

## Additives for ultraviolet-induced oxidative degradation of low-density polyethylene

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**ABSTRACT:** Polyethylene (PE) is one of the most widely produced and widely used plastics in the world. Saturated hydrocarbons cannot absorb the energy of the light reaching earth, so the degradation process is rather slow; this, in return, causes disposal problems. On the other hand, it was observed that in the presence of oxygen and impurities in the polymer matrix, the degradation could be reduced to shorter time intervals. In this study, vanadium(III) acetyl acetonate (VAc), serpentine (SE), and Cloisite 30B (CL) were used as additives, both together and alone, and we followed the photodegradation of PE. The amount of VAc was kept constant at 0.2 wt %, whereas the amounts of SE and CL were varied between 1 and 4 wt %. The samples were irradiated by UV light for up to 500 h. Mechanical and spectroscopic measurements were carried out during certain time intervals to monitor the degradation. VAc containing PE showed the fastest degradation. The elongation at break values of these samples were reduced to half of the initial value of elongation at break within five days. Combinations of the CL and SE additives were also proven to accelerate the degradation of PE; this was followed by an increase in the carbonyl index, which was observed to be at least 10 times greater than that of pure PE. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43354.

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### INTRODUCTION

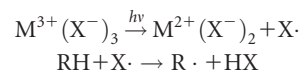
The degradation behavior of polyethylene (PE) has been studied from various perspectives, especially concerns on environmental problems. It is well known that in the absence of oxygen, PE with no additive is a relatively stable material. Degradation via chain scission and hydrogen abstraction can occur after it is exposed to short-wavelength UV light for a very long time.<sup>1</sup>

In many studies, it has been reported that after they are exposed to UV light, oxygen uptake is observed in these samples as well as the formation of many groups, such as carbonyl, hydroxyl, and vinyl groups, with evolution of acetone, acetaldehyde, water, carbon dioxide, and so on.<sup>2</sup> When the photons interact with the polymer chains, numerous complicated reactions start,<sup>3,4</sup> and the formed macroradicals are able to combine with oxygen by an addition reaction to form the peroxy radicals of polymers.<sup>4</sup> The rate of oxygen absorption is directly proportional to the surface area of the polymer, where it is inversely proportional to the thickness of the polymer film because of problems in oxygen diffusivity.<sup>5,6</sup>

It has been estimated that some transition metals that exist in the polymer matrix by coincidence or on purpose act as degradation

accelerators when the polymers are exposed to UV light, whereas some others show just the opposite effect. For example, nickel and cobalt complexes cause the polymer to become more stable to UV light, whereas ferric and copper complexes favor photodegradation. The excited ions of the latter metals behave as catalytic activators, and they cause radical degradation reactions to occur.<sup>7</sup> It has been stated that in the presence of metal complexes, the initiation of photoredox reactions via UV light can follow two different paths. These are as follows<sup>5,8</sup>:

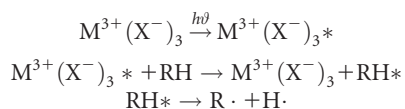
1. The transition-metal complex decomposes with the absorption of the energy of UV light. In our case, M is vanadium, X is acetyl acetonate, and RH stands for polymer chains:



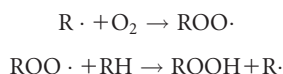
2. After excitation by UV, the energy of the complex may be transferred to a molecule in the polymer chain, so the following reactions occur:

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3. After degradation is initiated with the help of both transition-metal complexes and UV light, oxygen takes place in the following series of reactions<sup>9</sup>:



Then, the degradation goes on with the produced active radical via the formation of carbonyl compounds; this leads to an increase in the carbonyl index (CI).

There have been numerous studies on the degradation of polymers, but the effect of nanocomposites on these polymers, especially PE, has not been studied in detail yet. Superficial works on the degradability of polymer nanocomposites were carried out with the help of UV radiation in a biotic environment.<sup>10</sup> Finally, Huailiet *al.*<sup>11</sup> revealed that polymer nanocomposites showed higher degradability than pure samples. It is also known that composites of polymers with nanosized fillers, such as organomodified montmorillonite or bentonite, can improve the thermal and mechanical properties of a polymer significantly, even at very low concentrations, because of the interaction of fillers at the nanolevel scale with the polymer matrix.<sup>12</sup>

In this study, we investigated the effects of three different additives, vanadium(III) acetyl acetonate (VAc), nanoclay, and serpentine (SE), on the UV-induced oxidative degradation of PE; this was followed by spectroscopic and mechanical measurements. The aim of this study was to obtain PE films that could degrade faster in nature when exposed to UV light. The degradation of PE is a competition between crosslinking and chain scission. The physical properties of the polymer sample vary according to this competition.<sup>1</sup> The mechanical properties are very important properties of polymers that must be followed definitely because the use of polymers mostly depend on their mechanical properties. Spectroscopic techniques are also used for this purpose to follow the formation of vinyl, carbonyl, and hydroxyl groups during degradation. So far, the thermal behavior and properties were followed to determine the crystalline melting temperature and the heat of fusion.<sup>5</sup>

## EXPERIMENTAL

### Materials

Low-density polyethylene (LDPE) supplied from Exxon Mobil (Belgium) was used in this study. Its density was 0.925 g/cm<sup>3</sup>, and the melt flow index of the polymer was 2 g/10 min. VAc, SE, and Cloisite 30B (CL) were used to follow the photodegradation of PE, both together and alone. VAc was supplied by Sigma-Aldrich. The compound was a fine, powdered solid at room temperature, and its melting point was 181–184°C. Its color was dark brown, and its molecular weight was 348.27 g/mol. The supplier of CL<sup>13</sup> was Southern Clay Products. The physical state of the compound at room temperature was solid. It was a white powder with a typical dry particle size of 2 μm

**Table I.** Compositions of the Samples

Sample	VAc (%)	CL (%)	SE (%)
LDPE	—	—	—
A	0.2	—	—
B	—	2	—
C	—	—	2
D	0.2	2	—
E	0.2	—	2
F	0.2	1	3
G	0.2	2	2
H	0.2	3	1

when its concentration was less than 10 vol %. SE is a metamorphic rock that is formed in nature with a shiny appearance and slippery feel with a variety of colors. It is actually hydrated magnesium silicate with a similar structure to clays, having octahedral and tetrahedral sheets. The rock was ground in a ball mill into fine particles with an average size of 1.19 μm. Further information about SE was given in detail by Tan and Tinçer.<sup>14</sup>

### Compounding

The amount of VAc was kept constant at 0.2 wt %, whereas the amounts of SE and CL used were between 1 and 4 wt %. All of the compositions were prepared in a Brabender plasticorder torque rheometer at a constant temperature at 180°C and mixed at 45 rpm for 10 min. The samples were then compression-molded with an ATS FAAR pneumo-hydraulic press at 190°C for 5 min. The compression molds were quenched in tap water for less than 2 min to cool them to room temperature. The final thicknesses of the films were 220 ± 40 μm (Table I).

### UV Exposure Test and Characterization

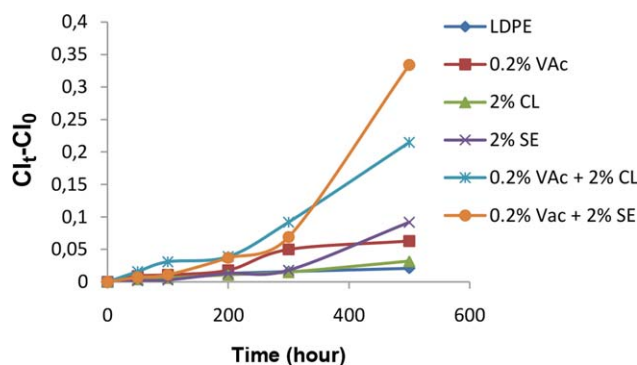
UV irradiation lasted for 500 h at 290 nm at a rate of 0.025 W/cm<sup>2</sup>. UV exposure was followed by the removal of the samples after 50, 100, 200, 300, and 500 h of irradiation. UV lamps, a product of Sylvania Mercury Lamp (medium mercury pressure, 100 W), were placed 25 cm away from both sides of the samples.

UV-induced oxidative degradation was followed by IR spectroscopy of the regions of the carbonyl band at 1730 cm<sup>-1</sup> and the crystalline CH<sub>2</sub> stretching band at 722 cm<sup>-1</sup>. IR spectra of samples were obtained with a Fourier transform infrared spectrometer (iS10 Thermo Scientific Smart Omni-Transmission, Nicolet).

The UV-exposed pristine PE and compounded films were then analyzed by Fourier transform infrared spectroscopy. The increase in the carbonyl band absorption around 1715–1730 cm<sup>-1</sup> was due to UV-enhanced oxidative degradation, and it was used to follow the degree of oxidative degradation.<sup>15</sup> So, the degradation was followed by the ratio of absorptions at 1715 and 722 cm<sup>-1</sup> ( $A_{1715\text{cm}^{-1}}/A_{722\text{cm}^{-1}}$ ), where this ratio was defined as CI<sup>16</sup>:

$$CI = \frac{A_{1730\text{cm}^{-1}}}{A_{722\text{cm}^{-1}}}$$

In this article, the results are expressed as the difference between the CI values at time *t* and 0 (CI<sub>*t*</sub> - CI<sub>0</sub>), respectively. Dogbone-shaped samples were exposed to UV light and mechanically tested before and after. The thickness of each sample was



**Figure 1.** Variation of the CI difference of various samples (0.2% VAc, 2% CL, 2% SE, 0.2% VAc + 2% SE, and 0.2% VAc + 2% CL) and pure LDPE with respect to time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

measured with a micrometer before we carried out the mechanical tests. A LLYOD LR5K mechanical tester was used for mechanical testing. The tests were carried out at room temperature, and the speed of the test was 10 cm/min.

A Scinco N-650 differential scanning calorimeter was used for differential scanning calorimetry (DSC) measurements, and nearly, 15 mg of each sample was analyzed. The temperature range was from 25 to 200°C, and a heating rate of 20°C/min was used.

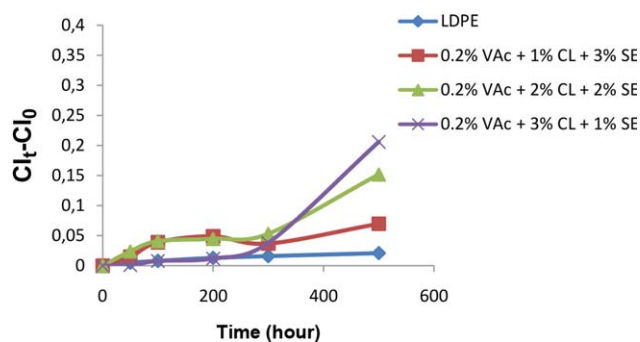
## RESULTS AND DISCUSSION

### CI Measurements

Figure 1 shows the change in CI of both the pristine PE and PE with a filled matrix as a function of the irradiation time. Transition-metal complexes are known to be very effective in photodegradation.<sup>5</sup> Fe, Co, Ni, and some metal complexes have been studied to enhance oxidative degradation and have been shown to be very effective.<sup>17</sup> The effect of vanadium metal on the degradation of PE has not been examined before. In this study, we filled the polymer matrix with 0.2 wt % VAc and found it to result in a degradation that was faster than that of unfilled PE (Figure 1).

Clay additives are a new class of materials that promote the degradation of the polymer to be higher than that of the pristine polymer, even when used in very small amounts up to 5 wt %.<sup>16</sup> First, 2 wt % of both additives was compounded in addition to VAc, as shown in Figure 1. A very significant increase in the degradation rate was obtained. Although the mechanism has not been clarified yet, this effect was due to the capture of oxygen in the polymer matrix. This effect was long enough to shorten the induction period of UV-induced oxidative degradation and also the exchange of alkyl ammonium cations with hydrogen in both the backbone and side chains, but no change was observed in the kinetics of the degradation.<sup>9,10,18,19</sup>

Therias *et al.*<sup>12</sup> stated that a higher amount of clay additive led to a faster increase in CI when only one clay product was used. A combination of two additives was tested both in the presence of a transition-metal complex and alone. In Figure 2, CL and SE additives with 0.2 wt % VAc are shown. The samples with CL and SE showed faster degradations than pure PE, as shown in Figure 1, in terms of CI, but combined VAc (which was kept constant at 0.2



**Figure 2.** Variation of the CI difference of various samples (0.2% VAc + 1% CL + 3% SE, 0.2% VAc + 2% CL + 2% SE, and 0.2% VAc + 3% CL + 1% SE) and pure LDPE with respect to time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

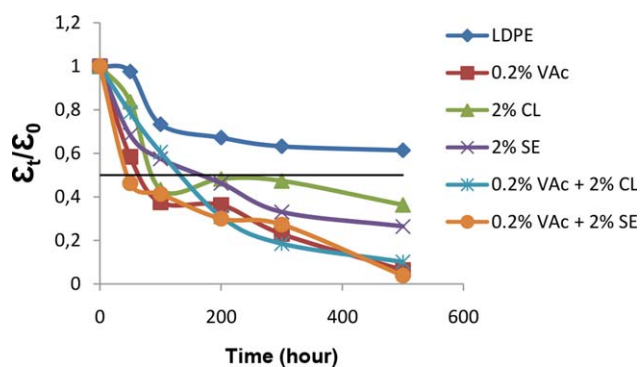
wt %), CL, and SE were found to show a higher oxidative degradation compared to the samples shown in Figure 1. Also, increases in the amounts of CL and SE did not lead to faster degradation; this may have been caused by unequal interactions of additives with each other (see Figure 2).

### Tensile Test Measurements

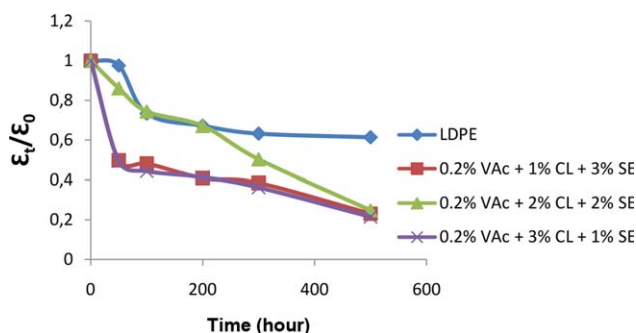
The percentage elongation at break of the degraded samples is a parameter affected the most by the variations in the structure and molecular level.<sup>18</sup> So, the decrease in the elongation at break during oxidative degradation was followed. The results are shown as the residual percentage elongation at break, which is the ratio of percentage strain at break at time  $t$  to time 0 that followed degradation. The results were found to be consistent with the CI change in the samples.

In Figure 3, it is obvious that the pure PE showed the slowest loss of strain, whereas the others, containing VAc, SE, and CL, were faster and almost the same. In general, it is accepted that when the value of the residual elongation at break decreases below 0.5 (a parallel line shown in Figures 3 and 4), the polymer is considered to be irreversibly degraded (Figure 3).

In Figure 4, the effects of the clay additive and metamorphic rock (up to 4 wt % total) in the presence of a transition-metal



**Figure 3.** Variation of the residual percentage elongation at break values ( $\epsilon_t/\epsilon_0$  is the ratio of elongation at break at time “t” to time “0”) of various samples (0.2% VAc, 2% CL, 2% SE, 0.2% VAc + 2% SE, and 0.2% VAc + 2% CL) and pure LDPE with respect to time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 4.** Variation of the residual percentage elongation at break values ( $\epsilon_t/\epsilon_0$  is the ratio of elongation at break at time “t” to time “0”) of various samples (0.2% VAc + 1% CL + 3% SE, 0.2% VAc + 2% CL + 2% SE, and 0.2% VAc + 3% CL + 1% SE) and pure LDPE with respect to time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

complex is shown. Pristine PE retained its mechanical strength in terms of elongation even after 500 h of irradiation time, whereas the filled PE matrix lost its mechanical properties after 100 h of UV exposure (Figure 4).

It is well known that there are two initial processes in the degradation of polymers, namely, chain scission and crosslinking.<sup>20</sup> These processes are considered to be competitive during degradation; this may be the reason for the initial slower loss of the strain profile of 0.2% VAc + 2% CL + 2% SE. Because chain scission is the continuous breakage of bonds in the polymer backbone because of light, heat, or molecular oxygen, decreases in the elongation at break and the polymer's average molecular weight occurred. In contrast to chain scission, in case of crosslinking, there was increase in the elongation at break of the polymer because of the formed crosslinking points, which could handle the applied stress.<sup>3,21</sup>

### Thermal Properties

DSC analysis was carried out to monitor the variations in the thermal properties in the samples studied, that is, the melting temperature (Table II). After we followed the DSC thermograms, we discovered that there was no significant change in the thermal properties of the samples. In all of the samples, the

**Table II.** Melting Point, Area under the Melting Peak, and Percent Crystallinity Values of the Samples

Sample	Melting point (°C)	Area under the peak (J/g)	% Crystallinity
LDPE	114.9	99.6	33.4
A	114.2	99.0	34.0
B	116.3	81.0	27.6
C	115.9	89.4	30.4
D	114.7	101.2	34.5
E	116.2	87.5	29.8
F	117.4	88.8	30.2
G	114.4	104.0	35.4
H	114.1	114.7	39.1

general trend of the melting temperature was in the range of a  $\pm 2^\circ\text{C}$  temperature change; this could not be accepted as an important change. In addition to these, the areas under the melting peaks of PE were almost similar and had almost the same energy of melting. However, the percentage crystallinity varied around 30%, and the sample H had the highest variation of 39%. In fact, the increased addition of CL enhanced the crystallization from 30 to 39% of the samples from F to G and H as well as sample D.

### CONCLUSIONS

The CI measurements showed that the addition of all additives either alone or in combination with each other led to an oxidative degradation that was faster than that of pristine PE. Because of oxygen capture in the matrix and hydrogen abstraction from the polymer chain,<sup>18,19</sup> higher amounts of CL and SE led to faster increases in CI. The combination of these two additives led to unequal interactions; however, the compositions showed faster degradations. The residual percentage elongation at break values were consistent with the variations of CI. Therefore, one of either variable could be used to follow the degradation. The degradation apparently did not affect the thermal properties. In conclusion, the used additives caused a faster photoinduced UV degradation of PE, and indeed, the action of VAc on the oxidative degradation was very effective when this chemical was added to PE.

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