaction causes degradation of PC chains bearing methyl carbonate chain ends, so one should expect a decrease in the thermal stability of PC in PC/PMMA blends. The low temperature shift for evolution of PC based fragments from the graft polymer and PC bearing methyl carbonate end groups should depend on the chain lengths. Furthermore, products bearing methyl carbonate chain ends should be detected.

On the other hand, Montaudo et al. found evidence that suggests an exchange reaction between carbonates of PC and esters of MMA, formed by depolymerization of PMMA above 300 °C, most likely due to diffusion of MMA at the interface or even into the PC domains, where it can react producing low molecular weight PC chains bearing methyl carbonate and methacrylate end groups, as shown in Scheme 4 [25]. They further suggested elimination of CO2 from the methyl carbonate chain ends of PC oligomers yielding compounds with methyl ether end groups. If such a reaction takes place, the relative intensities of PMMA based products should change; the relative intensity of the MMA molecular peak should decrease with respect to CH2=CCH3 (m/z = 41 Da) and CH2=CCH3CO (m/z = 69 Da) fragment peaks. The thermal decomposition of methacrylate bearing products should also generate 69 and 41 Da fragments directly during thermal degradation or/and dissociative ionization processes. Thus, significant changes in relative intensities of MMA, CH2=CCH3 and CH2=CCH3CO peaks are expected if an exchange reaction between carbonates of PC and esters of MMA, formed by depolymerization of PMMA, takes place.

As a result of all these processes, several compounds with hydroxide, methyl ether, methacrylate and methyl acrylate end groups should be generated, as summarized in Table 1, during the thermal degradation.

Detection of the products listed in Table 1 for both coalesced and physical PC/PMMA blends supported the existence of exchange reactions. However, the relative yields of these products, especially the dimers, were significantly low under our experimental conditions. Thus, in Fig. 5,
evolution profiles of the products from the coalesced and physical blends corresponding to the monomers listed in Table 1 are shown. Among these, the ions at \( m/z = 256, 300 \) and 344 Da, assigned to a series of molecules bearing only either methyl acetate or methyl ether end groups showed noticeably different trends when generated during the pyrolysis of the coalesced blend.

First of all, their relative yields were higher than those from the physical blend, although all other fragment peaks that can be related to products due to exchange reactions between PMMA and PC with hydroxide or methacrylate chain ends were more intense for the physical blend. Of utmost importance is the fact that the evolution profiles of products with methyl ether or methyl carbonate chain ends were shifted toward lower temperatures (\( \sim 15^\circ \text{C} \)), whereas all others were evolved at a later stage in the case of the coalesced blend. These findings suggest that methyl ether or methyl carbonate bearing products are generated through different routes during the pyrolysis of the coalesced blend.

The superimposable maxima in the evolution profiles of PMMA and PC based products, and the earlier evolution of more intense methyl ether and methyl carbonate bearing products from the coalesced blend indicate existence of ester–ester interchange reaction between PC and PMMA yielding a graft copolymer and low molecular weight PC chains bearing methyl carbonate end groups, together with exchange reactions between MMA and PC.

On the other hand, detection of products bearing methyl ether, methyl carbonate, and methacrylate end groups, the similarities in their evolution profiles, and evolution of PMMA based products, with significant changes in relative yields, at slightly lower temperatures than those of PC based ones, confirm that the only exchange reaction is the one between carbonates of PC and esters of MMA, formed by depolymerization of PMMA, in the case of the physical blend.

Actually, it has been shown that as a result of the coalescence process, intimately mixed blends having modified structures, morphologies, and even conformations can be formed \[27,29\]. Thus, as a result of this intimate mixing, the separation between PC and PMMA chains should decrease and enhance ester–ester exchange reactions between PC and PMMA in the coalesced blend. On the other hand, diffusion of MMA into the PC domains should be more effective for the phase segregated physical blend and thus the yield of methacrylate bearing products should be higher.

### 4. Conclusions

Direct insertion probe pyrolysis mass spectrometry analyses of coalesced and physical PC/PMMA blends indicated that an exchange reaction between carbonates of PC and esters of MMA, formed by depolymerization of PMMA above 300 °C, occur most likely due to diffusion of MMA at the

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**Table 1**

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>( m/z ) (Da)</th>
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<tbody>
<tr>
<td>OCH₃</td>
<td>OCH₃</td>
<td>242, 496</td>
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<tr>
<td>O–CO–OCH₃</td>
<td>O–CO–OCH₃</td>
<td>286, 540</td>
</tr>
<tr>
<td>O–COC(CH₃)═CH₂</td>
<td>O–COC(CH₃)═CH₂</td>
<td>296, 550</td>
</tr>
<tr>
<td>OCH₂₃</td>
<td>OCH₂₃</td>
<td>256, 510</td>
</tr>
<tr>
<td>O–CO–OCH₃</td>
<td>O–CO–OCH₃</td>
<td>300, 554</td>
</tr>
<tr>
<td>O–COC(CH₃)═CH₂</td>
<td>O–COC(CH₃)═CH₂</td>
<td>310, 564</td>
</tr>
<tr>
<td>O–CO–OCH₃</td>
<td>O–CO–OCH₃</td>
<td>344, 598</td>
</tr>
<tr>
<td>O–COC(CH₃)═CH₂</td>
<td>O–COC(CH₃)═CH₂</td>
<td>354, 608</td>
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<tr>
<td>OCOC(CH₃)═CH₂</td>
<td>OCOC(CH₃)═CH₂</td>
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interface or even into the PC domains, where it can react producing low molecular weight PC chains bearing methyl carbonate and methacrylate end groups. However, the results also suggested ester—ester interchange reaction between PC and PMMA yielding a graft copolymer and low molecular weight PC chains bearing methyl carbonate end groups in the case of the coalesced blend, which can be attributed to the presence of specific molecular interactions between the intimately mixed PMMA and PC chains.

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