Special Issue: Polycarbonates and Green Chemistry

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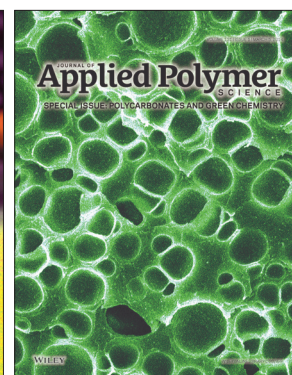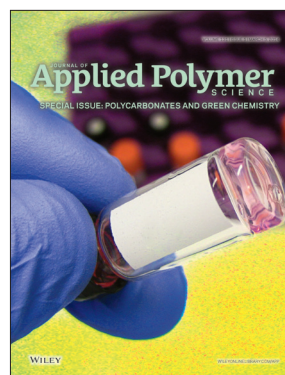Clay-induced degradation during the melt reprocessing of waste polycarbonate
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Clay-Induced Degradation During the Melt Reprocessing of Waste Polycarbonate

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ABSTRACT: The addition of small amounts of organoclays during the reprocessing of waste polycarbonates (WPCs) is a promising method for improving the properties of the recycled plastics. However, the clays can also induce the degradation of the polymer during the melt compounding and thus lower the properties of the final materials. This clay-induced degradation of polycarbonate (PC) was examined in this study. A WPC, a virgin PC (VPC) (that served as a comparison), and two commercial montmorillonites, Cloisite 15A and Cloisite 30B, were melt compounded in a twin-screw microextruder. The degradation of the polymer, which caused the formation of phenolic compounds and the reduction of the average molar mass, was monitored with UV spectroscopy, thermogravimetric (TG) analysis, and solution viscosimetry. The results reveal that the effect of the clays on the degradation depended on the amount of clay used and the chemical nature of the organic modification. When small amounts of the appropriate clay were used, the polymer degradation was minimized, and a net improvement of some properties of the recycled PC was achieved. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39997.

INTRODUCTION

Because of its excellent thermal, mechanical, and optical properties, bisphenol A polycarbonate is one of the most widely used engineering plastics. Large amounts of polycarbonate (PC) waste are generated every year; ideally, this material should be recycled.[1–7]

Melt reprocessing appears to be the most suitable recycling process, at least for those PC residues that are only moderately degraded or contaminated. However, different authors have pointed out that PC can suffer severe degradation during the mechanical processing at elevated temperatures, with a noticeable reduction in the average molar mass due to hydrolysis and chain scission.[1,2,7–9] This degradation explains the deterioration of some of the mechanical, thermal, and optical properties of the PC that takes place during reprocessing. Several authors have proposed the addition of different polymers and chain extenders during reprocessing to improve the properties of the recycled materials.[5–7]

de la Orden et al.[10] recently studied the effects of the addition of different organoclays during the melt reprocessing of a waste polycarbonate (WPC). The addition of small amounts (2 wt %) of clay allowed the improvement of some mechanical and thermal properties. However, the addition of greater amounts of clay was not useful because no significant additional improvements in the properties were obtained. In some cases materials recycled with 4 wt % of clay showed worse properties than those reprocessed with 2 wt % of clay.

This behavior was tentatively explained by the organoclays, which acted as a catalyst for the degradation of the PC during melt reprocessing.[10] Different polymers experience a noticeable
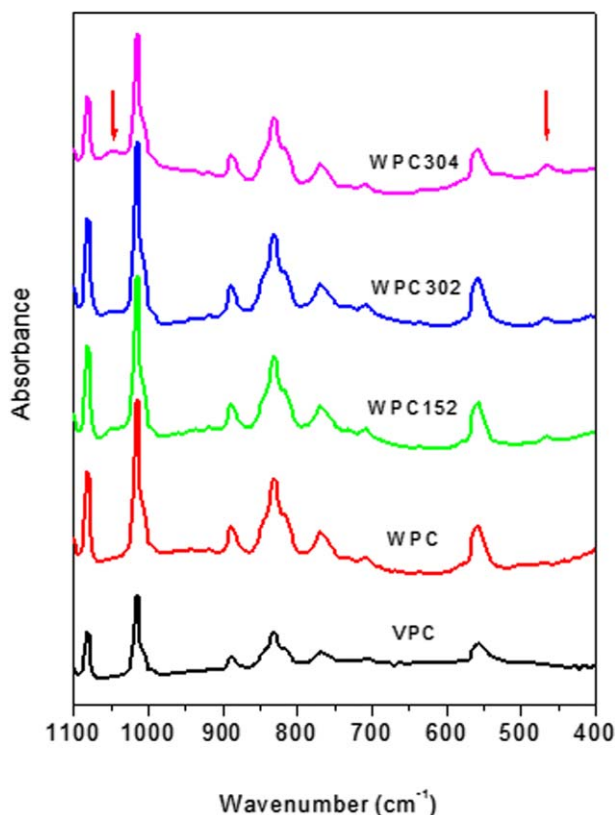
Figure 1. FTIR spectra of the PCs (VPC and WPC) and nanocomposites of WPC with C-15 and C-30. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

degradation under the severe conditions usually selected for the melt compounding of clay-reinforced nanocomposites.[11–16] This degradation reduces the overall performance of the final materials and especially affects polymers such as polyesters,[17] polyamides,[18,19] and PCs.[20,21] A recent article[22] we reported the effects of different modified montmorillonites, including clays that were modified in the laboratory, on the degradation of a virgin polycarbonate (VPC) during the melt compounding of nanocomposites. The results reveal that some organoclays caused a remarkable degradation in the polymer and that the organic modification of the clay played a main role in polymer degradation.

When recycling a used PC, the degradation during melt reprocessing may be substantially different because of the effect of previous damage to the polymer. The effects of the clay on the degradation of a VPC and a WPC may also be clearly different. The study of the effects of these clays on the degradation of the waste polymer during melt reprocessing is necessary to evaluate the usefulness of the addition of clays for improving the properties of the recycled material.

The main objective of this study was to examine the effect of different clays on the degradation of a WPC during melt reprocessing. Two commercial montmorillonites with different organic modifications, Cloisite 15A (C-15) and Cloisite 30B (C-30), were used to evaluate the effects of the chemical modifications of the clay. The WPC was obtained from the milling of

large bottles of water. A VPC was also studied for comparison. The structure of the nanocomposites compounded in a twin-screw microextruder was analyzed with transmission electron microscopy (TEM) and Fourier transform infrared (FTIR) spectroscopy. The degradation of PC during melt compounding was monitored with UV spectroscopy, thermogravimetric analysis (TGA), and solution viscometry. The results indicate that the two clays catalyzed the degradation of the WPC, but the severity of the degradation depended on the nature of the organic modification of the clay and the amount of clay used.

EXPERIMENTAL

Materials

The VPC used in this study, which was supplied by SABIC Innovative Plastics (Cartagena, Spain), was a polymer in powder form with no additives. The WPC studied, which was provided by Montsiaplastic (Tarragona, Spain), was a powder obtained during the mechanical recycling of PC bottles used in water dispensers. The starting WPC was composed of neat PC and impurities such as adhesive, paper, ink, and other unidentified substances. To remove the impurities, the waste was sieved and washed successively with water and 2-propanol. The absence of significant amounts of impurities in the purified waste was checked with FTIR spectroscopy. The close similarity between the spectra of VPC and WPC, both shown in Figure 1, revealed that the impurities in the starting waste were properly removed during the purification step.

Two organically modified montmorillonites with different quaternary ammonium salts, C-15 and C-30, were kindly supplied by Southern Clay Products. Figure 2 presents the chemical structures of the organic modifiers. C-15 contains two methyl groups and two dihydrogenated tallow (HT) groups in the organic modifier. C-30 has two 2-hydroxyethyl groups in the organic modifier that do not appear in C-15.

Melt Compounding

The raw materials were dried before extrusion to minimize the hydrolytic degradation of PC during the reprocessing. The WPC and VPC, in powder form, were dried in a vacuum oven at 110°C for 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%.[22] The clays were dried at a lower temperature, 70°C, in a vacuum oven, to prevent the degradation of the organic modifier. It is always important to preserve the organic modification of the clays before the extrusion process to obtain true nanocomposites from the polymers and layered silicates. Organic modification is applied to increase the separation between the clay platelets and, facilitating the
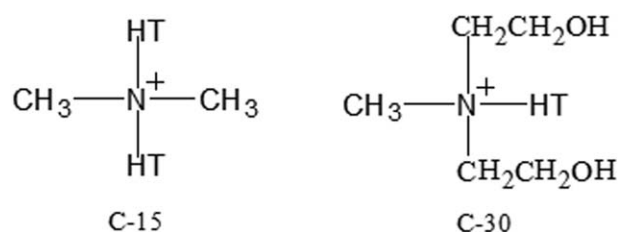

Figure 2. Chemical structures of the organic modification of each clay.

Table I. Code Names and Compositions of the Prepared Materials

Sample code	PC	Clay	Clay content (wt %)	Sample code	PC	Clay	Clay content (wt %)
VPC	Virgin	—	0	WPC	Waste	—	0
VPC152	Virgin	C-15	2	WPC152	Waste	C-15	2
VPC154	Virgin	C-15	4	WPC154	Waste	C-15	4
VPC302	Virgin	C-30	2	WPC302	Waste	C-30	2
VPC304	Virgin	C-30	4	WPC304	Waste	C-30	4

penetration of the polymer molecules and, hence, the formation of exfoliated or intercalated structures with good properties. To obtain good nanocomposites, the organic modifications must be degraded, removed, and substituted by the polymer molecules during the extrusion process, when clays and polymers are finally mixed in the extruder at high temperatures. However, if the organic modification is removed before the extrusion, the clay platelets collapse, and then the formation of the desired intercalated or exfoliated structures is very difficult.

The materials were processed with a corotating twin-screw microextruder (Rondol) with a screw temperature profile of 150, 220, 250, 250, and 225°C from the hopper to the die. The length-to-diameter ratio was 20:1. The compounding temperature was limited at 250°C to minimize the degradation of the polymer. The pelletized nanocomposites were dried at 150°C and then compression-molded at 250°C in a hot-plate hydraulic press. The clay concentrations in the nanocomposites were 0, 2, and 4 wt %. Table I gives the code names and compositions of the polymers and nanocomposites obtained by this method.

The presence of the clays in the nanocomposites was tested with FTIR spectroscopy and TEM. Figure 1 shows the spectra of the nanocomposites obtained from WPC, CV-15, and C-30 in addition to the spectra of the neat polymers. The spectra of the nanocomposites showed two characteristic IR absorption bands centered at 465 and 1043 cm^{-1}; these revealed the presence of the clays in the final composite. The weak absorption band centered at 1043 cm^{-1} was assigned to a Si—O—Si stretching vibration mode corresponding to the reinforcing clays.[22–24] The two bands became more accentuated as the clay content increased from 2 to 4%.

Characterization of the Materials

Microtomed sections of the different materials were examined by TEM at room temperature. A JEOL JEM-2100 transmission electron microscope, operated at 200 kV, was used to obtain images of the nanocomposite specimens. The UV absorption spectra of the sample films, obtained by casting from dilute solutions in dichloromethane, were measured in a PerkinElmer Lambda 35 UV–vis spectrophotometer at room temperature. The 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. The TGA of the different materials was carried out with a TA Instruments TGA2050 thermobalance. Samples of about 10 mg were heated at 10°C/min from room temperature to 800°C in dry air or dry nitrogen (30 cm^3/min). Two characteristic temperatures were chosen to compare the thermal degradation of the different materials:

the onset degradation temperature (T_{onset}), which corresponds to 5% weight loss, and the temperature of maximum weight loss rate (T_{max}). The viscometry was carried out at 25 ± 0.5°C with an Ubbelohde 0B viscometer and chloroform as the solvent. The intrinsic viscosity ($[\eta]$) was calculated by extrapolation with the equations proposed by Kraemer and Huggins.[25] The viscosity-average molar mass (M_v) was calculated from $[\eta]$ with the Mark–Houwink–Sakurada equation.

RESULTS AND DISCUSSION

Morphological Characterization

Figure 3 shows the TEM micrographs of different nanocomposites (WPC152, WPC302, and VPC302. See code names in Table 1). The set of three images allowed an overview of the morphology of the nanocomposites obtained from WPC, VPC, C-15, and C-30. The images show that the clay was well-dispersed in the polymer in the three nanocomposites and gave a mixture of intercalated and exfoliated nanostructures. In the three cases, the TEM images revealed effective polymer intercalation into the clay galleries. The nanostructures observed in the nanocomposites obtained from the WPC were very similar to those found in the nanocomposites obtained from the VPC [Figure 3(b,c), respectively]. However, the morphology of the nanocomposites depended on the nature of the organic modification of the clay. While WPC302 and VPC302 [Figure 3(b,c)] showed more intercalated structures, more exfoliation was seen in the composites made from C-15 [WPC152; Figure 3(a)].

Other authors have found similar structures in nanocomposites obtained from different VPCs and clays.[21,26–33] In all cases, the presence of exfoliated and intercalated morphologies was associated with high-performance nanocomposites. A good dispersion of the clay also implied close contact of the clay surfaces with the polymer.

TGA

The results obtained in the TGA of the nanocomposites reveal information about the degradation of the VPC and WPC during the melt processing of the clay-reinforced composites. Figure 4 shows the TGA curves of the WPC and WPC matrix nanocomposites that were obtained under a dry air atmosphere at 10°C/min. The TGA curve corresponding to the VPC is included for comparison.

The thermooxidative decomposition of PC in an air atmosphere occurred in two distinct steps. The first step corresponded to the weight loss caused by the thermooxidative decomposition of the polymer, while the second step corresponded to the combustion of the char formed in the first step. The formation of
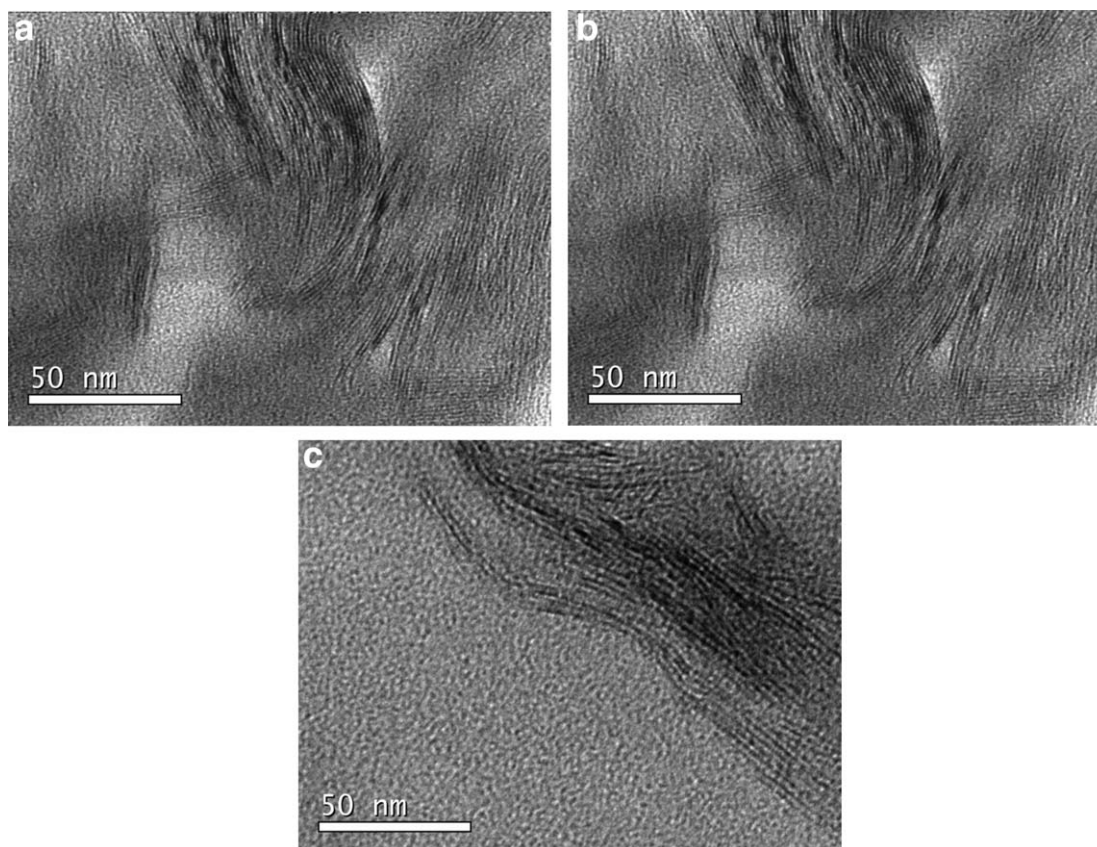
Figure 3. TEM images for (a) WPC152, (b) WPC302, and (c) VPC302.

char, which was due to the crosslinking reactions that took place during the decomposition,[34] reduced the permeability and hindered the output of the volatile decomposition products; this increased the decomposition temperature.

These two steps are shown in Figure 5, which contains the differential thermograms [differential thermogravimetry (DTG) curves] corresponding to the WPC and WPC302. The DTG curves allowed the determination of T_{max} for each degradation
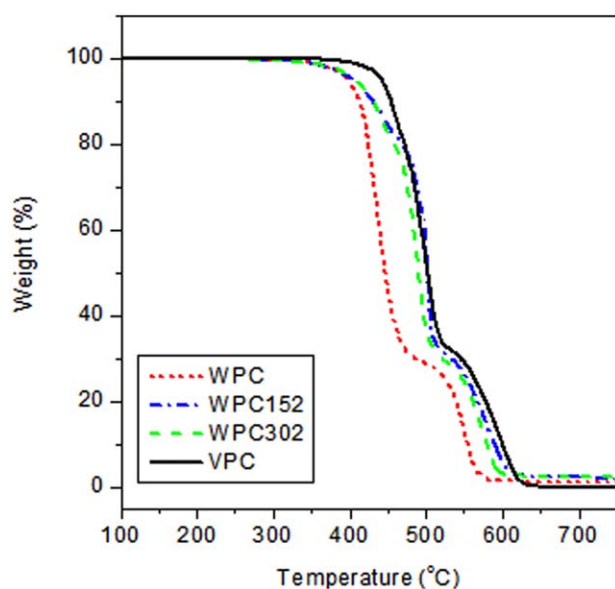

Figure 4. TGA curves of the VPC, WPC, and nanocomposites made from WPC and 2 wt% of clays (dry air atmosphere). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
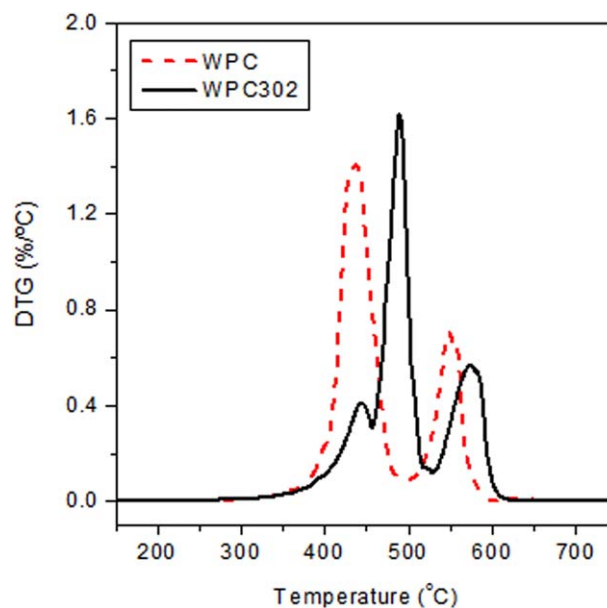

Figure 5. DTG curves in air for the WPC and WPC reinforced with 2 wt% of C-30. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Representative TGA Data for the VPC, WPCs, and Nanocomposites Obtained from WPC and 2 wt% C–15 and C–30 in a Dry Air Atmosphere

Sample	T_{onset} (°C)	T_{max1} (°C)	T_{max2} (°C)	Char residue at 700°C (%)
VPC	443	503	598	0.1
WPC	398	438	548	1.1
WPC302	408	490	575	2.5
WPC152	405	502	582	2.4

step. These T_{max1} and T_{max2} values, which could be used to compare the degradation of the different materials examined in this study, are collected in Table II. They also included the values of T_{onset}, the initial decomposition temperature, and the values of the char residues (weight percentages) measured at 700°C.

As shown in Figure 4 and Table II, the WPC showed lower resistance to thermooxidative degradation than the VPC. A similar result was obtained when the degradation in nitrogen was studied; this revealed that WPC had, in general, a lower thermal stability than the virgin polymer. This result can be explained by the WPC, which suffered some degradation during its processing and use, and also during the recovery and milling processes. Similar results have been obtained by other authors. For example, Pérez et al.[2] showed that there was a loss of thermal stability during the reprocessing of PC. This decrease in the thermooxidative stability is a severe disadvantage for the recycled PC because the thermal stability is one of the key properties of PCs.

However, Figures 4 and 5 and Table II also show that the thermooxidative stability of the waste could be strongly improved with low amounts of clays. The onset temperature increased from 398 to 408 or 405°C with the addition of 2 wt % C-30 or C-15, respectively, although these values were still well below the value measured for the VPC (443°C). The increases in the thermal stability caused by the addition of organoclays were clearer when the T_{max} values were compared. The values of T_{max1} and T_{max2} (502 and 582°C, respectively) of WPC152, were clearly higher than those corresponding to WPC (438 and 548°C, respectively) and were comparable with the values corresponding to the VPC (503 and 598°C, respectively). Analogous results were found in an inert atmosphere.

Other authors have reported similar positive effects of organoclays on the thermal and thermooxidative stability of VPC and other polymers.[11,12,35,36] These authors have proposed that the added clay acts as a mass-transport barrier and, thus, hinders the output of the volatile products generated during decomposition. When the thermal degradation takes place in air, the layered silicates contribute to the stability of the polymer by hindering the input of oxygen. These thermal stability improvements are more important when the nanocomposites present exfoliated structures.

The enhancement of the thermal stability depends on the chemical nature of the clay modifiers. Table I shows that T_{max} values

corresponding to nanocomposites obtained from C-30 were slightly lower than those corresponding to the nanocomposites obtained from C-15. This behavior could have been related to the difference observed in the characteristic morphology of each material; as mentioned previously, exfoliated clay is more effective as a barrier to the input and output of gases during the decomposition of the polymer, and WPC152 showed more exfoliation than WPC302 (Figure 3).

Table II shows that the increases in T_{onset} due to the introduction of clays were clearly less important than the increases observed in the values of T_{max}. The analyses of the TGA and DTG curves shown in Figures 4 and 5 give an explanation for this behavior. In addition to the two weight loss steps characteristic of the thermooxidative degradation of PCs (WPCs or VPC), the clay-reinforced nanocomposites showed a third step that appeared near 455°C as a weak shoulder in the TGA curves (Figure 4) or as small peak in the DTG curves (Figure 5). This third weight loss, which could explain the unexpectedly low values of T_{onset} in the nanocomposites, could have been related to a polymer degradation caused by the clays during the melt processing of the nanocomposites.

The organic modifiers of the montmorillonites C-15 and C-30 were both quaternary ammonium salts (Figure 2). Because of their low thermal stability, these modifiers underwent Hoffman elimination to form an amine and the corresponding olefin; this left an acidic site on the silicate layer.[34,37] This process took place at temperatures even lower than those used in the melt processing of PC nanocomposites. Thus, during the melt compounding of the nanocomposites, some acidic sites were generated on the silicate layers; these catalyzed the degradation of the PC and other polymers.[11,13,20,21,28] This clay-catalyzed degradation in the nanocomposites caused the appearance of chains of lower molecular mass, which were responsible for the characteristic weight loss at 455°C. This effect, which has also been observed in the nanocomposites of VPC, depended on the amount of clay used and, thus, acted as a limiting factor for the addition of clay to the WPC.[22]

Finally, Table I shows the amount of char residue observed in each material after the end of the thermooxidative degradation at 700°C. As expected, the amount of char residue was very low, 0.1%, for the VPC. The clay nanocomposites generated higher amounts of char and corresponded to materials where only the organic modification of the clay is eliminated during the thermooxidative degradation. The value observed for waste (1.1%) revealed the presence of some impurities in the waste polymer, which could not be detected in the IR spectrum. These impurities could have played a significant role in facilitating the thermal and thermooxidative degradation of the WPCs.

The decrease in the thermal stability observed in the waste polymer as compared with the virgin material was completely compensated for by the positive effect caused by the addition of low amounts of clay. The experimental results demonstrate that the thermal and thermooxidative stabilities of the WPC reinforced with low amounts of clay were similar to those corresponding to the VPC used for comparison.
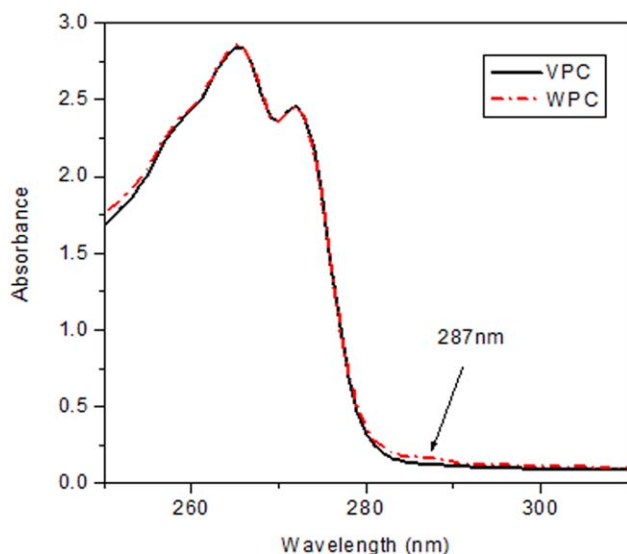
Figure 6. UV absorption spectra VPC and WPC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

UV Spectroscopy

The degradation of PC was also studied with UV spectroscopy. Figure 6 shows the normalized UV spectra of the VPC and WPC. There was a clear difference at 287 nm, where the spectrum of the waste polymer showed a weak shoulder.

The band at 287 nm has been previously assigned to phenolic compounds in the polymer[38] and has been used by different authors to characterize the degradation of PC.[20,22] Taking into account this assignment, the shoulder observed at 287 nm in the spectrum of the WPC was explained as the result of the degradation of PC molecules during use and during the recycling process, which generated phenolic units.

Figure 7 shows the normalized spectra corresponding to the nanocomposites obtained from WPC and C-30. The absorbance at 287 nm increased with the amount of clay; this showed that the clays catalyzed the degradation of the polymer during melt compounding. Similar results were obtained when the clay was C-15.

These results were in good agreement with those obtained in the TGA. The compounds generated as a result of the degradation, as revealed by the UV spectra, were fragments of lower molecular weight and, hence, of lower thermal stability than the original macromolecules. These fragments could have been responsible for the weight loss observed at moderate temperatures in the TGA and DTG curves.

Viscometry

The results obtained by UV spectroscopy and TGA indicate that the two clays examined in this study cause the degradation of the waste polymer during recycling. To quantify the effect of the clays on the M_v of the polymer, the changes in $[\eta]$ were measured, as determined by dilute solution viscometry. The values of M_v were calculated from $[\eta]$ with the Mark–Houwink–Sakurada equation with the recommended values of K and α, two constants dependent on polymer–solvent–temperature system (0.0301 mL/g and 0.74, respectively):[39]

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

Figure 8(a,b) shows that M_v decreased during the mechanical reprocessing of VPC and WPC in the presence of clay; this revealed a severe degradation of the PC during reprocessing. Other authors have reported that clays can induce the degradation of PCs[20–22] and other polymers, such as different polyamides, poly(lactic acid) and poly(ethylene-co-vinyl acetate).[11,13–16,20,21,28] Figure 8 shows that the decreases in M_v were slightly more important in the WPC than in the VPC. This result was explained as a result of the previous degradation of WPC, which facilitated the subsequent degradation of the material. The decreases in M_v were strongly dependent on the clay content and especially on the nature of the organic modification of the clay. Figure 8 also shows that C-15 caused a stronger degradation than C-30. A molar mass reduction higher than 30% was observed in PC reprocessed with 4% C-15.

These results agreed with those obtained with thermogravimetric and spectroscopic techniques. The clay-catalyzed degradation of PC during the reprocessing explained the reductions in M_v, the formation of compounds with lower thermal stability observed in the TGA curves (Figures 4 and 5), and the appearance of phenolic compounds, which were responsible for the new absorption band centered at 287 nm in the UV spectra of the nanocomposites (Figure 7).

To explain the different effects of C-15 and C-30 on the degradation of the polymer, different factors were considered, including the water content of the clay, the nature of the organic modification, and the degree of dispersion of the clay platelets into the polymer. We previously studied the effects of clays with different organic modifications and water contents on the degradation of a VPC during melt compounding.[22] The results show that the water content of the clay was not a significant matter in the degradation of the polymer. However, the nature of the organic modification of the clay and the degree of dispersion appeared to play important roles.
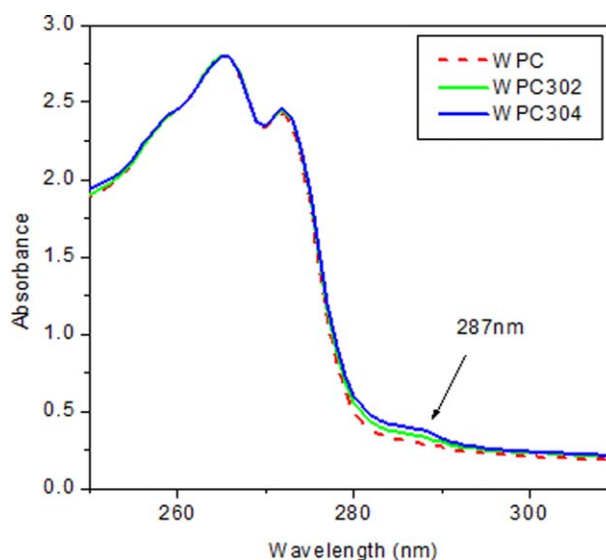

Figure 7. UV absorption spectra of the WPCs reinforced with 2 and 4 wt % C-30. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
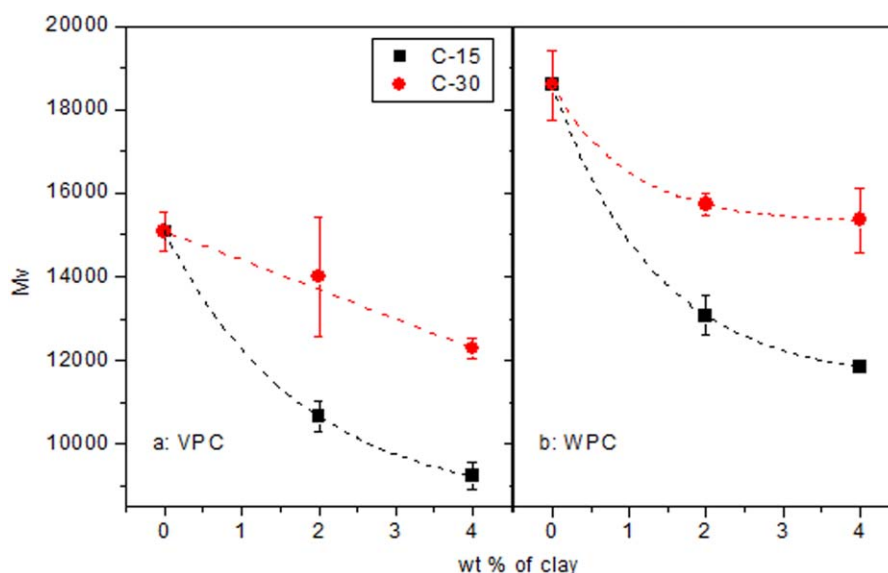
Figure 8. Values of M_v measured in the VPC and WPCs and their nanocomposites with C-15 and C-30. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The organic modifiers C-15 and C-30 were both quaternary ammonium salts that suffered Hoffman elimination during the melt compounding of the nanocomposites. This process is important because the acidic sites generated on the silicate layers induced the degradation of the polymer.

The higher activity of C-15 can be explained, at least in part, by taking into account the differences in the nature of the organic modification. While C-30 contained two 2-hydroxyethyl groups and only one HT group (Figure 2), C-15 contained two HT groups. The better dispersion of C-15 into the polymer matrix, as shown in the TEM analysis (Figure 3), must also be considered. As previously mentioned, the better dispersion of the clay favored the contact of the silicate layers with the polymer and, hence, the catalytic effect of the clay on the polymer degradation.

CONCLUSIONS

WPCs were mechanically reprocessed with the addition of small amounts of C-15 and C-30, two montmorillonites with different organic modifications. The obtained materials were characterized with different spectroscopic techniques, TEM, TGA, and dilute solution viscometry. The results indicate that true nanocomposites were obtained with the two clays. In addition to the improvement of some mechanical properties, as observed in a previous work, the use of small amounts of clay allowed great improvement in the thermal stability of the waste polymer. The waste showed, after being reinforced with 2 wt % of clay, a thermooxidative stability close to that corresponding to the virgin polymer.

However, the clays also showed some detrimental effects. The two clays catalyzed the degradation of PC, which explained the reduction in the average molar mass of PC that was observed by viscometry, the weight loss step at low temperatures that was observed by TGA, and the appearance of phenolic compounds that was observed in the UV spectra of the nanocomposites. The

catalytic effect was explained by the fact that the organic modification of the clays suffered Hoffmann degradation during the melt compounding of the nanocomposites. This degradation generated acidic sites on the silicate layers, which catalyzed the degradation of the PC. The different behavior of the two clays was explained the nature of the organic modification and the degree of dispersion. A better dispersion of the clay in the nanocomposite implied a closer contact with the polymer, which favored the catalytic action of the clay on the degradation.

The degradation of the WPC during the melt compounding had a well-known negative effect on the performance of the recycled materials. The relative importance of this degradation depended on the amount and nature of the clay used. When small amounts of the appropriate clay were used, recycled PCs with improved thermal and mechanical properties were obtained.

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