

Photochemistry of Low-Density Polyethylene–Montmorillonite Composites

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ABSTRACT: Photo-oxidation at the exposed surfaces of low-density polyethylene/montmorillonite composites was analyzed with attenuated total reflection/Fourier transform infrared spectroscopy. It was found that the clay particles were dispersed but not exfoliated in the polymer matrix. The extent of oxidative degradation of the low-density polyethylene matrix was slightly greater when montmorillonite was present and was greatest for the blend of low-density polyethylene and organically modified montmorillonite. The Fourier transform infrared measurements demonstrated that the rate of photo-oxidation in the bulk was lower than that observed at the surface, but the oxidation chemistry was similar at the surface and in

the bulk. The distribution of the photo-oxidation products was somewhat modified in the presence of montmorillonite and organically modified montmorillonite in comparison with pure low-density polyethylene, with the yield of acidic products higher and the yield of double bonds lower. These observations were attributed to a slightly higher yield of radicals and some modification of the quantum yield for the processes leading to the formation of double bonds when the clay filler was present. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 381–389, 2009

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INTRODUCTION

The photo-oxidation of polyolefins has been extensively studied over the past 50 years. These studies have principally attributed the degradation to the formation of hydroperoxides and have focused on the mechanisms of their formation and the fate and roles of catalyst residues and adventitious impurities. The parts played by additives, fillers, and stabilizers in the formation and degradation of hydroperoxides have also been widely investigated. It is believed that some hydroperoxides and other photoactive species can be formed as byproducts during the synthesis or processing of polyolefins, and these act as the initiators for photo-oxidation. The results of this enormous body of work have been periodically reviewed.^{1–9}

Although much has been reported on the oxidative degradation of polyolefins, this field of research remains highly active. Clough and coworkers^{6,7} reported that at least 11 oxidation products are formed and that they fall into the general categories of ketones, carboxylic acids, esters, peresters, ketals, hemiketals, peroxides, and alcohols. Salvalaggio et al.⁹ used Fourier transform infrared (FTIR) transmission spectroscopy to study the thermal oxidation of low-density polyethylene (LDPE) in an oxygen atmosphere. They used spectral curve fitting to identify 10 components that absorb in the FTIR carbonyl region of 1650–1800 cm⁻¹. They assigned these components to a variety of ketones and aldehydes, carboxylic acids and esters, peracids and peresters, lactones, and unsaturated groups.

Thus, the methods of oxidation initiation in air and the photo-oxidation products for polyolefins have been well characterized, and mechanisms have been formulated to account for their formation.^{1–5}

Over the past few years, there has been increased interest in the incorporation of nanosized particles into polymers, including polyolefins, to modify properties, particularly thermal, tensile, and barrier properties.^{10,11} If these composites are to find applications in outdoor environments, their photo-oxidation stability is of interest. Yang et al.¹² examined the

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effects of nanosized inorganic particles on the photo-oxidation of linear low-density polyethylene (LLDPE). They found that there was a significant difference in the stabilizing effect of the nanoparticles between the surface and the bulk, with the rate of oxidation at the surface being significantly higher than that in the bulk.

In contrast, Allen et al.¹³ and Zan et al.¹⁴ found a different effect for the photo-oxidation of LDPE composites containing TiO₂ nanoparticles. This was attributed to the ability of TiO₂ to generate active oxygen species, such as superoxide, upon photolysis in the presence of oxygen. These active oxygen species can be converted into peroxides and hydroxyl radicals that accelerate the rate of photo-oxidation of the polymer.

A different type of composite is formed by the incorporation of clay particles into polymers. The clay particles often have micrometer dimensions, but when the clay galleries are exfoliated in a polymer composite, the clay sheets have nanometer dimensions.¹⁵ The extent of intercalation and exfoliation of the clay within a polymer can be enhanced if the surfaces of the clay sheets are made more hydrophobic with a charged organic modifier, such as a quaternary amine salt, to replace some of the surface metal ions.^{15–17} At low filler contents, these clay composites exhibit enhanced polymer properties, including properties such as Young's modulus, flammability, and small-molecule permeability.¹⁷ A wide range of clay types have been studied as polyolefin fillers, including both synthetic and natural clays.¹⁷

Studies of the photo-oxidation of polyolefin/clay composites are of considerable interest because they are being widely used in outdoor applications, such as agricultural mulches.¹⁸ It has been shown that the rate of photo-oxidation of LDPE is enhanced in the presence of natural clays and that the rate of oxidation depends on several factors, including the extent of intercalation or exfoliation of the clay layers, the presence of transition-metal ions, and the presence of active sites on the clay surfaces.^{19,20} Qin et al.²⁰ and Gournis et al.²¹ proposed that these active sites can lead to the formation of superoxides, which enhance degradation through the formation of peroxides. Natural clays will contain Fe²⁺/Fe³⁺, for example, and these are known to accelerate the degradation of hydroperoxides.²¹

Recently, Qin and coworkers^{19,20} reported studies of the photo-oxidation of LDPE in the presence of natural montmorillonite (MMT) clay that was surface-modified with dialkyldimethylammonium chlorides. They found that the rate of photo-oxidation of the LDPE composite, assessed by the changing area of the carbonyl band in the transmission FTIR spectrum, was much (up to 10 times) greater than that for pure LDPE. They also found that the extent of photo-

oxidation increased with an increase in the clay content over the clay content range of 0–10%. However, the largest change in the rate of oxidation was observed over the range of 0–2%, after which the change was linearly dependent on the amount of clay present. Qin and coworkers concluded that the extent of dispersion of the clay within the matrix did not play the key role in the degradation of the LDPE matrix. Rather, they proposed that the presence of active sites on the clay surfaces was responsible for the accelerated photo-oxidation of the polymer. In this respect, they suggested that ammonium ions, formed through thermal degradation of the organic modifier during processing, played the vital role.

Qin and coworkers^{19,20} focused on oxidation of the bulk LDPE/MMT matrix, as they carried out their analyses with transmission FTIR spectroscopy. However, Yang et al.¹² reported a difference in the behavior between photo-oxidation at the surface and in the bulk for composites of LLDPE and some inorganic nanoparticles. For many applications of polymers, surface behavior plays a pivotal role. Therefore, in this article, the work of Qin et al.¹⁹ is extended to an examination of the photo-oxidation at the exposed surfaces of LDPE/MMT composites.

EXPERIMENTAL

LDPE (Alkathene LDN248) was obtained from Qenos (Sydney, Australia). Alkathene is an extrusion-grade product with a melt flow index of 8.5 at 190°C for a mass of 2.16 kg and a density of 0.922 g/cm³. The MMT clay samples were obtained from Southern Clay Products, Inc. (Austin, TX). The two samples were (1) Cloisite Na⁺ (MMT), which is an unmodified natural clay with 90% of the clay particles less than 13 μm in diameter and a spacing between the clay galleries of $d_{001} = 1.17$ nm, and (2) Cloisite 20A [organically modified montmorillonite (OMMT)], which is a modified natural clay with 90% of the clay particles less than 13 μm in diameter and a spacing between the clay galleries of $d_{001} = 2.42$ nm. The modifier used in the OMMT is a dimethyldialkylammonium chloride, with the alkyl groups being hydrogenated tallow consisting of 65% C18, 30% C16, and 5% C14 alkyl chains. The concentration of the modifier in OMMT is 950 mequiv/kg.

MMT and OMMT were separately blended with the LDPE in a Brabender model PL 2000 blender with 1, 3, or 5 wt % clay at a temperature of 170°C and a mixing frequency of 60 min⁻¹ for a mixing time of 5 min. After blending, the virgin LDPE and the composite mixtures were pressed into sheets approximately 1 mm thick. This was done in a hydraulic press fitted with stainless steel compression plates and with a load of 30 tons at 210°C. After the pressing, the polymer sheets were cooled in the

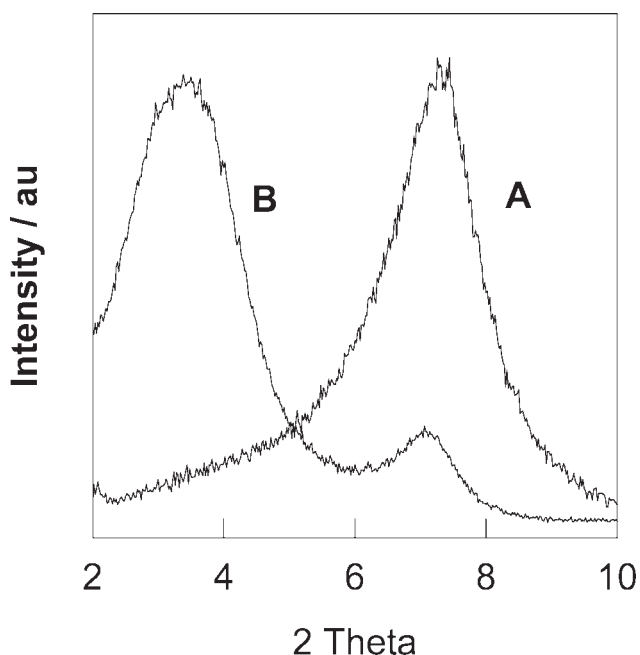


Figure 1 XRD patterns for (A) MMT and (B) OMMT particles before blending with LDPE.

compression mold to the ambient temperature by water circulating through the heater plates. Samples of the appropriate size for exposure and analysis were cut from these sheets.

The samples were exposed in air at room temperature to UV light in a Q-Panel QUV accelerated weathering tester fitted with an array of Q-Panel UV-B 313-nm fluorescent tube lamps. The photon flux from the lamp array was measured at the position of the samples during exposure and was 0.15 W/m^2 . After exposure, the samples were removed, and their surface spectra were delineated with a Nicolet 5700 FTIR spectrometer fitted with a diamond attenuated total reflection (ATR) accessory. The spectra were acquired over the wavelength range of $500\text{--}4500 \text{ cm}^{-1}$ after correction for the background. The spectra were collected at room temperature at a resolution of 2 cm^{-1} and averaged over a total of 64 scans to improve the signal-to-noise ratio. All the spectra were indexed with the intensity of the C–H peak at 1461 cm^{-1} , which was assigned an absorbance of unity. The X-ray diffraction (XRD) analyses were performed with a Bruker D8 Advance X-ray diffractometer equipped with a graphite monochromator, a copper target, and a scintillation counter detector. The analyses were performed on powdered clay samples over the 2θ range of $2\text{--}10^\circ$ at intervals of 0.02° with a step time of 20.3 s.

RESULTS AND DISCUSSION

The d_{001} spacing for the MMT used in the LDPE/MMT composite was calculated from XRD measure-

ments to be 1.2 nm (see Fig. 1), and this was in good agreement with that reported by the manufacturers. In the LDPE composites, the MMT particles were dispersed as micrometer-sized particles in the matrix, with no intercalation of the LDPE between the clay galleries. On the other hand, the d_{001} spacing for the OMMT used in the LDPE/OMMT composites was calculated from XRD measurements to be 2.6 nm (see Fig. 1). This spacing was slightly greater than that reported by the manufacturers (2.4 nm). XRD of OMMT also shows that a small proportion of the clay layers were not modified by the tallow, with these layers having a spacing of about 1.2 nm. OMMT has been found^{17,19,20,22,23} to be dispersed as micrometer-sized particles in a polyolefin matrix with some intercalation of the olefin chains between the clay galleries but no significant exfoliation of the OMMT into clay sheets with nanometer dimensions. This was confirmed for these OMMT/LDPE blends by XRD and TEM measurements.

ATR–FTIR spectra typical of those obtained for pure LDPE before and after UV exposure in the Q-panel instrument for 333 h are shown in Figure 2(A,B). Indexation of the spectra with the polyethylene (PE) peak intensity at 1461 cm^{-1} ensures that the ATR spectra are representative of the same amount of LDPE in each case. The general features of these two ATR spectra are similar to those that have been reported by other workers, such as Costa

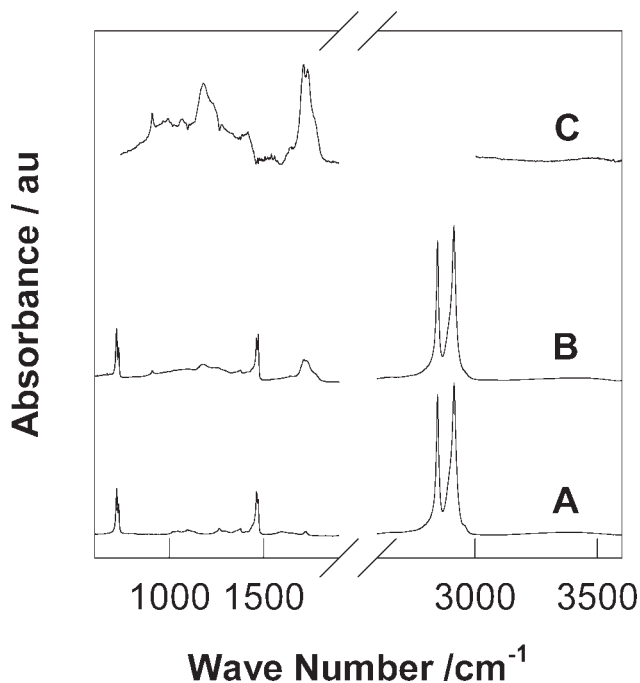


Figure 2 (A,B) ATR–FTIR spectra of the surfaces of samples of LDPE before room-temperature UV photolysis and after UV photolysis, respectively, and (C) the difference spectrum (expanded 5 times), which shows new bands that appear after photolysis.

TABLE I
Observed Bands and Bands Assigned by Salvalaggio et al.⁹ to Carbonyl Oxidation Products for PE

Oxidation product	Reported wave number (cm ⁻¹)	Observed band wave number (cm ⁻¹)
Ketones and α,β -unsaturated acids	1684	1687, shoulder
γ -Keto acids, keto group	1698	1698, shoulder
γ -Keto acids, acid group	1707	1702, shoulder
Associated carboxylic acids	1714	1713, peak
Ketones	1721	Hidden
Esters and aldehydes	1737	1733, peak
Peracids	1750	—
Isolated carboxylic acids	1767	1769, shoulder
Peresters	1779	1780, shoulder
γ -Lactones	1788	1791, shoulder

et al.²⁴ and Lacoste and Carlsson,²⁵ for virgin PE and PE after photo-oxidation to a similar extent during exposure to natural or UV-B radiation. However, the spectra are somewhat better resolved than the transmission spectra reported by Qin et al.,¹⁹ which were obtained after photo-oxidation of LDPE in air with 300-nm UV radiation for 200 h.

On the basis of a comparison of the relative intensities of the C=O band at 1718 cm⁻¹ and the C—H band at 1461 cm⁻¹, the extent of photo-oxidation of the bulk of LDPE reported by Qin et al.¹⁹ in their Figure 2 was lower than that observed in this study for oxidation at the LDPE surface. Qin et al. used a much shorter UV exposure time (200 vs 333 h) but somewhat higher energy photons than the average of those used in this work (peak wavelength = 313 nm). More importantly, Qin et al. did not report the photon flux incident on their LDPE samples, so it was impossible to compare exposure doses. It is possible that the photon flux used by them was much lower than that used in this study and that this also partially accounts for the different extents of oxidation.

The new bands that appear in the ATR spectrum of LDPE after exposure are highlighted in the difference spectrum shown in Figure 2(C). The absorbance scale for this spectrum has been expanded 5 times with respect to Figure 2(A,B). The major new bands that appear in the region around 1000–1300 cm⁻¹ arise principally from new C—O groups, and those in the region around 1650–1900 cm⁻¹ arise from new C=O groups.²⁵ Other small new bands also appear; the peak at 909 cm⁻¹ and the shoulder at approximately 1600–1650 cm⁻¹ arise from vinyl groups, and the broad, low-intensity band observed in Figure 2(B) at approximately 3400–3500 cm⁻¹ arises from new O—H groups formed during photo-oxidation.²⁵

It is well accepted that the photo-oxidation process in LDPE occurs via the formation of radical sites on the polymer chains followed by the addition of oxygen to these polymer radicals.^{24–26} The resulting peroxy radicals subsequently abstract hydrogen atoms

to form alkyl hydroperoxides and new polymer radicals. The alkyl hydroperoxides are photolabile and decay to form carbonyl and hydroxyl radicals that undergo further reactions leading to the final photo-oxidation products. Thus, the process of photo-oxidation occurs via a branching chain mechanism. The final products of the photo-oxidation of LDPE include carboxylic acids, aldehydes and esters, secondary alcohols, and double bonds.^{24–26}

The C—O bands in the spectrum are not very useful for identifying these photo-oxidation products, but the carbonyl bands have been widely used for this purpose. Two distinct broad peaks and several small but reproducible shoulders are clearly identifiable in the heavily overlapped carbonyl band shown in Figure 2(C). These features are summarized in Table I, which also contains the band assignments reported by Salvalaggio et al.⁹ As can be seen from the table, all of the major bands are identifiable in Figure 2(C), except that for ketone, which overlaps and is hidden by the strong neighboring bands for acids and esters.

When the LDPE/MMT and LDPE/OMMT blends were exposed to UV radiation, the new bands that appeared after photo-oxidation were similar to those found for virgin LDPE after 333 h of exposure. This is revealed in Figure 3 for the 800–1900-cm⁻¹ region of the spectrum through the difference spectra for virgin LDPE, LDPE/5 wt % MMT, and LDPE/5 wt % OMMT. A comparison of the carbonyl bands in the three spectra shows that the component bands observed for LDPE are present, but there is a change in the relative intensities of the two major peaks. For the same incident dose of UV radiation, the extent of LDPE oxidation was greater when MMT was present and was greatest for the LDPE/OMMT blend, but the differences in the carbonyl indices were small. For both the MMT and OMMT composites, the extent of photo-oxidation also increased slightly at higher clay concentrations, as revealed in Figure 4 for the LDPE/OMMT blends.

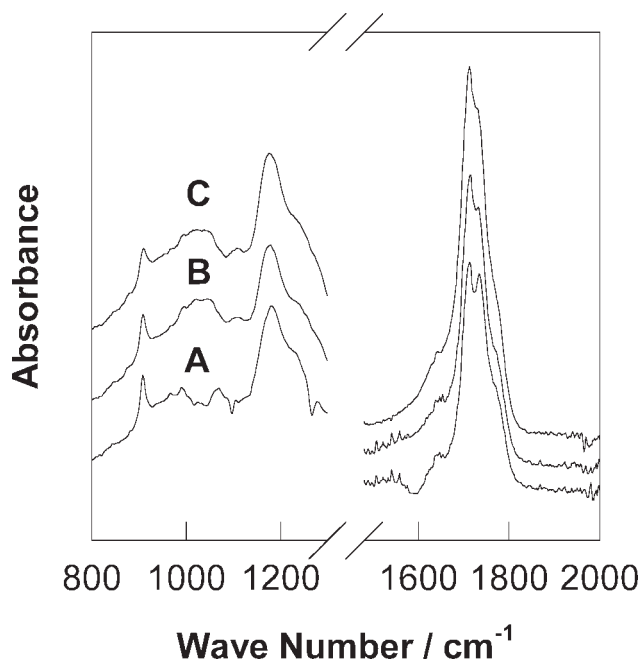


Figure 3 Before and after difference spectra showing new bands that appear after room-temperature UV photolysis: (A) LDPE, (B) LDPE/5 wt % MMT, and (C) LDPE/5 wt % OMMT.

Qin et al.¹⁹ previously observed an increase in the rate of photo-oxidation of LDPE in the bulk matrix when MMT was present and especially for an LDPE/OMMT blend. They also showed that the rate of photo-oxidation in the bulk is dependent on the concentration of the clay in the blend and on the nature of the clay surface.^{19,20} However, the extent of oxidation of the LDPE/OMMT blend over that for virgin LDPE (ca. 10 times greater) was much larger than that found here at the surfaces of exposed samples that had a similar clay content. Qin et al. concluded, from a comparison of their observed relative rates of photo-oxidation for LDPE/MMT and LDPE/OMMT blends, that acidic sites (ammonium ions), formed by thermal decomposition of the alkylammonium chloride modifier during processing, were principally responsible for this large enhancement of the LDPE/OMMT photo-oxidation rate.

A large increase in the photo-oxidation rate would not be anticipated if there were only an increase in the interlayer spacing of the clay particles for LDPE/OMMT with respect to LDPE/MMT, indicating partial intercalation of some LDPE chains but essentially no exfoliation of the clay. Hence, Qin et al.¹⁹ proposed that ammonium ions are involved in initiating the photo-oxidation of LDPE/OMMT composites. If this is the case, then the mixing conditions, including the time and temperature, for blending LDPE and OMMT will determine the extent of modifier decomposition that occurs and

hence the photo-oxidation characteristics for the blends.

Herein, only a small enhancement of the extent of surface photo-oxidation was observed for the OMMT composites over the MMT composites, and this is consistent with what might be expected if the clay layers were intercalated but not exfoliated by the LDPE. This is in stark contrast to the reported observations of Qin et al.¹⁹

In making comparisons between the observations made herein and those of Qin et al.,¹⁹ we must remember that the MMT clays are natural clays and that they were obtained from different suppliers. Thus, the impurities present in the MMT used by Qin et al. were probably different in nature and concentration from those used in this study. In addition, Qin et al. prepared the OMMT samples themselves using pure dioctadecyldimethylammonium chloride, whereas the OMMT samples used herein were commercial materials modified with a mixture of dialkyldimethylammonium chlorides. These differences could lead to different behaviors of the clays with respect to the extent of intercalation of LDPE chains and photo-oxidation.

The three spectra in Figure 3 reveal that there were changes in the distribution of photo-oxidation products when the MMT clays were present. The difference in the distribution of oxidation products is more clearly highlighted in Figure 5 for the LDPE/MMT blend. Figure 5(A) is the difference spectrum of Figure 3(A,C). To aid in the visual

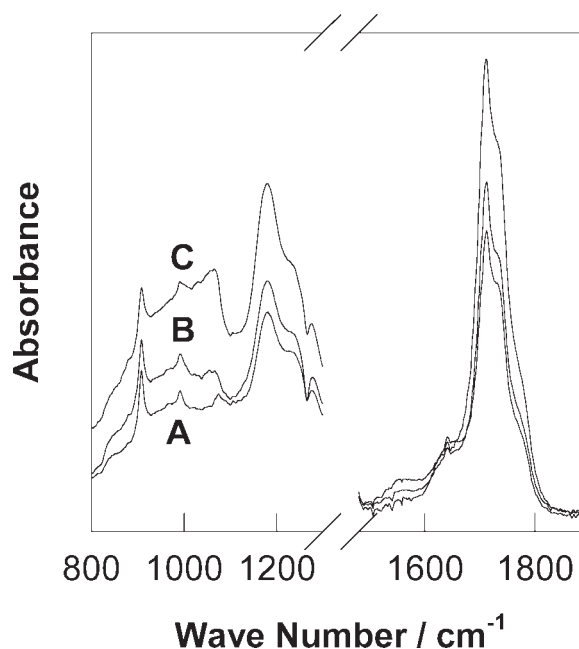


Figure 4 Before and after difference spectra showing new bands which appear after room-temperature UV photolysis of LDPE plus (A) 1 wt % OMMT, (B) 3 wt % OMMT and (C) 5 wt % OMMT.

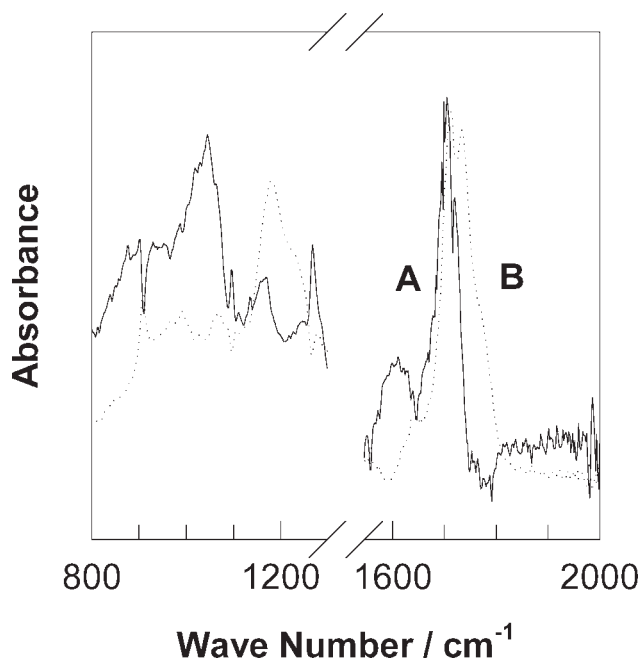


Figure 5 Difference spectra showing new bands that appear after room-temperature UV photolysis: (A) the difference between spectra of LDPE/5 wt % MMT and virgin LDPE after exposure and (B) the spectrum of the new bands that appear after the exposure of virgin LDPE. The intensity of the peak at 1715 cm^{-1} in spectrum B was attenuated to make the intensity the same as that of the corresponding peak in spectrum A.

identification of the difference in the distribution of the oxidation products, the spectrum for photo-oxidized virgin LDPE is also shown in Figure 5(B).

Figure 5(A) shows that when micrometer-sized MMT particles were present, with respect to virgin LDPE, there was either no change or perhaps a small decrease in the absorbance between 1750 and 1800 cm^{-1} . However, there was a large increase in the absorbance between 1650 and 1750 cm^{-1} . Corresponding changes can also be seen in the C—O band region of the spectrum. Thus, the band profiles in Figure 5(A) indicate that there was a change in the distribution of the oxidation products when MMT was present. Similar conclusions were drawn for the LDPE/OMMT blends. From Table I, these spectral differences indicate that the extent of formation of acid products increased with respect to that for esters and lactones.

The origin of the broad peak in the range of 1550 – 1650 cm^{-1} in Figure 5(A), which corresponds to higher absorbances in the tails of the carbonyl bands in this region of Figure 3(B), is not known with certainty. However, carboxylate ions absorb in this region of the spectrum. These ions could be formed by the reaction of some carboxylic acid oxidation products with species on the surface of the MMT particles. It is also possible that the peak could arise

through physical interactions of some of the carbonyl oxidation products with the clay surfaces. It is known²⁵ that interactions of carbonyl groups, such as hydrogen bonding, can modify significantly the absorption characteristics of these groups. Importantly, there are no bands due to MMT located in this region of the spectrum.²⁷ Therefore, the higher absorbances in the 1550 – 1650 cm^{-1} region must arise from new photo-oxidation products.

Another observation that can be drawn from the difference spectrum in Figure 5(A) is that the extent of formation of vinyl groups in LDPE was lower in the presence of MMT. This is clearly evident from the negatively oriented peaks at 1558 and 909 cm^{-1} in Figure 5(A) and the corresponding positive peaks for LDPE in Figure 5(B). A similar observation was made for the LDPE/OMMT blends.

Finally, in the LDPE/MMT and LDPE/OMMT blends, the broad OH peak at 3400 – 3500 cm^{-1} after photo-oxidation was more intense than in virgin LDPE and shifted toward lower wave numbers. This is demonstrated in Figure 6 for the LDPE/OMMT composite. It is most likely that the clay surfaces act as scavengers for the various polar OH species that are produced during photo-oxidation, including water.

Comparison with bulk

Although the principal focus of this study was the photo-oxidation of the surface of the polymer matrices, the oxidation of the bulk polymer was also

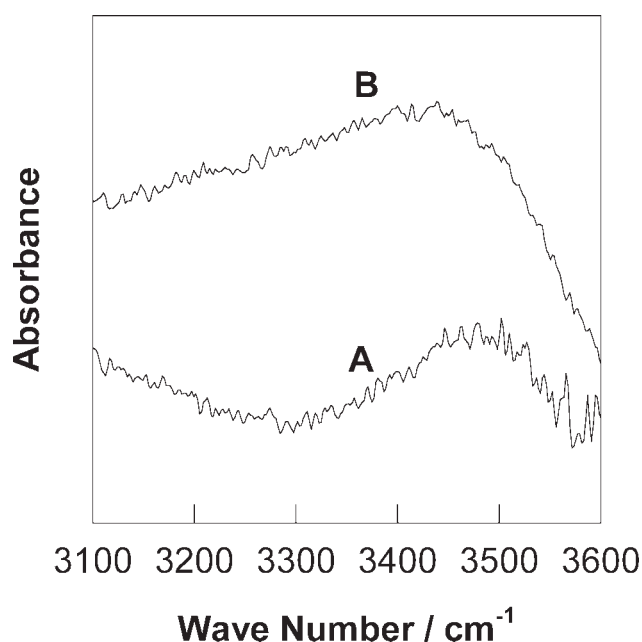


Figure 6 Before and after difference spectra showing new bands that appear after room-temperature UV photolysis: (A) LDPE and (B) LDPE/3 wt % OMMT.

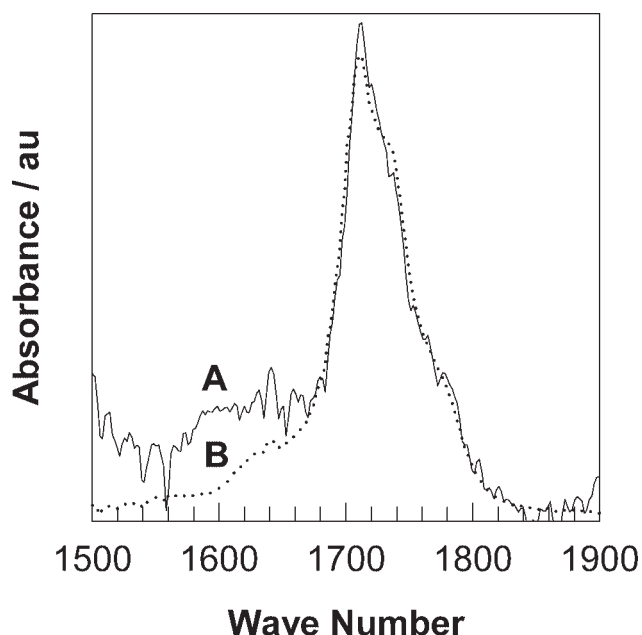


Figure 7 Spectra of LDPE/5 wt % OMMT samples showing new carbonyl bands that appear after room-temperature UV photolysis: (A) for the bulk of the matrix and (B) for the surface after attenuation of the spectrum by a factor of 6.5 times.

investigated. To examine the bulk, thin slices of the polymer matrices were cut at right angles to the sample surface, and the interiors of these slices were examined by ATR–FTIR analysis.

The new bands that appeared in the ATR spectra of the bulk of the LDPE, MMT/LDPE, and OMMT/LDPE samples following UV photolysis were the same as those that appeared in the ATR spectra of the surface of the corresponding samples. However, the band intensities were significantly lower for the bulk of the samples, as demonstrated in Figure 7 for the ATR spectrum for the carbonyl region of the bulk of an OMMT/LDPE composite containing 5 wt % OMMT. In this figure, the intensity of the spectrum of the OMMT/LDPE surface has been attenuated 6.5 times, and this is indicative of the difference between the photo-oxidation rates at the surface and in the bulk. Similar observations were made for the UV photolysis of virgin PE and the MMT/LDPE composites.

The good correspondence between the band profiles of the two ATR spectra shown in Figure 7 for the surface and bulk of the composite indicates that similar oxidation chemistry occurred at the surface and in the bulk, but the rate of oxidation was much higher at the surface. This conclusion is similar to that reported previously¹² for other nanocomposites of PE and results from the greater availability of oxygen and the higher photon flux at the surface of the samples. However, no very large differences were found between the rates of photo-oxidation for

the bulk of virgin LDPE and MMT/LDPE or OMMT/LDPE composites, as was also observed and reported previously for the surfaces of these composites.

Thus, the results of this study of the photo-oxidation of the bulk of the MMT/LLDPE and OMMT/LLDPE matrices are not in agreement with those of Qin and coworkers^{19,20} in this respect. Possible explanations for this disagreement have already been presented.

Mechanistic implications

Transition-metal ions, such as $\text{Fe}^{2+}/\text{Fe}^{3+}$, which are present as impurities in natural clays, are well known to promote the decomposition of hydroperoxides,²⁸ and thus they could account for an increase in the rate of photo-oxidation of LLDPE in the presence of MMT or OMMT. However, Gardette and coworkers^{29,30} found that transition-metal impurities do not play an important role in increasing the photo-oxidation rates of polyolefins in the presence of natural MMT clays. In addition, Qin et al.¹⁹ proposed that ammonium ions, formed by the decomposition of the alkyl ammonium salts during processing, play a pivotal role in the photo-oxidation of LDPE/OMMT composites by providing active oxidation sites at the surfaces of the clay sheets. Edwards et al.³¹ recently showed that some thermal degradation of the modifier can occur when OMMT is subjected to elevated temperatures (e.g., during processing). Finally, other workers^{20,21} have suggested that superoxide radicals can be formed on the clay surfaces during photo-oxidation and that these radicals enhance the rate of oxidation of the LDPE by the formation of hydroxyl radicals. It is likely that all of these possibilities play some part in enhancing the photo-oxidation rate in the clay blends, but they do not directly explain the changes that are observed in the concentration distribution of oxidation products in the presence of MMT.

Vinyl group formation is a characteristic of photo-oxidation of PE but not of thermal oxidation. Thus, it has been proposed that in PE, photoexcitation of in-chain ketones is responsible for the formation of unsaturated groups. The photoexcitation of the ketone is followed by LDPE chain scission through a Norrish type II mechanism with the formation of vinyl groups at the scissioned chain ends. However, Guillet and coworkers^{32,33} reported that the quantum yields for the Norrish type I and type II processes in PE are approximately the same. The Norrish type I process also involves chain scission, but as suggested by Costa et al.,²⁴ it can lead to the formation of chain-end carboxyl groups, but not vinyl groups. Hence, if a role of MMT in the composites is to modify the relative quantum yields for the Norrish

type I and II pathways, making the quantum yield for the former mechanism greater than that for the latter, it would be possible to account for both a lower yield of vinyl groups and a higher yield for carboxylic acids. However, if the role of MMT is simply to lower the quantum yields for both the Norrish type I and II mechanisms, by providing a route for de-excitation of ketone groups without chain scission, the yields of both vinyl groups and carboxyl groups would decrease.

It has also been proposed²⁵ that carboxylic acids are principally formed during the photolysis of PE by abstraction of the α -hydrogen at the site of an in-chain peroxide group. The resulting α -carbon radical then can undergo chain scission with the formation of an alkyl radical and the chain-end carboxyl group. The probability for this process to occur would be enhanced if the local radical concentration is increased by the presence of MMT in the LDPE composites. This would be the case if the role of MMT is to increase the hydroxyl and other radical concentrations in LDPE via superoxide formation at the clay surface.

Unfortunately, it is not possible to distinguish between the two possible explanations for an increase in the yield of carboxylic acid, for the same incident dose of UV light, when MMT is present in LDPE.

CONCLUSIONS

Photo-oxidation at the surface of LDPE/MMT and LDPE/OMMT composites has been investigated. In the former composites, there is no intercalation of the LDPE chains between the clay layers, whereas some intercalation of LDPE chains does occur for the LDPE/OMMT composites, but the clay layers are not exfoliated. Only a slight enhancement of the extent of surface photo-oxidation of LDPE was observed after an exposure time of 333 h in the presence of MMT and OMMT, with the extent of oxidation being higher for the OMMT composite. This is contrary to the previously reported order of magnitude increase in the photo-oxidation rate of bulk LDPE when OMMT was present.

Qin et al.¹⁹ attributed the significant increase in the photo-oxidation rate of LDPE in the presence of OMMT to acidic sites on the clay originating from the organic alkyl ammonium modifier. However, in this study of OMMT/LDPE, no large enhancement of the photo-oxidation rate was observed, and this indicated that the quaternary alkyl ammonium salt itself does not significantly enhance the oxidation rate under the conditions used herein. This could be explained by the method used to blend OMMT and LDPE, which was designed to minimize degradation of the organic modifier during processing.

It was observed that for the same exposure dose, the concentration distribution of photo-oxidation products was different when MMT or OMMT was present in the LDPE. More carboxylic acid products than ester products were formed, but the yield of unsaturated groups was reduced. These observations suggest that the MMT and OMMT particles must modify the pathways for the formation of these groups. One of their roles must be to reduce the quantum yield for the Norrish type II process for photodegradation of in-chain ketones, which leads to the formation of unsaturated products. A second role might be to increase the local radical concentration in the vicinity of an MMT particle and hence increase the probability for in-chain hydroperoxides to decay into carboxylic acids.

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References

1. Carlsson, D. J.; Wiles, D. M. *J Macromol Sci Rev Macromol Chem* 1976, 14, 65.
2. Ranby, B.; Rabek, J. F. *Photodegradation, Photo-Oxidation and Photostabilization of Polymers*; Wiley: New York, 1975.
3. George, G. A. *Dev Polym Degrad* 1981, 3, 173.
4. Pospíšil, J. Activity mechanisms of amines in polymer stabilization. In *Polymer Durability Degradation, Stabilization and Lifetime Prediction*; Clough, R. L., Billingham, N. C., Gillen, K. T., Eds.; *Advances in Chemistry Series*; ACS: Washington, DC, 1996, Vol.249, p.712.
5. (a) Allen, N. S. *Photochemistry* 2007, 36, 232; (b) Allen, N. S. *Photochemistry* 2004, 35, 206; (c) Allen, N. S. *Photochemistry* 2003, 34, 197; (d) Allen, N. S. *Photochemistry* 2002, 33, 339; (e) Allen, N. S. *Photochemistry* 2001, 32, 343.
6. Mowery, D. M.; Assink, R. A.; Derzon, D. K.; Klamo, S. B.; Bernstein, R.; Clough, R. L. *Radiat Phys Chem* 2007, 76, 864.
7. Adam, T. M.; Celina, M.; Assink, R. A.; Clough, R. L. *Radiat Phys Chem* 2001, 60, 121.
8. Gulmine, J. V.; Akcelrud, L. *Polym Test* 2006, 25, 932.
9. Salvalaggio, M.; Bagatin, R.; Fornaroli, M.; Fanutti, S.; Pulmary, S.; Battistel, E. *Polym Degrad Stab* 2006, 91, 2775.
10. Zhao, C.; Qin, H.; Gong, F.; Feng, M.; Zhang, S.; Yang, M. *Polym Degrad Stab* 2005, 87, 183.
11. Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1179.
12. Yang, R.; Li, Y.; Yu, J. *Polym Degrad Stab* 2005, 88, 168.
13. Allen, N. S.; Edge, M.; Ortega, A.; Sandoval, G.; Liauw, C. M.; Verran, J.; Stratton, J.; McIntyre, R. B. *Polym Degrad Stab* 2004, 85, 927.
14. Zan, L.; Fa, W.; Wang, S. *Environ Sci Technol* 2006, 40, 1681.
15. Pinnavaia, J.; Beal, G. W. *Polymer-Clay Nanocomposites*; Wiley: New York, 2000.
16. Awad, W. H.; Gilman, J. W.; Nyden, M.; Harris, R. H.; Sutto, T. E.; Callahan, J.; Trulove, P. C.; Delong, H. C.; Fox, D. M. *Thermochim Acta* 2004, 409, 3.
17. Zhao, C.; Feng, M.; Gong, F.; Qin, H.; Yang, M. *J Appl Polym Sci* 2004, 93, 676.
18. Scoconi, M.; Cimmino, S.; Kaci, M. *Polymer* 2000, 41, 7969.
19. Qin, H.; Zhao, C.; Zhang, S.; Chen, G.; Yang, M. *Polym Degrad Stab* 2003, 81, 497.

20. Qin, H.; Zhang, Z.; Feng, M.; Gong, F.; Zhang, S.; Yang, M. *J Polym Sci Part B: Polym Phys* 2003, 42, 3006.
21. Gournis, D.; Karakassides, M. A.; Petridis, D. *Phys Chem Miner* 2002, 29, 155.
22. Tidjani, A.; Wilkie, C. A. *Polym Degrad Stab* 2001, 74, 33.
23. Huang, W.; Han, C. D. *Macromolecules* 2006, 39, 257.
24. Costa, L.; Luda, M. P.; Trossarelli, L. *Polym Degrad Stab* 1997, 58, 41.
25. Lacoste, J.; Carlsson, D. J. *J Polym Sci Part A: Polym Chem* 1992, 30, 493.
26. Tidjani, A. *Polym Degrad Stab* 2000, 68, 465.
27. Cervantes-Uc, J. M.; Cauich-Rodriguez, J. V.; Vazquez-Torres, H.; Garfias-Mesias, L. F.; Paul, D. R. *Thermochim Acta* 2007, 457, 92.
28. Oyama, N.; Anson, F. C. *J Electroanal Chem* 1986, 199, 467.
29. Morlat-Therias, S.; Mailhot, B.; Gardette, J.-L.; Da Silva, C.; Haidar, B.; Vidal, A. *Polym Degrad Stab* 2005, 90, 78.
30. Morlat-Therias, S.; Fanton, E.; Tomer, N. S.; Rana, S.; Singh, R. P.; Gardette, J.-L. *Polym Degrad Stab* 2006, 91, 3033.
31. Edwards, G.; Halley, P.; Kerven, G.; Martin, D. *Thermochim Acta* 2005, 429, 13.
32. Li, S. K. L.; Guillet, J. E. *J Polym Sci* 1980, 18, 2221.
33. Hartley, G. H.; Guillet, J. E. *Macromolecules* 1968, 1, 165.