

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 organoclays 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.

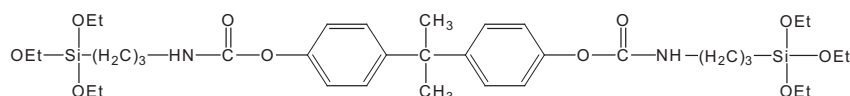


Fig. 1. Silane used to obtain CBPAS.

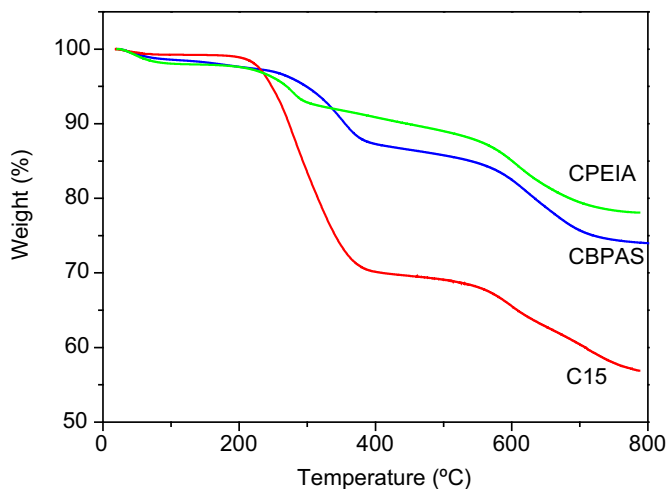


Fig. 2. TG curves (in nitrogen atmosphere) corresponding to C15, CBPAS and CPEIA.

2.3. Material characterization

The UV absorption and the fluorescence emission spectra of sample films were measured in a Perkin–Elmer Lambda 35 UV–Vis spectrophotometer and a Perkin–Elmer LS-5 luminescence spectrometer, respectively, at room temperature. Sample films were obtained by casting from dilute solutions in dichloromethane. FTIR spectra were recorded in a Nicolet iS10 spectrometer in transmission mode. Each spectrum was recorded at a resolution of 4 cm^{-1} , with a total of 25 scans. Microtomed sections of the different materials were examined by transmission electron microscopy (TEM) at room temperature. A transmission electron microscope (JEOL JEM-2100) operated at 200 kV was used to obtain images of the nanocomposite specimens. Thermogravimetric analysis of the different clays was carried out using a TA Instruments TGA2050 thermobalance. Samples of $\sim 10\text{ mg}$ were heated at $10\text{ }^{\circ}\text{C}/\text{min}$ from room temperature to $900\text{ }^{\circ}\text{C}$ in dry nitrogen ($30\text{ cm}^3/\text{min}$). The viscosity-average molar mass (M_v) of polycarbonate was determined by dilute solution viscosimetry at $25 \pm 0.5\text{ }^{\circ}\text{C}$ using an Ubbelohde 0B viscosimeter and chloroform as a solvent. The intrinsic viscosity was calculated by extrapolation using the equations proposed by Kraemer and Huggins [37]. M_v was

calculated from the intrinsic viscosity using the Mark–Houwink–Sakurada equation.

3. Results

3.1. Characterization

The knowledge of the degree of dispersion of the clay platelets into the polymer can aid to explain the effect of the clay on the degradation of the polymer. A better dispersion of the clay implies a larger surface area of the clay in close contact with the polymer and available for specific interactions. In this work the morphology of the different materials has been characterized using Transmission Electron Microscopy. Representative images of the TEM micrographs of PC/C15, PC/CBPAS, and PC/CPEIA composites with 2 wt% of organoclays are shown in Fig. 3a–c, respectively. It is clearly seen that in the PC/C15 nanocomposites many organoclay aggregates were fairly well dispersed and intercalated/exfoliated structures were developed. Materials obtained with the silane-modified clay (Fig. 3b) show a different morphology; some intercalated and exfoliated structures are still seen, but most clay appears as aggregates. The micrographs corresponding to PC/CPEIA (Fig. 3c) reveal the presence of few or none exfoliated layers, with almost all the clay forming aggregates. These images confirm that the organic modifier plays a major role in dispersing the clay aggregates and obtaining intercalated or exfoliated structures. Among the organically modified clays studied in this work, C15 allows better dispersion than CBPAS and CPEIA.

Fig. 3 also shows that, whilst the layers of C15 appear almost clean in the micrograph of PC/C15, the layers of CBPAS and, specially, those of CPEIA appear surrounded by a dark impurity, which may be the rests of the chemical modification of the clays. In the case of C15, most of the chemical modification appears to be eliminated during the melt compounding of the nanocomposite.

The materials obtained were also characterized using FTIR spectroscopy. Fig. 4 shows the FTIR spectra of polycarbonates reinforced with the different clays studied in this work. In addition to the strong polycarbonate characteristic absorptions, the spectra corresponding to the nanocomposites show a weak characteristic absorption band centred at 1043 cm^{-1} , which can be assigned to a Si–O–Si stretching vibration mode corresponding to the reinforcing clays [38,39]. The only other difference appears as a weak shoulder at 1730 cm^{-1} in the spectrum of PC/C15 (see also the

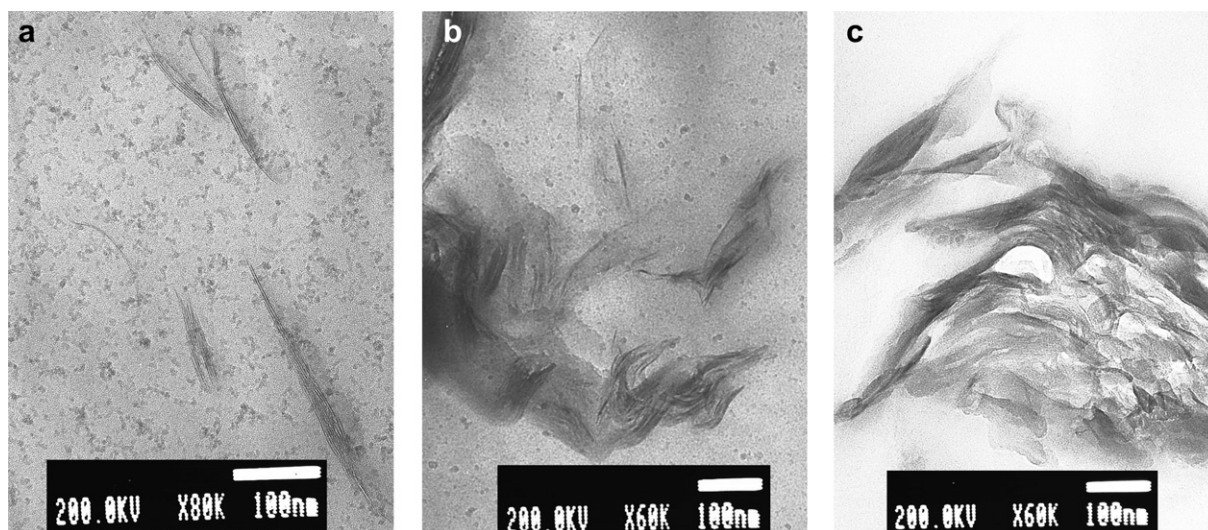


Fig. 3. TEM images corresponding to PC/C15 (a), PC/CBPAS (b) and PC/CPEIA (c) (2% by weight of clay).

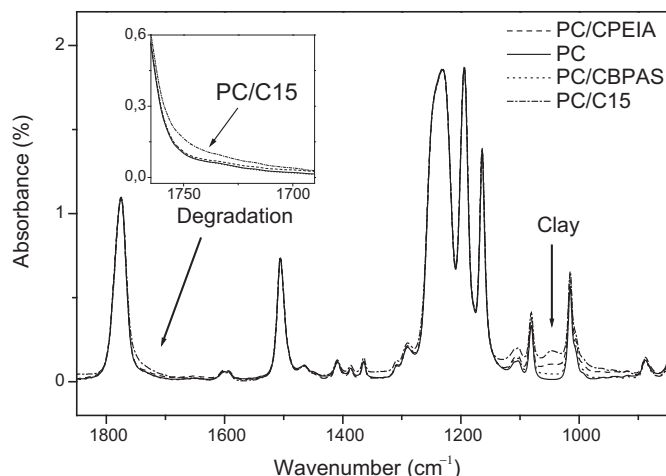


Fig. 4. FTIR spectra of the starting polycarbonate and the composites of PC with C15, CBPAS and CPEIA.

inset). This weak absorption can be assigned to oxidation products (C=O stretching vibrations) formed as a result of the degradation of the polymer during the melt processing of the composites. This difference is only significant in the spectra of the materials obtained with C15, thus revealing that the degradation processes depend on the organic modification of the clay.

3.2. Thermogravimetric analysis (TGA)

The polycarbonate degradation during the melt processing of the clay-reinforced composites has been studied using various experimental techniques, including thermogravimetric analysis. Fig. 5 shows the TGA curves corresponding to pure PC and its composites with 2% of C15, CPEIA and CBPAS, measured in dry nitrogen with a heating rate of 10 °C/min.

The thermal decomposition of pure PC occurs in two distinct steps. The first of them corresponds to the weight loss caused by the thermal decomposition of the polymer, while the second step corresponds to the decomposition of the char formed in the first step. The formation of char, due to the cross-linking reactions that take place during the decomposition [31], reduces the permeability

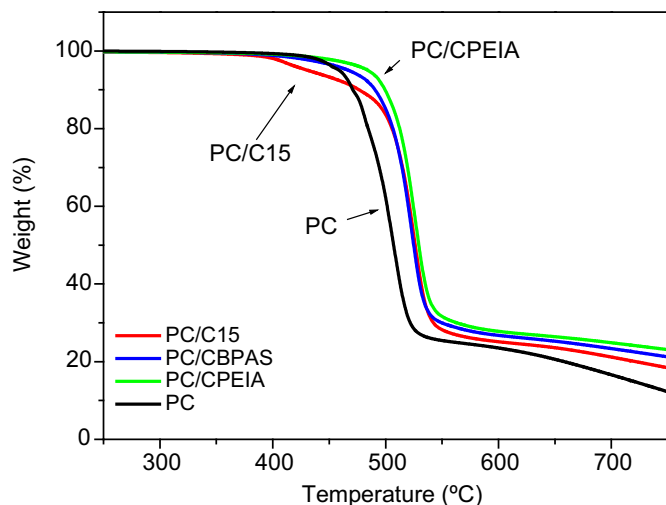


Fig. 5. TG curves corresponding to the starting polycarbonate and the composites of PC with 2% of C15, CBPAS or CPEIA.

and hinders the output of the volatile decomposition products, thus increasing the decomposition temperature. As can be seen in Fig. 5, the presence of clay causes the formation of larger amounts of char, with higher thermal stability, which explains in part the improved flame resistance of the layered silicate nanocomposites, one of the most important advantages of these materials.

Fig. 5 also shows that the thermal stability of the polymer is clearly improved by adding 2% of clays. The values of the temperature of maximum weight loss rate, T_{max} , of the nanocomposites, which can be used to compare the relative thermal stability of the different materials, are clearly higher than those corresponding to pure PC. Similar results were found in dry air atmosphere. This is an expected result because several authors have reported previously similar positive effects of organoclays on the thermal stability of polycarbonate and other polymers [1,3,40,41]. In general, the incorporation of clay into the polymer matrix enhances the thermal stability because clay acts as a mass-transport barrier, thus hindering the output of the volatile products generated during the decomposition.

Fig. 5 also contains information concerning the degradation of polycarbonate during the melt processing of the nanocomposites. The TGA curves corresponding to PC nanocomposites show a characteristic weight loss step at low temperatures, which do not appear in the curve corresponding to the pure polymer (see inset in Fig. 5). This weight loss can be also clearly seen in the first derivative curves (TGD) shown in Fig. 6, where it appears as a small peak at ~400 °C.

The low-temperature weight loss step has been sometimes assigned to the thermal elimination of the organic modification of the clay, but this is not possible because in the case of PC/C15 with 2% by weight of clay, this low-temperature weight loss step implies at least the 5% of the total mass of the nanocomposite. Therefore, this weight loss must include, in addition to the loss of the organic modification of the clays, the loss of a polymer fraction of low thermal stability, which must be the result of the polycarbonate degradation caused by the clays during the melt processing of the nanocomposites.

Fig. 5 shows that the effect of the clay on the polycarbonate thermal degradation, as revealed by the low temperature weight

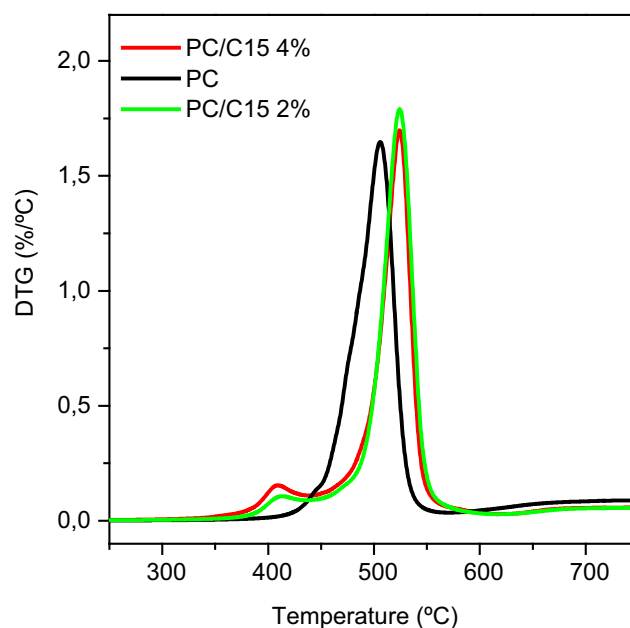


Fig. 6. TGD curves corresponding to the starting polycarbonate and the composites of PC with 2 and 4% of C15.

loss step, depends on the organic modification of the clay. In good agreement with the results observed in the IR analysis, the highest level of degradation is seen in the materials reinforced with C15, while no significant effect is observed in PC/CPEIA. Finally, Fig. 6 shows that the low-temperature weight loss step is clearly more important in the sample with 4% of C15, thus revealing that the effect of the clay on the polycarbonate degradation increases with the amount of clay used. These results are important because the degradation of polycarbonate reduces the performance of its nanocomposites.

3.3. Fluorescence

The fluorescence of bisphenol-A polycarbonate subjected to thermal degradation was studied by Rufus et al. [42]. These authors reported that thermal degradation of PC produces different compounds with important fluorescence emission and the emission intensity increases with the temperature of the degradation process. Moreover, they pointed out the interest of the fluorescence techniques in the study of the degradation, derived from the high sensibility of these techniques, which allows the detection of small amounts of polycarbonate thermal degradation products.

Fig. 7 shows the emission spectra, with excitation at 250 nm, corresponding to films of polycarbonate and its composites with C15, CBPAS and CPEIA. All the materials were compounded in the Minilab at 230 °C.

The PC film (solid line) shows a complex structured emission spectrum, with several emission bands between 300 and 330 nm and another set of bands between 330 and 370 nm. The presence of such a number of bands in the emission spectrum of PC can be explained by taking into account that this spectrum does not correspond only to the pure polymer, but also to the presence of different impurities and products of the degradation (thermal and photochemical), as has been shown by Itagaki and Umeda [43], and Rufus et al. [42]. Itagaki and Umeda assigned a band at 298 nm to the emission of pure PC in the film (this band appears at 288 nm in solution). Other bands may be assigned to phenolic compounds (for example, compounds such as bisphenol-A and 4-phenoxyphenol show emission peaks at 303 and 322 nm, respectively [43]) present in the PC film as impurities or degradation products. Other emission peaks, at longer wavelengths, may be assigned to different products of the thermal degradation of PC. Rufus et al. [42] assigned

emissions centred at ~330 and ~350 nm to compounds like dibenzofuran and phenyl-2-phenoxybenzoate, respectively, produced in the thermal degradation of PC. Finally, other emission bands, mainly those appearing at higher wavelengths in the fluorescence spectrum of PC, can be related to products formed in the photochemical degradation of the polymer [43].

The spectra shown in Fig. 7 can be explained by taking into account the above band assignments. The emission spectra of PC/C15 and PC/CBPAS show, with respect to PC, significantly increased emissions at low wavelengths, between 300 and 330 nm. As these emissions may be assigned, at least in part, to phenolic compounds produced in the hydrolysis and thermal degradation of PC, we can conclude that the fluorescence results confirm that some of the clays can favor the degradation of PC. The catalytic effect is stronger for C15 than for CBPAS, while no effect is observed at these wavelengths for CPEIA. These results agree with those obtained by infrared spectroscopy and thermogravimetric analysis (Figs. 4–6), which shows that the degradation is stronger in the materials that contain C15.

The effect of the clays on the set of emission bands at high wavelengths is clearly different. The spectrum of PC/CBPAS in this spectral region is similar to the spectrum of pure PC; however, the spectra of the composites that contain C15 and CPEIA show emissions of very low intensities at wavelengths higher than 340 nm. The compounds responsible for the emission peaks at higher wavelengths are not formed (or disappear) during the melt processing of PC/CPEIA and PC/C15. Taking into account that the differentiating characteristic of C15 and CPEIA is the presence of amine (CPEIA) or ammonium groups (which can form amine groups upon thermal degradation, as will be discussed later), we propose that a reaction with these groups must explain the anomalously low intensities observed at high wavelengths in the spectra of the nanocomposites made with C15 and CPEIA. However, we do not have more results that support the above hypothesis and additional investigation is needed at this point.

3.4. UV spectroscopy

The UV spectroscopy can also provide useful information about the degradation of polycarbonate during the melt processing of its nanocomposites. Fig. 8 gives the UV spectra of pure PC and various composites with 2% of clay. Although the spectra are normalized, there is a clear difference at 287 nm, where the spectrum of the nanocomposite made with C15 shows a noticeable shoulder. However, pure PC and even the composites made with CBPAS or CPEIA show very weak absorption at 287 nm.

The band at 287 nm was used by Yoon et al. [16] to characterize the degradation of PC because this band was previously assigned to phenolic units in the polymer [44]. Following this assignment, the appearance of a new absorption at 287 nm was explained as the result of the degradation (by chain scission) of the PC molecules, which generates phenolic units during the melt compounding. Using as an internal reference the absorption band at 265 nm, which was assigned to the ester moiety of the carbonate groups [44], the normalized absorbance at 287 nm ($R = A_{287}/A_{265}$) was used to study the degradation of PC [16]. In this work we have used the same ratio to study the effect of the different clays on the degradation of PC during the melt processing.

Fig. 9 shows the values of the normalized absorbance at 287 nm, measured in films of PC and its nanocomposites, all compounded at 230 or 250 °C in the Haake Minilab. The values of R increase with the temperature (as should be expected) and the amount of clay, revealing the main role of the clays in the degradation of the polymer. C15 is the clay that causes a greater effect on the polycarbonate degradation, in good agreement with the results

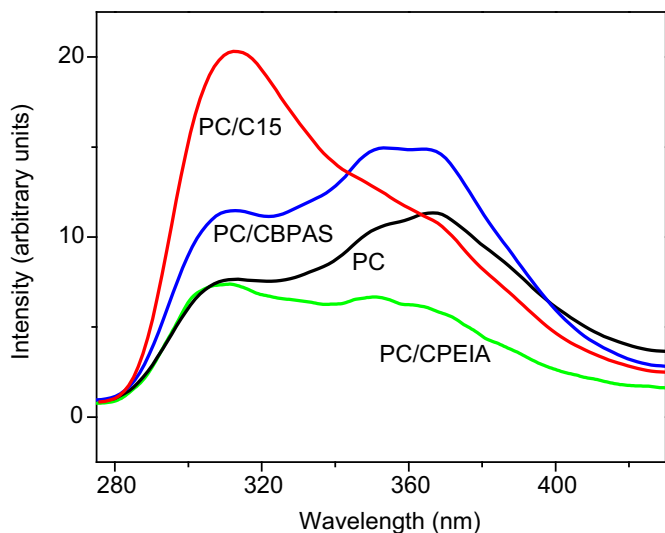


Fig. 7. Fluorescence emission spectra ($\lambda_{\text{ex}} = 250$ nm) corresponding to the starting polycarbonate and the composites of PC with 2% of C15, CBPAS or CPEIA.

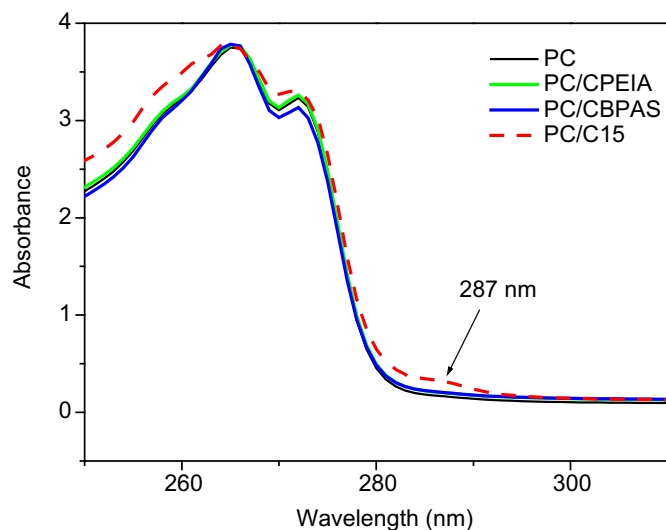


Fig. 8. UV absorption spectra measured in the starting polycarbonate and the composites of PC with the three studied clays (2% by weight).

obtained in the thermogravimetric analysis, as well as in the fluorescence study.

4. Discussion

The above results indicate that the three clays studied in this work cause the degradation of polycarbonate during the melt processing of the nanocomposites. The effect depends on the organic modification of the clay, being C15 the most active of the three clays. The results of the fluorescence study appear to indicate that the clays favor the formation of fluorophores which may be, at least in part, phenolic compounds. The results obtained in the thermogravimetric analysis reveal a degradation during the compounding that causes the appearance of fragments of lower molecular weight and, hence, lower thermal stability. Finally the UV spectroscopic analysis appears to indicate the hydrolysis of the polycarbonate molecules, with formation of phenolic units. All these results are coherent.

In order to quantify the effect of the clays on the degradation, we have measured the changes in the average molar mass determined

by dilute solution viscosimetry (M_v). The values of the intrinsic viscosity, $[\eta]$, were determined by extrapolation to infinite dilution in chloroform at $25 \pm 0.5^\circ\text{C}$ and the values of M_v were calculated according to the Mark–Houwink–Sakurada equation,

$$[\eta] = K(M_v)^\alpha$$

using the recommended values of K (0.0301 mL/g) and α (0.74) [45].

The values of M_v show a great reduction of the molar mass during the processing of certain nanocomposites, revealing a severe degradation of the polycarbonate. The value measured for the unprocessed PC was 24.1 kDa. Fig. 10 shows that the reduction in M_v (ΔM_v) increases with the temperature and the clay content and is strongly dependent on the nature of the organic modification of the clay. A molar mass reduction higher than 40% was observed in composites with 4% of C15. Other authors have reported similar effects of various clays on the PC degradation. Yoon et al. [16] and Cui et al. [35] studied the effect of different clays on the degradation of the polycarbonate molecules and Mitsunaga et al. [17] reported that the molecular weight change observed in clay reinforced PC nanocomposites is due to the hydrolysis of the PC chains.

These results are in good agreement with those above reported, obtained using thermogravimetric and spectroscopic techniques. The reductions in M_v can explain the formation of compounds with lower thermal stability, observed in the TGA curves (Fig. 5). The hydrolysis of the PC molecules can explain the appearance of phenolic compounds, which are responsible for the new absorption band centred at 287 nm in the UV spectra of the nanocomposites (Fig. 8). These phenolic compounds can be also responsible, at least in part, for the increased emission at 320 nm observed in the fluorescence spectra (Fig. 7).

The concordance between the experimental results can be also observed by comparing Figs. 9 and 10. The effects of the different clays on both the increase of R (A_{287}/A_{265}) and the decrease in M_v are so similar that the existence of a correlation between R and M_v should be investigated. Fig. 11 shows the variation of M_v with the values of R and confirms the existence of a strong correlation between the appearance of the absorption band at 287 nm and the PC degradation. This is an interesting result because confirms that the degradation of PC during the melt processing of its nanocomposites can be quantitatively studied using a fast, simple and inexpensive experimental technique, such as UV spectroscopy.

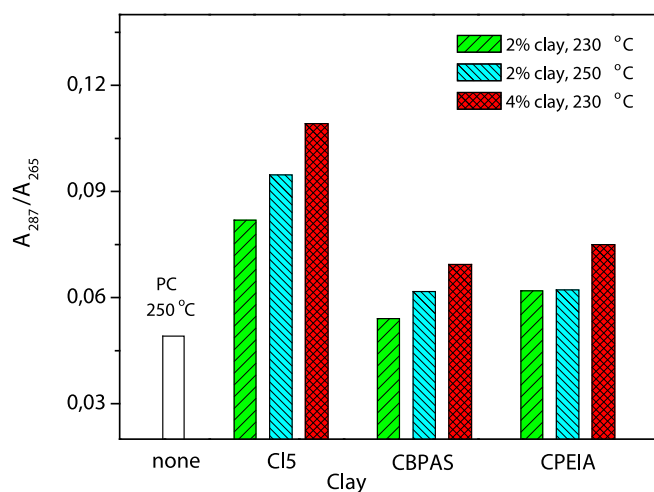


Fig. 9. Values of the A_{287}/A_{265} ratio measured in films of pure PC and nanocomposites of PC with 2% of C15, CBPAS or CPEIA.

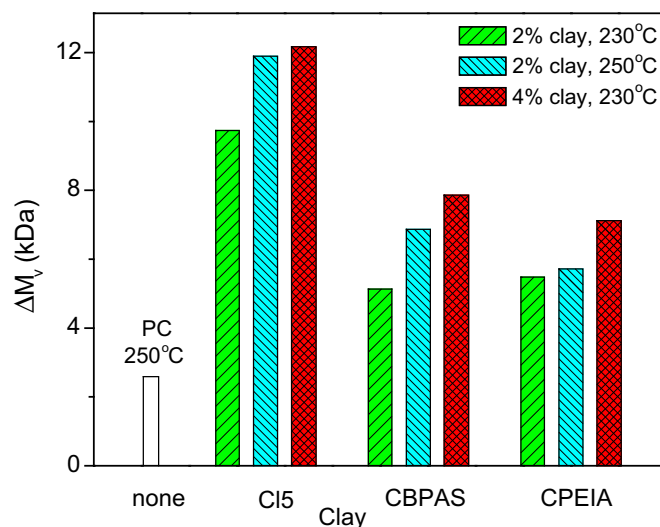


Fig. 10. Reductions in the average molar mass (M_v) measured in pure PC and nanocomposites of PC with 2% of C15, CBPAS or CPEIA.

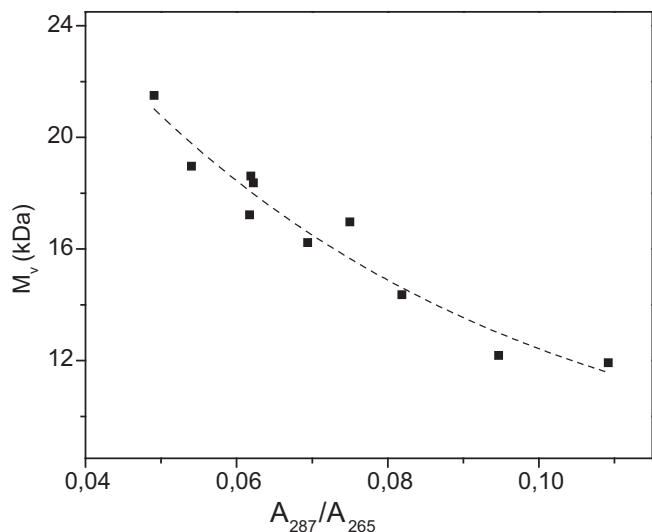


Fig. 11. Relationship between the reduction in the average molar mass and the A_{287}/A_{265} ratio. The dashed line is only a guide to the eye.

All the results obtained in this work indicate that C15 causes greater degradation than CBPAS and CPEIA. In order to explain this result, and taking into account the key role of the hydrolysis in the degradation of PC, we firstly must consider the water content of the three clays. This water content can be compared using Fig. 2, which shows the weight losses at low temperatures (between 50 and 150 °C) of the three clays. Fig. 2 shows that C15 is the clay with smaller weight loss at low temperatures, so we can consider that the content of free water is lower in C15 than in the other clays. In this case, the water content of the clays does not appear to play a main role in the degradation of PC.

The high activity of C15 as degradation catalyst must be explained by taking into account other factors. It must be considered, on one hand, that the organic modifier of C15 is a quaternary ammonium salt. Due to its low thermal stability, this modifier will suffer the Hoffmann elimination to form an amine and the corresponding olefin, thus generating acidic sites on the clay [20,31], in a process which takes place at temperatures similar to those used in the melt processing of polycarbonate nanocomposites. Thus, during the melt compounding of the nanocomposites, some acidic sites are generated on the silicate layers, which catalyze the hydrolytic degradation of PC. A similar clay catalyzed hydrolysis has been observed in other polymers such as PA6, PLA and EVA [1,16–18,25–28]. This clay-catalyzed degradation in the nanocomposites can explain the appearance of the low-temperature weight loss step observed in the TGA and TGD curves of PC/C15, as well as the appearance of the phenolic compounds responsible for the changes observed in the absorption and emission spectra. On the other hand, the superior effect of C15 may be also due to the better dispersion of this clay into the polymer matrix, which has been shown in the TEM analysis. As has been mentioned above, a better dispersion of the clay implies a better contact of the silicate layers with the polymer, which favors the clay catalytic effect.

The clays modified in the laboratory, CBPAS and CPEIA, show a considerably lower effect on the PC degradation. The different behavior of these clays, in relation with C15, can be explained by taking into account that the chemical modifications of CBPAS and CPEIA do not contribute to the generation of acidic sites during the melt processing of the nanocomposites. On the other hand, the TEM images reveal a poor dispersion of CBPAS and CPEIA into the polymer, as well as the presence of a dark impurity around the clay in the corresponding composites (see Fig. 3). This impurity can be

explained by the presence of degraded rests of the chemical modification of these clays, which are only partially eliminated during the melt processing of the nanocomposites at 250 °C. These degraded rests can hinder the dispersion of the clays into the polymer and the good contact necessary for the catalytic effect on the polycarbonate degradation.

The above results indicate that the nature (and especially some degradation processes) of the chemical modification of the clays plays a main role in the degradation of PC during the melt processing of the nanocomposites. Thus, the above results confirm that the organic modification and the amount of the layered silicate must be carefully selected in order to minimize the polymer degradation during the melt processing of the nanocomposites.

5. Conclusions

The degradation of polycarbonate during the melt-compounding with three montmorillonites, with different organic modifications, has been studied using different spectroscopic techniques, thermogravimetric analysis and dilute solution viscosimetry. The selected clays were two montmorillonites modified in the laboratory, with a bisphenol-A containing silane and a polyethylenimine, respectively, and a commercial montmorillonite, Cloisite™ 15A. The results indicate that the three clays catalyze the hydrolytic degradation of polycarbonate, which explains the great reduction in the average molar mass of PC, observed by viscosimetry, as well as the appearance of phenolic compounds, observed in the UV spectra and in the fluorescence emission. There is a strong correlation between the normalized absorption at 287 nm, assigned to the phenolic units, and the reduction in the average molar mass. The degradation catalyzed by the clays explains also the appearance in some nanocomposites of a weight loss step at low temperatures, observed in the thermogravimetric analysis. The fluorescence spectroscopy has been found to provide useful information about the clay-induced degradation of PC.

All the experimental techniques indicate that the commercial clay used as a reference causes a most severe degradation than the clays modified in the laboratory. This result has been explained taking into account that, on one hand, the organic modification of the commercial clay suffers the Hoffmann degradation during the melt compounding of the PC nanocomposites, thus generating acidic sites on the silicate layers which catalyze the hydrolytic degradation of the polymer. On the other hand, the commercial clay gives a better exfoliation than the laboratory ones, and the close contact with the polymer is necessary for the clay action on the degradation. Moreover, the TEM analysis reveals that the two clays modified in the laboratory appear in the composite surrounded by dark impurities, tentatively explained as degraded rests of the chemical modifications of the clays, which hinder the close contact with the polymer.

The degradation of polycarbonate also depends on the amount of clay and the processing temperature. However, the apparent water content of the clay does not appear to play a significant role in this case.

The obtained results indicate that the degradation of PC during the melt processing of the clay-reinforced nanocomposites may be characterized using fluorescence emission and UV absorption spectroscopic techniques. The clays modified by us in the laboratory cause substantially less degradation of the polymer than the commercial clay used as a reference.

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