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Reaction to fire of recycled poly(ethylene terephthalate)/polycarbonate blends

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Abstract

In the present paper, we study the effect of both morphology and compatibilization on the reaction to fire of blends of recycled poly(ethylene terephthalate) (PETr) with recycled polycarbonate (PCr). It is shown that while the flame retardancy of blends containing less than 50% w/w of PCr increases almost linearly with PCr content, blends containing more than 50% w/w of PCr react to fire like pure PCr. This change of reaction to fire correlates with the formation of a continuous PCr phase in the blend.

The compatibilization of the blend by a trans-esterification reaction leading to the formation of copolymers at the interface decreases the overall fire performances due to PETr chain breaking as a side effect which results in a strong decrease of blend viscosity and of the temperature at which mass loss begins.

Keywords: Poly(ethylene terephthalate); Recycling; Fire; Blends

1. Introduction

Little is known about the effects of the morphology and the compatibility of a blend of two polymers on its fire retardancy. This is particularly important when the two polymers, taken separately, have very different fire resistances. A certain number of articles deal with the effect of blending polymers on their thermal degradation [1], in some cases showing a positive but small effect on thermal stability of compatibilization in immiscible blends. For example, in the case of polypropylene (PP)/polyamide blends (PA) mixtures, the thermal stability of PP rich blends is slightly enhanced by the presence of a compatibilizer despite a significant change of blend morphology from spherical PA domains in a PP matrix to co-continuous morphology.

Very few articles try to address the effect of blending on fire behaviour. Lizymol and Thomas [2] briefly studied and compared the fire behaviour of different blends of poly(vinyl chloride) (PVC) and ethylene-*co*-vinyl acetate (EVA). These polymers have different fire behaviours, while EVA has a weak resistance to fire with limiting oxygen index (LOI) of 17, PVC is intrinsically fire retardant due to the presence of chlorine and has an LOI of 38. PVC and EVA are also partially miscible depending on blend composition: a PVC/EVA blend of composition 50/50 w/w is immiscible (two phases blend), while an EVA/PVC blend of composition 30/70 w/wweight by weight is miscible (one phases blend). Lizymol and Thomas found that the LOI value (and of other fire properties such as smoke density or static thermal stability) of EVA/PVC blends only depends on composition and not on blend miscibility. Therefore, they conclude that the miscibility was not an important factor when dealing with flame retardancy properties.

Renaut et al. [3] and Almeras et al. [4] studied the fire retardancy of PP blends with PC and PA-6, respectively. In both cases, they observed that the introduction of an interfacial agent allowing compatibilization of the blend (for example PP-*g*-MA) led to an improvement of flame retardancy

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(decrease of maximum of heat release rate curve in cone calorimeter tests).

In the present paper, we report a study on the case of blends of recycled polycarbonate (PCr) and recycled poly(ethylene terephthalate) (PETr), this work being part of a wider research project aiming to recycle PET in engineering applications involving enhanced flame retardancy.

PC typically has an LOI of 28 and produces a large fraction of char upon combustion, whereas PET has an LOI of 22, with serious dripping during combustion. When they are mixed, PC and PET are immiscible over the entire range of composition, phase inversion occurring around 50/50 w/w composition [5]. However, the miscibility behaviour of PC/PET blends was controversial for a long time [5], many authors having found contradictory results, depending both on the experimental conditions used to prepare the blends and on the residues of the polycondensation catalysts present in the PET. Actually, PC/PET blends can be compatibilized and even become miscible in certain conditions due to a trans-esterification reaction between the two polymers (Fig. 1). This reaction can occur in the molten state, but is rather slow and requires suitable catalyst in order to allow complete blend compatibilization to be performed during melt blending in a twin screw extruder [6].

In the present work, we study the thermal degradation and fire behaviour of PETr/PCr blends of various compositions and morphologies, with and without compatibilization.

2. Experimental

2.1. Materials

The recycled PET (post-consumer bottles flakes) was supplied by Valorplast (France) ($\eta_{PET} = 0.76$ dl/g, in 2-chlorophenol at 25 °C). Recycled PC (CD production waste) was supplied by MPO (France) ($\eta_{PC} = 0.37$ dl/g, in 2-chlorophenol at 25 °C). The CDs have been ground using a rotary cutter mill in order to obtain PC flakes of typically 8 mm. Samarium acetyl acetonate ($Sm(aca)_3 \cdot xH_2O$ $x = 3-4$) supplied by Acros Organics was used as catalyst for trans-esterification reaction [6].

2.2. Processing

PETr/PCr blends were compounded using a twin screw extruder (Clextral BC 21, $L = 1200$ mm, $L/D = 48$, 6 kg/h, 350 rpm, 270 °C) and pelletized. PET and PC flakes were mechanically mixed prior to feeding the extruder. Fig. 2 shows the screw configuration used, for which the residence time in the extruder was about 90 s. Five different compositions have been processed: pure PETr, 90/10, 80/20, 70/30 and 50/50 PETr/PCr blends, and pure PCr. Samarium acetyl acetonate catalyst was used for the compatibilization of the blends during melt mixing. Catalyst was directly dispersed in PETr/PCr pellets in order to obtain catalyst weight contents of 0.025% and 0.05%.

Due to the great sensitivity of PETr to water, the following protocol was used before melt mixing: PETr flakes, PCr flakes were dried in vacuum at 120 °C during 16 h and the catalyst was dried overnight in an oven at 105 °C. The choice of these drying conditions was based on a preliminary study on the evolution of residual water content measured using the following: Karl Fisher titration was performed using a potentiometric titration device (Metrohm Titrino) based on a redox reaction between iodine and water molecules. Water molecules were desorbed from the polymer by heating a sample at 270 °C under nitrogen and then carried by the gas flow to the titration cell.

Curves presented in Fig. 3 allowed us to determine the minimum drying time leading to a residual water quantity below 100 ppm (0.01%) as recommended in several publications [7,8]: above 6 h for PCr and 11 h for PETr.

Standard ISO 527-2 type 1A tensile test specimens and $100 \times 100 \times 4$ mm^3 specimens were injection moulded (95 Tons Sandretto AT press, 170 °C) from the pellets, after air drying at 105 °C during 24 h followed by drying under vacuum at 120 °C during 16 h. All the samples used for testing were cut from these specimens.

2.3. Scanning electron microscopy

A Quanta 200 FEG environmental Scanning Electron Microscope (FEI) was used. Samples were previously submitted

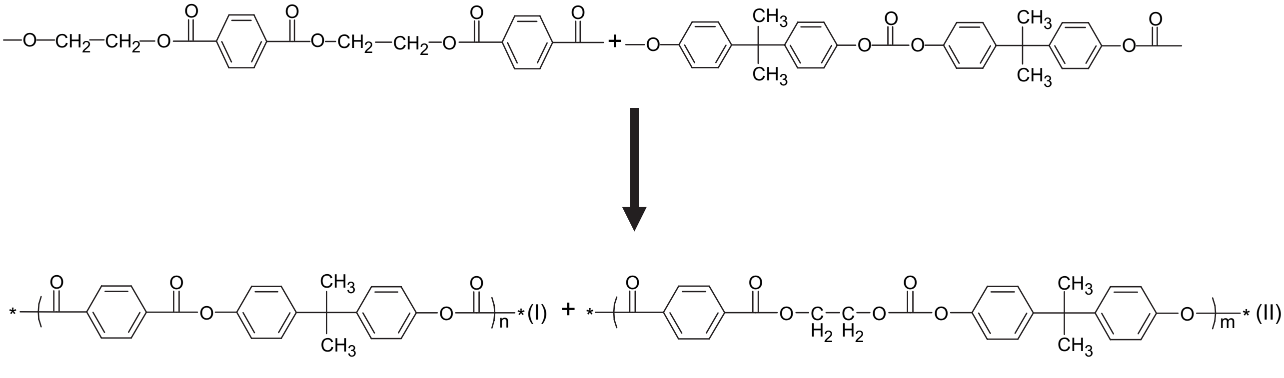

Fig. 1. Predominant trans-esterification reaction for PET/PC blends. (I) and (II) are PET/PC copolymer more or less alternate and depends on reaction progress.