Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polymer Degradation and Stability 86 (2004) 1–9
Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

Surface chemistry changes of weathered HDPE/wood-flour composites studied by XPS and FTIR spectroscopy☆

Nicole M. Stark[a,*], Laurent M. Matuana[b]

[a]U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53726-2398, United States
[b]Department of Forestry, Michigan State University, East Lansing, MI 48824-1222, United States

Received 7 August 2003; received in revised form 3 November 2003; accepted 4 November 2003

Abstract

The use of wood-derived fillers by the thermoplastic industry has been growing, fueled in part by the use of wood-fiber–thermoplastic composites by the construction industry. As a result, the durability of wood-fiber–thermoplastic composites after ultraviolet exposure has become a concern. Samples of 100% high-density polyethylene (HDPE) and HDPE filled with 50% wood-flour (WF) were weathered in a xenon arc-type accelerated weathering apparatus for 2000 h. Changes in surface chemistry were studied using spectroscopic techniques. X-ray photoelectron spectroscopy (XPS) was used to verify the occurrence of surface oxidation. Fourier transform infrared (FTIR) spectroscopy was used to monitor the development of degradation products, such as carbonyl groups and vinyl groups, and to determine changes in HDPE crystallinity. The results indicate that surface oxidation occurred immediately after exposure for both the neat HDPE and WF/HDPE composites; the surface of the WF/HDPE composites was oxidized to a greater extent than that of the neat HDPE. This suggests that the addition of WF to the HDPE matrix results in more weather-related damage. The results also show that while neat HDPE may undergo crosslinking in the initial stages of accelerated weathering, WF may physically hinder the ability of HDPE to crosslink, resulting in the potential for HDPE chain scission to dominate in the initial weathering stage.

Keywords: Polyethylene (PE); Ultraviolet; Weathering; Photodegradation; Composites; Wood-flour; FTIR; XPS

1. Introduction

Although inorganic fillers currently dominate the thermoplastic industry, the use of wood-derived fillers is growing. Growth has been fueled in part by the use of wood-fiber–thermoplastic composites (WTPCs) in the non-structural (siding, roofing, etc.) or semi-structural (decking) construction market. This is apparent as WTPCs make dramatic inroads into the residential decking market. In 2000, WTPC made up 8% of the decking market. This percentage is projected to increase to 19% by 2005 [1]. Other residential construction applications, such as windows, siding, and roof tiles, are quickly entering the market or are under development.

The use of WTPC by the construction industry has resulted in concern about the durability of these products when exposed to outdoor environments. Of particular concern is the durability of WTPC after ultraviolet (UV) exposure. Scientists have begun to investigate the UV durability of WTPC [2–7]. Work with wood-flour-filled polyolefin composites has focused mainly on changes in appearance and mechanical properties [2–5]. Little work has provided insight into

☆ The Forest Products Laboratory is maintained in cooperation with the University of Wisconsin. This article was written and prepared by U.S. Government employees on official time and is therefore in the public domain and not subject to copyright. The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

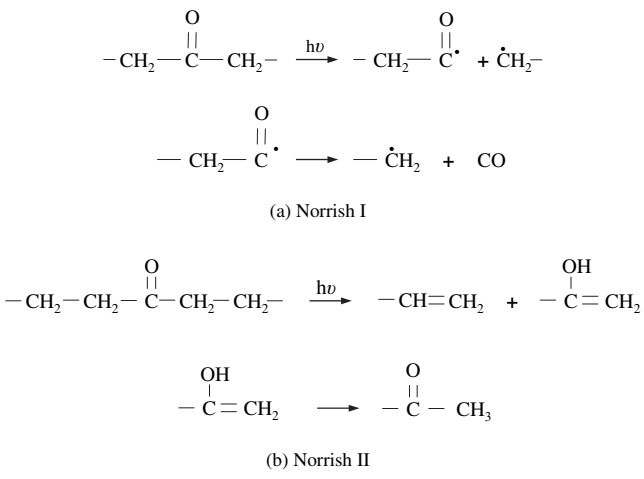
* Corresponding author. Tel.: +1-608-231-9392; fax: +1-608-231-9582.
E-mail address: nstark@fs.fed.us (N.M. Stark).

0141-3910/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2003.11.002

the surface chemistry changes of wood-flour-filled polyolefin composites after UV exposure.

The photodegradation of polyolefins is mainly caused by the introduction of chromophores, such as catalyst residues, hydroperoxide groups, carbonyl groups, and double bonds, during polymer manufacture [8]. Carbonyl groups are postulated to be the main light-absorbing species responsible for the photochemical-induced degradation reactions of UV-exposed polymers [9]. The degradation reactions proceed from carbonyl group precursors according to Norrish type I and II reactions [9,10]. If degradation of the carbonyl groups proceeds according to the Norrish I reaction, the resultant free radicals can attack the polyolefin (Fig. 1a), which may lead to termination via crosslinking or chain scission [10]. If the degradation proceeds according to the Norrish II reaction, carbonyl groups and terminal vinyl groups are produced (Fig. 1b) and chain scission occurs. In addition, the carbonyl group formed is capable of further degradation. During the course of accelerated polyethylene photodegradation, the two mechanisms, chain scission and crosslinking, compete [9–11]. Chain scission lowers molecular weight, whereas crosslinking raises molecular weight by increasing the bonding between polymer chains.

Ketones, carboxylic acids, and vinyl groups are the three major functional groups that accumulate with the photodegradation of polyethylene [10]. The formation of carbonyl groups and vinyl groups can be studied as a direct indication of main chain scission [11,12]. The weathering of polyethylene results in an increase in crystallinity [13], which also indicates that chain scission has occurred. The shorter chains produced during chain scission are more mobile and are able to crystallize more readily, which increases crystallization and associated embrittlement [9,10]. In contrast, crosslinking does not affect polymer crystallinity.



(a) Norrish I

(b) Norrish II

Fig. 1. Norrish I and Norrish II degradation mechanisms: (a) Norrish I degradation can lead to chain scission or crosslinking; (b) Norrish II degradation leads to chain scission.

Polyethylene is a semi-crystalline polymer. The packing of the crystalline phase is much tighter than that of the amorphous phase and is impermeable to oxygen [8]. The degradation reactions therefore occur predominantly in the amorphous region and are controlled by the diffusion of oxygen in this region [10]. While chain scission occurs in the amorphous phase of the polymer, UV-induced crosslinking occurs in imperfect crystalline regions [14].

Fourier transform infrared (FTIR) spectroscopy has been recently used to study changes in the surface chemistry of polyethylene after weathering. FTIR spectroscopy has been used to monitor carbonyl group formation [9,11,12,14–17], vinyl group formation [9,11,14], and changes in crystallinity [13,18–21] of weathered polyethylene. X-ray photoelectron spectroscopy (XPS) has also been found useful to study the concentration of carbon to oxygen atoms of aged polyethylene [22,23] and wood-flour-filled polyvinyl chloride [7].

We used XPS and FTIR spectroscopy to monitor the changes in surface chemistry of high-density polyethylene (HDPE) and wood-flour/HDPE (WF/HDPE) composites after accelerated weathering. We also used FTIR spectroscopy to monitor changes in crystallinity. The comparison of surface chemistry changes of neat HDPE samples to that of WF/HDPE composites provides important information on how the addition of wood-flour to HDPE changes the mechanisms of UV degradation.

2. Methods

2.1. Materials

The materials used in this study were wood-flour (WF) and HDPE. The WF, a 40-mesh ponderosa pine, was supplied by American Wood Fibers (Schofield, Wisconsin). The HDPE, virgin material with a melt index of 0.72 g/10 min and density of 0.963 g/cm^3 (60 lb/ft^3), was supplied by Solvay Polymers, Inc. (Fortiflex A60-70-162, Houston, Texas).

2.2. Processing

The HDPE samples were molded into flexural bar test samples using a 33 ton (30 metric ton) Cincinnati Milacron (Batavia, Ohio) injection molder. The mold nozzle temperature was 204 °C (400 °F) and the injection pressure reached a peak of 12.4 MPa (1800 lb/inch^2). The dimensions of the American Society for Testing and Materials (ASTM) mold cavity used for the flexural samples were 120×3×12 mm (4.7×0.1×0.5 inches) [24].

The WF was dried for 24 h at 105 °C (221 °F) and then dry-blended with HDPE at 50% by weight.

Compounding was accomplished using a 32-mm (1.2 inches) Davis Standard (Pawcatuck, Connecticut) twin-screw extruder to produce homogeneous WF/HDPE composite pellets. The melt temperature at the die was 200 °C (392 °F) and the melt pressure was 2.96 MPa (430 lb/inch^2). The pellets were dried at 105 °C (221 °F) for at least 24 h prior to injection molding into flexural bar test samples. The injection molding conditions were the same as those for the manufacture of neat HDPE.

3. Testing and analysis

3.1. Weathering

Both the neat HDPE and WF/HDPE composite samples were placed in a xenon arc-type light-exposure apparatus operated according to ASTM D2565 [25]. Samples were mounted in four rows on a drum that rotated around the xenon arc lamp at 1 rpm. The samples were repositioned on the drum periodically to ensure that all were exposed to the same irradiance. The exposure cycle consisted of 108 min of light and 12 min of simultaneous water spray and light [25]. Samples were removed for analysis after 250, 500, 1000, and 2000 h of exposure.

3.2. X-ray photoelectron spectroscopy

X-ray photoelectron spectra were collected using a Leybold MAX-200 X-ray photoelectron spectrometer (Leybold, Cologne, Germany). Three types of spectrum were collected: a survey spectrum, a low-resolution spectrum from 0 to 1100 eV binding energy, and a high-resolution spectrum of the C_{1s} region from 280 to 300 eV. The samples were analyzed at a take-off angle of 90°. The ratio of elemental oxygen to carbon (O/C) was determined from the low-resolution spectra. To determine the types of oxygen–carbon bonds present, chemical bond analysis of carbon was accomplished by curve fitting the C_{1s} peak from the high-resolution spectra and deconvoluting it into four subpeaks corresponding to an unoxidized carbon, C1, and various oxidized carbons, C2, C3, and C4 using ESCA Tools (version 4.2, Mountain View, California). An oxidized to unoxidized carbon ratio ($C_{ox/unox}$) was calculated (Eq. (1)) [7].

$$C_{ox/unox} = \frac{C_{oxidized}}{C_{unoxidized}} = \frac{C2+C3+C4}{C1} \quad (1)$$

3.3. Fourier transform infrared spectroscopy

FTIR spectroscopy was conducted on a Mattson Genesis II spectrophotometer (Mattson Instruments, Madison, Wisconsin) to provide detailed information of the functional groups present at the surface of the samples. Scans were run at a resolution of 4 cm^{-1}. Each sample recorded consisted of 100 scans recorded in absorbance units from 4000 to 700 cm^{-1}. The spectra were obtained using attenuated total reflectance (ATR). The surfaces of the samples analyzed were in contact with a ZnSe crystal with a 45° angle of incidence. The peaks were analyzed without smoothening the data. Net peak heights were determined by subtracting the height of the baseline immediately before the peak from the total peak height. Both carbonyl index and vinyl index were calculated using the following equations:

$$\text{Carbonyl index} = \frac{I_{1715}}{I_{2912}}(100) \quad (2)$$

$$\text{Vinyl index} = \frac{I_{908}}{I_{2912}}(100) \quad (3)$$

where I represents the peak intensity. The peak intensities were normalized using the peak at 2912 cm^{-1}, which corresponds to alkane CH stretching vibrations of the methylene groups. This peak was chosen as a reference peak because it changed the least during weathering.

Crystallinity of HDPE was determined using the method described by Zerbi et al. [18]. The doublet peaks observed at 1474–1464 cm^{-1} and 730–720 cm^{-1} correspond to polyethylene crystalline content (1474 and 730 cm^{-1}) and amorphous content (1464 and 720 cm^{-1}). The percentage of the crystalline content, X, can be calculated using Eq. (4):

$$X = 100 - \frac{(1 - I_a/I_b)/1.233}{1 + I_a/I_b}(100) \quad (4)$$

where I_a and I_b can be determined from the bands at either 1474 and 1464 cm^{-1} or 730 and 720 cm^{-1}, respectively [18]. Colom et al. [19] examined the crystallinity changes of aspen fiber filled HDPE composites using the FTIR method and differential scanning calorimetry (DSC). They determined that the bands at 730 and 720 cm^{-1} were the most appropriate to study, because a peak from cellulose fibers at 1430 cm^{-1} interferes with the 1474 and 1464 cm^{-1} peaks [19]. Kaci et al. [13] studied the crystallinity changes of low-density polyethylene films after weathering using FTIR and DSC. They concluded that using the bands at 1474 and 1464 cm^{-1} to determine crystallinity leads to unreliable results because these bands are asymmetric [13]. In the work reported here, crystallinity was calculated using the doublet peaks at 730 and 720 cm^{-1}.

3.4. Statistics

Statistical analysis was conducted on the FTIR data to determine the significance of the changes in carbonyl

index, vinyl index, and crystallinity after weathering. Five replicate samples were analyzed, and average and standard deviation were calculated to represent the data. In addition, significant changes between the exposed and unexposed samples were determined by conducting a one-tail *t*-test assuming equal variance at a level of $\alpha = 0.05$.

4. Results and discussion

4.1. X-ray photoelectron spectroscopy

A low-resolution scan was run to determine the percentages of the elements present at the surface. The relative elemental compositions of the samples are presented in Table 1. The main elements detected using XPS were oxygen and carbon. Small amounts of sodium, nitrogen, and silicon were also present, possibly arising from the additives introduced during polymer manufacturing or from contamination during sample preparation. An O/C atomic ratio was calculated as an initial indication of surface oxidation. The O/C ratio was slightly higher for the unexposed WF/HDPE samples than for unexposed HDPE samples, primarily as a result of the hydroxyl groups and some carbonyl groups in the wood-flour. An increase in the concentration of oxygen atoms occurred after weathering. As a result, after 2000 h of weathering the O/C ratio increased for both the neat HDPE and WF/HDPE samples, indicating that the surface of the material had oxidized.

A high-resolution scan was conducted on the C_{1s} region for each unexposed sample and for each sample weathered for 2000 h to determine the types and amounts of carbon–oxygen bonds present. The C_{1s} peak was deconvoluted into four subpeaks, C1, C2, C3, and C4. The theoretical binding energy and corresponding bond type are shown in Table 2. The C1 peak does not have a carbon–oxygen bond, whereas C2, C3, and C4 all possess a carbon–oxygen bond. The corresponding graphs and deconvolution peaks for unexposed and exposed neat HDPE and WF/HDPE samples are presented in Figs. 2 and 3, respectively. A drop in the C1 peak is clearly seen for the neat HDPE samples weathered for 2000 h (Fig. 2b), indicating a decreased concentration of unoxidized carbon atoms. This drop was even more apparent for the WF/HDPE composites. As illustrated in Fig. 3, the peak intensity corresponding to C1 decreased dramatically while an increase in C2 was observed as a shoulder peak. This trend implies that surface oxidation had occurred. To quantify the degree of surface oxidation, the area under each peak was integrated and an oxidized to unoxidized carbon ($C_{ox/unox}$) ratio was calculated (Eq. (1)). These results are presented in Table 3.

Table 1
Relative amount of atoms at sample surface determined by low-resolution XPS scan and calculated oxygen-to-carbon atomic ratio

Element	HDPE		WF/HDPE	
	0 h	2000 h	0 h	2000 h
Na	0.58	0.29	0.57	0
O	13.28	25.44	14.12	29.99
N	1.41	1.26	1.07	0.62
C	82.96	63.63	82.59	66.67
Si	1.78	9.38	1.64	2.71
O/C	0.160	0.400	0.171	0.450

Table 2
Deconvoluted peak assignments with corresponding theoretical binding energy and bond type for high-resolution XPS scan of C_{1s} region

Carbon group	Binding energy (eV)	Bond
C1	285.0	C–C or C–H
C2	286.5	C–OH
C3	288.0	O–C–O or C=O
C4	289.5	O–C=O

Differences in the oxidized-to-unoxidized carbon ratio for the unweathered samples (0 h) were apparent (Table 3). The addition of WF to the HDPE matrix increased the concentration of carbon–oxygen bonds (C2 + C3 + C4) in the samples. This was expected since the major components of wood, i.e., cellulose, hemicelluloses, and lignin, have a larger percentage of oxidized carbon in their chemical structure than does manufactured neat HDPE. Hydroxyl groups are the main carbon–oxygen functional groups in wood [26]. This is most evident as a larger C2 value for the WF/HDPE composites than for the neat HDPE before weathering (Table 3).

As expected, weathering significantly increased the $C_{ox/unox}$ ratio for both neat HDPE and WF/HDPE composites (Table 3), proving that substantial surface oxidation occurred after 2000 h of exposure. The increase in the $C_{ox/unox}$ ratio for both the neat HDPE and WF/HDPE composites appears to be mainly due to an increase in hydroxyl groups (i.e., increase in C2). These results confirm the trend observed with the low-resolution data, which showed an increase in elemental oxidation (O/C ratio) after weathering (Table 1). In addition, surface oxidation due to weathering was more pronounced for WF/HDPE composite samples than for the neat HDPE samples. The $C_{ox/unox}$ ratio increased dramatically for WF/HDPE composites after weathering, resulting in an 80% increase compared with a 5% increase for neat HDPE samples, which suggests that the addition of WF to HDPE matrix exacerbates the photo-oxidation of the sample surface. The surface of the entire composite sample was analyzed for oxidation. These methods cannot differentiate between oxidation of HDPE or WF independently.

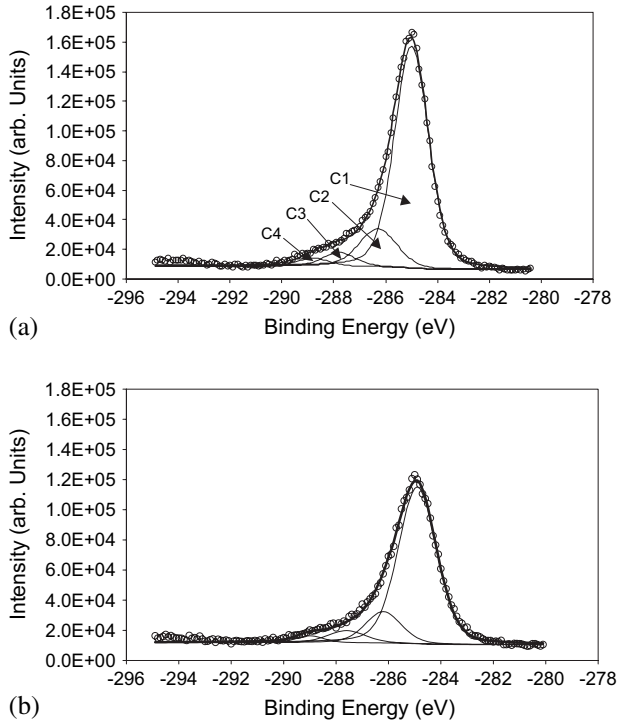


Fig. 2. XPS scan of C_{1s} region for neat HDPE: (a) unexposed samples, (b) samples subjected to 2000 h UV/water spray cyclic exposure.

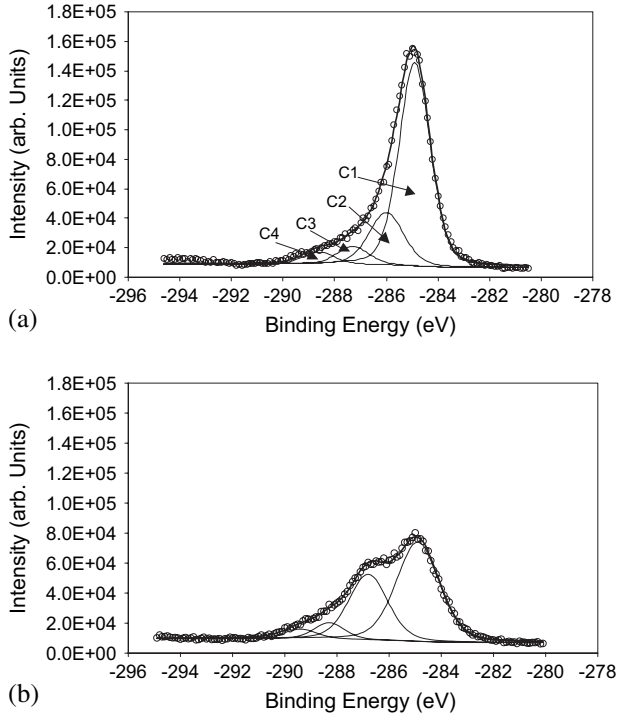


Fig. 3. XPS scan of C_{1s} region for WF/HDPE composites: (a) unexposed samples, (b) samples subjected to 2000 h UV/water spray cyclic exposure.

Table 3
Relative amount of different carbon-to-oxygen bonds at sample surface determined by high-resolution XPS

Carbon group	HDPE		WF/HDPE	
	0 h	2000 h	0 h	2000 h
C1	78.01	77.23	69.54	55.85
C2	14.74	15.55	19.9	33.49
C3	4.63	5.08	6.34	6.52
C4	2.62	2.14	4.22	4.14
$C_{ox/unox}$	0.282	0.295	0.438	0.791

4.2. Fourier transform infrared spectroscopy

FTIR spectroscopy was used to verify the occurrence of surface oxidation of the samples through the investigation of a carbonyl group change. In addition, structural changes in the matrix after weathering were investigated by following vinyl group formation and crystallinity changes of both HDPE and WF/HDPE composite samples. Table 4 shows the wavenumbers of the peaks monitored with their corresponding functional groups and vibrational types. Fig. 4 is an example of the shape and location of the carbonyl band for WF/HDPE composites after various exposure times. In the carbonyl region (1750–1700 cm^{-1}), a sharp peak formed at 1715 cm^{-1} with a shoulder peak at 1735 cm^{-1} corresponding to carboxylic acid and ester groups, respectively [11]. Figs. 5–7 summarize the FTIR results for both HDPE and WF/HDPE composites.

4.3. Carbonyl group formation

The increase in carbonyl group concentration (calculated from Eq. (2)) over exposure time is plotted in Fig. 5. Initially, the carbonyl index was higher for WF/HDPE composites than for the neat HDPE composites. This supports the XPS data, as the addition of WF to the HDPE matrix increased the amount of oxygen in the sample, including carbonyl functionality. As the exposure time increased, the carbonyl index increased at approximately the same rate for WF/HDPE composite samples and neat HDPE samples. The increase in carbonyl group formation for polyethylene after weathering is known to be proportional to the number of chain scissions that occur in the polyethylene [10]. Our results indicate that chain scission may have occurred immediately upon exposure and that the number of chain scissions increased with increasing exposure time (Fig. 5).

4.4. Vinyl group formation

Like carbonyl group formation, vinyl group formation is an indication of polymer chain scission [9] of either HDPE or WF, which can be a result of carbonyl degradation via Norrish II. Fig. 6 shows the increase in

Table 4
Wavenumbers of peaks used for FTIR analysis and corresponding functional groups and vibrational types[a]

Wavenumber (cm^{-1})	Functional group	Vibrational type
2912	$-CH_2-$	C–H stretching
1715	R(C=O)OH	C=O stretching
1474	$-CH_2-$	C–H bending, crystalline
1464	$-CH_2-$	C–H bending, amorphous
908	$RCH=CH_2$	C–CH_2 out of plane bending
730	$-CH_2-$	C–H rocking, crystalline
720	$-CH_2-$	C–H rocking, amorphous

[a] Sources: Refs. [9,21].

vinyl group concentration based on the peak at 908 cm^{-1}. The concentration of vinyl groups was generally much larger for the neat HDPE composites than for the WF/HDPE composites. This suggests that vinyl group formation may be important for the degradation of only the polymer, not the wood.

There was no significant vinyl group formation during exposure of neat HDPE through the initial 250 h (Fig. 6). After 250 h, vinyl group formation significantly increased with UV exposure time, leveling after 1000 h. Other investigators have also found an initial delay in vinyl group formation in the early stages of naturally weathered HDPE [9], followed by a steep increase as weathering progressed. The plateau experienced in the production of vinyl groups at longer exposure times (1000–2000 h) is thought to be due to degradation via the Norrish type II mechanism, which causes vinyl groups to be the major products in the first stage followed by a slower conversion to carbonyl groups [9].

Similarly, for WF/HDPE composites, the vinyl group concentration was not significantly larger than that of the unexposed sample through 250 h of exposure, then increased in concentration to 1000 h. Again the concentration appeared to remain levelled between 1000 and 2000 h of exposure. The change in vinyl group concentration is thought to be mainly due to degradation of the HDPE matrix as a component of WF/HDPE composites.

4.5. Crystallinity changes

The addition of WF to HDPE matrix changes the crystallinity of HDPE. The crystallinity of HDPE in the unweathered samples was higher for neat HDPE samples than for WF/HDPE composites (Fig. 7). Although wood-fiber can act as a nucleating site for crystallization, it has been found to physically hinder crystal growth, resulting in lower polymer crystallinity [27]. Colom et al. [19] studied the changes in crystallinity of HDPE matrix filled with aspen fiber and reported that increasing the fiber content from 10% to 40% decreased crystallinity [19]. A similar effect has also been

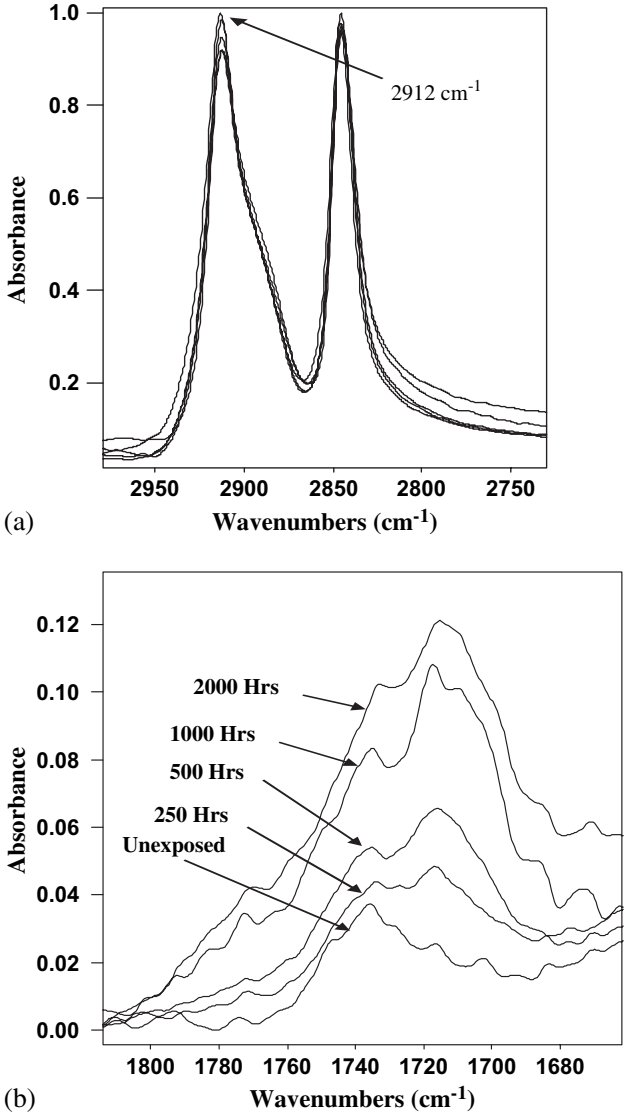


Fig. 4. FTIR spectra of WF/HDPE composites exposed to various weathering times: (a) methyl group region, (b) carbonyl group region.

shown in sisal fiber/polypropylene composites. When the sisal content is low (<20%), the sisal fiber acts as a nucleating site, increasing crystallinity. However, when the sisal content is above 20%, crystallinity decreases as the fiber begins to hinder the molecular motion of polypropylene [27].

An increase in crystallinity can also be used as an indicator of polyethylene chain scission during photodegradation. Chain scissions resulting from degradation via Norrish I and II reactions reduce the density of the entanglements in the amorphous phase, which allows shorter molecules to crystallize because of their higher mobility [9]. Therefore, secondary crystallization takes place in the amorphous phase of polyethylene. The effect of UV exposure time on the crystallinity of neat HDPE and WF/HDPE composites is shown in Fig. 7. As the

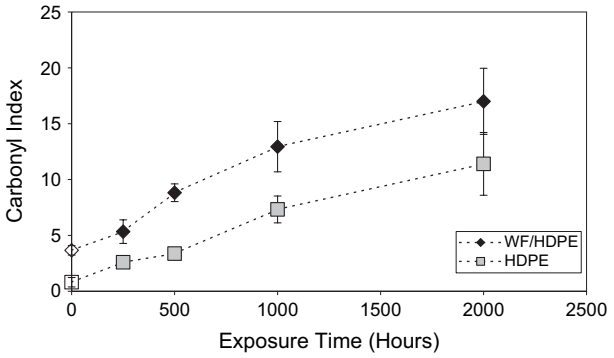


Fig. 5. Carbonyl group formation as a function of exposure time for neat HDPE and WF/HDPE samples. Each data point represents average of five samples; error bars represent one standard deviation. Solid symbols indicate that data point was significantly different from unexposed data point at that exposure level. Open symbols indicate that data point at that exposure level was not significantly different from data point corresponding to unexposed sample.

samples underwent photodegradation, differences in the crystallinity of neat HDPE and WF/HDPE samples became apparent. The crystallinity of HDPE appeared to remain constant through 500 h of exposure, at which point it began to decrease, resulting in a significant decrease at 2000 h (Fig. 7). Alternatively, the crystallinity of the HDPE matrix in the WF/HDPE composites increased with increasing exposure time to 1000 h, at which point crystallinity dropped.

Because chain scission occurs during exposure, as evidenced by the growth of carbonyl and vinyl groups, we expected that crystallinity would increase. Indeed, others have found increases in crystallinity after weathering. Kaci et al. [13] used FTIR to determine the crystallinity of low-density polyethylene after natural weathering. Crystallinity increased with increasing exposure time until a plateau was reached after 400 days. The authors attributed this trend to secondary crystallization in the amorphous phase [13].

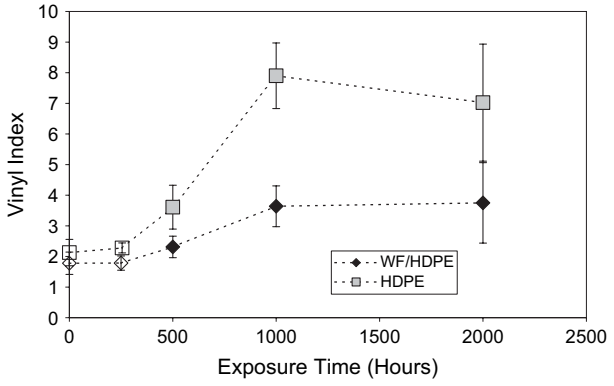


Fig. 6. Vinyl group formation as a function of exposure time for neat HDPE and WF/HDPE samples. Each data point represents average of five samples; error bars represent one standard deviation. See legend to Fig. 5 for explanation of symbols.

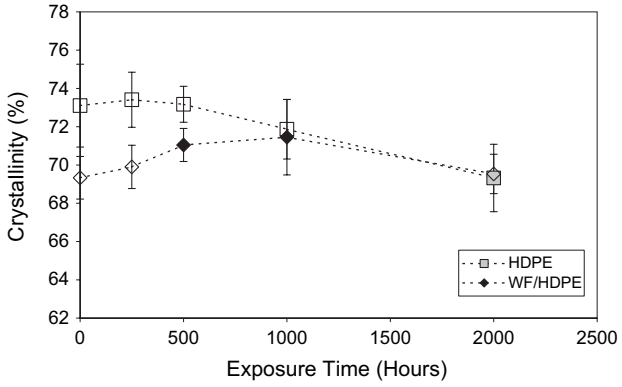


Fig. 7. Crystallinity as a function of exposure time for neat HDPE and WF/HDPE samples. Each data point represents average of five samples; error bars represent one standard deviation. See legend to Fig. 5 for explanation of symbols.

While chain scission may be an important mode of polyethylene degradation, crosslinking begins to predominate as the temperature increases [10,12]. In accelerated weathering, temperatures are elevated above that of the exposure temperatures of natural weathering. Hamid and Amin [14] studied both natural and accelerated weathering of low-density polyethylene (LDPE). They concluded that crosslinking and chain scission reactions take place simultaneously. Tidjani [11] adds that under accelerated weathering, crosslinking reactions reduce the concentration of free radicals taking part in the oxidation process. Oxidation damage can also occur at the tie molecule region. Tie molecules are polymer molecules that form a part of a folded crystalline region and extend through an amorphous region into another crystalline region. A small amount of oxidation products in polyethylene can cause great damage to the tie molecules [17], resulting in a breakdown of crystallization.

The WF/HDPE composite experienced an increase in crystallinity due to chain scission, rather than a decrease in crystallinity and crosslinking, which was the preferred method for neat HDPE degradation. Although we do not know the reasons for this difference in the degradation mechanism, we believe that WF particles may physically hinder crosslinking in the composite during the initial stages of accelerated weathering, which would allow for more chain scission and a corresponding increase in crystallinity. As with the unfilled HDPE samples, chain scission in the HDPE matrix of the composite eventually affected the tie molecules and the crystallinity was decreased.

5. Concluding remarks

Both XPS and FTIR spectroscopy can be used to effectively study the surface oxidation of weathered WF/HDPE composites. A low-resolution XPS scan quickly

demonstrated an increase in oxygen atoms at the surface of both HDPE and WF/HDPE samples after 2000 h of weathering. A high-resolution scan was used to determine the type and amount of carbon–oxygen bonds formed after 2000 h of weathering. Through the calculation of an oxidized-to-unoxidized carbon ratio, the results point toward an increase in oxidized carbon atoms. In addition, the WF/HDPE composites showed a dramatic increase in the oxidized-to-unoxidized carbon ratio, compared with that of unfilled HDPE (80% versus 5%, respectively). This is evidence of the damaging effect of adding wood to HDPE, which effectively increases the surface oxidation of composite samples after weathering.

FTIR spectroscopy was used to determine carbonyl group formation, vinyl group formation, and crystallinity changes during weathering. An increase in the calculated carbonyl index denotes an increase in polymer chain scission. Initially, the carbonyl index was higher for WF/HDPE composites but it increased at approximately the same rate for both WF/HDPE composites and neat HDPE samples. The calculated vinyl group index can also be used to indicate polymer chain scission. The vinyl index remained constant through 250 h of exposure time, increased through 1000 h, and then reached a plateau for both WF/HDPE composites and neat HDPE samples. The concentration of vinyl groups was much larger for neat HDPE than for WF/HDPE composites, suggesting that vinyl group formation takes place mainly in the polymer component of the composite. Increases in matrix crystallinity can occur if chain scission occurs. The shorter, more mobile chains recrystallize in the amorphous phase of the polymer. Our data show differences between crystallinity changes for neat HDPE and WF/HDPE composites. Crystallinity of HDPE samples remained statistically unchanged through 1000 h of exposure, then decreased. Conversely, crystallinity of the HDPE matrix in the WF/HDPE composites increased with exposure time through 1000 h before decreasing.

The neat HDPE samples may have predominantly undergone crosslinking as opposed to chain scission during the initial stages of accelerated weathering, which favors the Norrish I degradation mechanism over the Norrish II mechanism (Fig. 1). The free radicals produced during Norrish I degradation are free to react with free radicals on other chains to terminate and crosslink the polymer chains. While some chain scission occurs initially, the delay in vinyl group formation suggests that early in weathering the Norrish II degradation mechanism is not as important as the Norrish I mechanism. The favoring of crosslinking over chain scission does not change overall crystallinity. However, as exposure increases the vinyl group formation increases, confirming an increase in polymer chain scission. Chain scission begins to affect the tie molecules, resulting in a net decrease in crystallinity.

The WF/HDPE composites initially had a higher surface oxygen concentration compared to that of unfilled HDPE as a result of the hydroxyl groups on the wood surface. The rate of carbonyl group was similar for WF/HDPE composites and unfilled HDPE samples. This suggests that each component of the WF/HDPE composite is oxidizing. Although the initial crystallinity in the polymer matrix of WF/HDPE composites was lower than the crystallinity of the neat HDPE because the wood-fiber hindered crystal growth, crystallinity increased through 1000 h of exposure. At 2000 h of exposure, crystallinity declined somewhat. This implies that chain scission in the polymer phase may predominate over crosslinking almost immediately, possibly because the wood-fiber hinders crosslinking of the matrix as well as crystal growth.

Acknowledgements

This research was supported by the School of Forest Resources and Environmental Science at Michigan Technological University. The authors gratefully acknowledge American Wood Fibers of Schofield, Wisconsin, for supplying the wood-flour.

References

[1] Smith P. Proceedings of Progress in Wood Fiber–Plastic Composites; 2002.
[2] Lundin T. Effect of accelerated weathering on the physical and mechanical properties of natural-fiber thermoplastic composites. M.S. thesis, University of Wisconsin–Madison; 2001.
[3] Falk RH, Felton C, Lundin T. Proceedings of the Third International Symposium on Natural Polymers and Composites; 2000.
[4] Rowell RM, Lange SE, Jacobson RE. Weathering performance of plant-fiber/thermoplastic composites. Mol Cryst Liq Cryst 2000; 353:85–94.
[5] Stark NM, Matuana LM. Ultraviolet weathering of photostabilized wood flour–HDPE composites. J Appl Polym Sci 2003;90(10):2609–17.
[6] Matuana LM, Kamdem DP, Zhang J. Photoaging and stabilization of rigid PVC/wood-fiber composites. J Appl Polym Sci 2001;80(11):1943–50.
[7] Matuana LM, Kamdem DP. Accelerated ultraviolet weathering of PVC/wood-flour composites. Polym Eng Sci 2002;42(8): 1657–66.
[8] Gugumus F. Light stabilizers. In: Gächter F, Müller H, editors. Plastics additives handbook. Munich, Germany: Hanser Publishers; 1990 [chapter 3].
[9] Jabarin SA, Lofgren EA. Photooxidative effects of properties and structure of high-density polyethylene. J Appl Polym Sci 1994;53(4):411–23.
[10] Wypych G. Handbook of material weathering. 2nd ed. Ontario, Canada: ChemTec Publishing; 1995.
[11] Tidjani A. Comparison of formation of oxidation products during photo-oxidation of linear low density polyethylene under different natural and accelerated weathering conditions. Polym Degrad Stab 2000;68(3):465–9.
[12] David C, Trojan M, Daro A, Demarteau W. Photodegradation of polyethylene: comparison of various photoinitiators in

natural weathering conditions. Polym Degrad Stab 1992;37(3): 233–45.
[13] Kaci M, Sadoun T, Cimmino S. Crystallinity measurements of unstabilized and HALS-stabilized LDPE films exposed to natural weathering by FT-IR, DSC and WAXS analyses. Int J Polym Anal Charact 2001;6(5):455–64.
[14] Hamid SH, Amin MB. Lifetime prediction of polymers. J Appl Polym Sci 1995;55(10):1385–94.
[15] Tidjani A, Arnaud R, Dasilva A. Natural and accelerated photoaging of linear low-density polyethylene: changes of the elongation at break. J Appl Polym Sci 1993;47(2):211–6.
[16] Gijsman P, Dozeman A. Comparison of the UV-degradation chemistry of unstabilized and HALS-stabilized polyethylene and polypropylene. Polym Degrad Stab 1996;53(1):45–50.
[17] Torikai A, Shirakawa H, Nagaya S, Fueki K. Photodegradation of polyethylene: factors affecting photostability. J Appl Polym Sci 1990;40(9–10):1637–46.
[18] Zerbi G, Gallino G, Del Fanti N, Baini L. Structural depth profiling in polyethylene films by multiple internal reflection infrared spectroscopy. Polymers 1989;30(12):2324–7.
[19] Colom X, Canavate J, Pagès P, Saurina J, Carrasco F. Changes in crystallinity of the HDPE matrix in composites with cellulosic fiber using DSC and FTIR. J Reinf Plast Comp 2000;19(10):818–30.
[20] Camacho W, Karlsson S. Simultaneous determination of molecular weight and crystallinity of recycled HDPE by infrared spectroscopy and multivariate calibration. J Appl Polym Sci 2002;85(2):321–7.
[21] Pagès P, Carrasco F, Saurina J, Colom X. FTIR and DSC study of HDPE structural changes and mechanical properties variation when exposed to weathering aging during Canadian winter. J Appl Polym Sci 1996;60(2):153–9.
[22] Maatoug MA, Anna P, Bertalan G, Ravadits I, Marosi G, Csontos I, et al. Role of pigments in the stability of polyethylene systems. Macromol Mater Eng 2000;282(9):30–6.
[23] Banik I, Kim KS, Yun YI, Kim DH, Ryu CM, Park CE. Inhibition of aging in plasma-treated high-density polyethylene. J Adhes Sci Technol 2002;16(9):1155–69.
[24] ASTM. Annual book of ASTM standards, 8.01. Conshohocken, PA: American Society for Testing and Materials; 2001.
[25] ASTM. Annual book of ASTM standards, 8.02. Conshohocken, PA: American Society for Testing and Materials; 2001.
[26] Hon DNS. In: Wood and cellulose chemistry. New York: Marcel Dekker, Inc.; 2001. p. 513–46.
[27] Xie XL, Li RKY, Tjong SC, Mai Y-W. Structural properties and mechanical behavior of injection molded composites of polypropylene and sisal fiber. Polym Comp 2002;23(3): 319–28.