



Polymer degradation during the melt processing of clay reinforced polycarbonate nanocomposites

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ABSTRACT

During the melt processing of nanocomposites with layered silicates, polycarbonates (PC) suffer a severe degradation which causes a great reduction of the mechanical and thermal properties. With the overall goal of obtaining clays that cause less degradation of PC, we have studied in this work the degradation of a PC during the melt compounding with three organically modified clays, a commercial one (Cloisite™ 15A) and two clays modified in our laboratory. The laboratory clays were obtained by treating sodium montmorillonite with polyethylenimine or a novel silane which contains the bisphenol-A group. The composites were characterized by Fourier Transform Infrared Spectroscopy and Transmission Electron Microscopy. The PC degradation was measured by Ultraviolet Spectroscopy, Thermogravimetry, Dilute Solution Viscosimetry and Fluorescence Spectroscopy. The second goal of this work was to study the relationships between the results obtained from the different experimental techniques. Some of the studied clays cause a significant increase in the hydrolytic degradation of PC during the melt processing, as shown by the reduction of the average molar mass as well as the appearance of a weight loss step at low temperatures in the thermogravimetric analysis. The formation of phenolic compounds in the degradation process was observed in the fluorescence emission and the UV absorption spectra. The relative effect of the different clays on the PC degradations depends more on factors such as the chemical nature of the organic modification of the clay or the degree of dispersion of the clay into the polymer, than on other factors such as the apparent water content of the clay.

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1. Introduction

Polymer nanocomposites have received great attention in the last years, as many of these material present very interesting properties, including high mechanical strength, improved gas barrier properties and decreased flammability [1–6]. Among the polymer matrices, polycarbonate (PC) is one of the most interesting ones, due to characteristic properties like high toughness and strength, excellent ballistic impact strength and good optical clarity. It could be expected that the addition of relatively low percentages of nano-reinforcements will result into remarkable improvements in mechanical and thermal properties. In fact,

several authors have reported the development of new polycarbonate nanocomposites with improved properties [7–20].

Among the nano-reinforcements, layered silicates as montmorillonite and other clays have received much attention due to their high aspect ratio and low cost. Usually, clays are chemically modified for expanding the clay interlayer space and improving the miscibility with the polymer. The modification allows the entry of the large polymer molecules into the clay galleries and the good dispersion of the clay platelets in the polymer matrix, which is needed in order to achieve the expected properties of the nanocomposites [21–24].

Many polymer/layered silicate (PLS) nanocomposites are obtained by melt-compounding. Under the severe conditions usually selected for these melt-compounding processes, some PLS nanocomposites can experiment a remarkable degradation, in both the polymer matrix and the organic modification of the silicate, as has been reported by several authors [1,3,25–28]. It must be taken into account that the nanocomposites of polymers like polyamides or polycarbonates require temperatures near 250 °C for an effective

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melt-compounding. These temperatures are clearly higher than the onset temperatures for the degradation of most of the organic modifications usually introduced in the silicates. Thus, parameters like the surface free energy, the surface polarity and, even, the basal spacing of organically modified clays can severely change during the melt blending of the composites [15,29–31].

On the other hand, many polymers can also suffer a severe degradation during the melt processing, which would significantly alter the properties of the final nanocomposites. Moreover, the organic modification of the clay can play a significant role in the polymer degradation. Xu et al. [32] found that poly(ethylene terephthalate) suffered a significant molecular weight reduction during the compounding with different clays, which depended on both the clay structure and the organic modification. Clays with more edge hydroxyl groups caused more degradation. Similarly, Fornes et al. [33] and Davis et al. [34] reported that the molecular weight degradation of nylon-6, observed during the melt compounding with different clays, depends on the chemical structure and modification of the clays. Yoon et al. [16] and Mitsunaga et al. [17] have reported similar effects on the degradation of polycarbonate during the melt processing with clays modified with alkyl ammonium surfactants. In general the studies about the polymer degradation during the melt processing of the nanocomposites appear to indicate that the level of the degradation depends on the chemical nature of both the clay and the organic modification. Cui et al. [35] studied the PC degradation caused by two clays with organic modifications of very different thermal stability. Their results prove that a higher thermal stability of the modified clay does not reduce the degradation of PC.

The water content of the material plays a main role in the hydrolytic degradation during the compounding of polymers such as polycarbonates. It should be noted that the addition of clays necessarily involves the introduction of a small amount of water in the system. Therefore, the water content of the clays may be one of the factors that influence the degradation.

The main objective of this work was to examine the effect of clays with different organic modifications on the degradation of polycarbonate during the melt compounding of the nanocomposites. One commercial montmorillonite (Cloisite™ 15A, C15) and two novel organo-montmorillonites obtained in our laboratory were used in order to evaluate the effect of the chemical modification of the clay. The first laboratory organoclay, CPEIA, was prepared by treating in aqueous solutions sodium montmorillonite with polyethylenimine (PEI), a cationic polyelectrolyte with primary, secondary and tertiary amine groups. This organic modification was selected because it has been reported that amines can catalyze the degradation of polycarbonate [12]. The second laboratory clay (CBPAS) was obtained treating the natural clay with a novel bisphenol-A silane (BPAS) synthesized by us. BPAS, obtained from 3-isocyanatopropyltriethoxysilane and bisphenol A, was synthesized in order to improve the chemical compatibility of the clay with bisphenol-A polycarbonate. The characterization of the two modified clays has been reported in detail in a previous work [36].

The different nanocomposites were compounded in a twin-screw microextruder. The structure of the materials was analyzed using Transmission Electron Microscopy (TEM) and Fourier Transform Infrared (FTIR) Spectroscopy, and the degradation of polycarbonate was characterized using a set of experimental techniques

including UV Spectroscopy, Thermogravimetric (TG) Analysis, Dilute Solution Viscosimetry and Fluorescence Spectroscopy.

2. Materials and methods

2.1. Materials

In this study, a commercial bisphenol-A PC (Lexan LS1, kindly supplied by Sabic, Cartagena, Spain) with a melt mass-flow of rate of 6.5 g/10 min (1.2 kg at 300 °C) was used. The commercial organoclay used, C15, as well as the unmodified clay, CLN, were kindly supplied by Southern Clay Products, Inc. CLN was a sodium montmorillonite (Cloisite™ Na⁺) with a cationic exchange capacity of 92.6 mequiv/100 g of clay. C-15 is the organically modified montmorillonite Cloisite™ 15A (C15), obtained using a dimethyl, dihydrogenated tallow, quaternary ammonium chloride surfactant as an organic modifier. Two montmorillonites chemically modified in our laboratory were also used. CPEIA was obtained by treating sodium montmorillonite with a branched polyethylenimine (Lupasol® PR 8515, active matter > 98%; M_w: 2000; CAS No.: 25987-06-8; ratio of primary, secondary and tertiary amines: 1:0.92:0.70), kindly supplied by BASF Española S.A. (Barcelona, Spain). The polyethylenimine was used as received and the treatment of the silicate was made in aqueous solution at pH = 8. The second organoclay developed in the laboratory, CBPAS, was obtained by treating sodium montmorillonite with a novel alkoxy silane obtained from bisphenol-A and 3-isocyanatopropyltriethoxysilane. Fig. 1 shows the chemical structure of this silane, as revealed by RMN and FTIR spectroscopy. The modification processes, as well as the characterization of the two modified clays, CPEIA and CBPAS, have been described in detail in a previous work [36]. In the two cases, the organic modifier was successfully introduced in the clay and remarkable increases of the basal spacing of the silicate were observed.

2.2. Melt compounding

Nanocomposites with different clay contents were prepared through melt processing, at 230 or 250 °C and 120 rpm for 10 min, in a Haake Minilab (Thermo Electron Corporation) twin-screw microcompounder with a volumetric capacity of 7 cm³, using corotating conical screws. Mild conditions for the processing were selected in order to minimize the intrinsic degradation of the pure PC. This choice allows a better study of the effect of the clay on the degradation of the polymer.

The PC, in powder form, was dried before compounding at 110 °C in a vacuum oven during 24 h. It was previously shown that this drying process removes most of the water, as it leads to a constant weight with a variation of less than 0.01%. In order to avoid the degradation of the organic modification, the modified clays were dried in the vacuum oven at only 70 °C during 24 h. This procedure does not allow the complete removing of the water. Fig. 2 shows the TG curves of the three clays recorded after the drying at 70 °C. The three curves show a small weight loss at low temperatures, between 50 and 150 °C, which can be mostly assigned to the elimination of water. This weight loss accounts for the 0.7% of the total mass in C15, and for the 2% in the case of CPEIA.

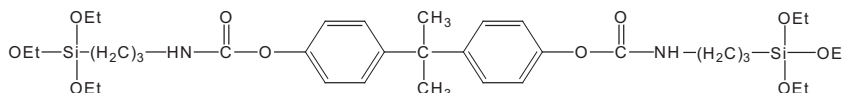


Fig. 1. Silane used to obtain CBPAS.

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