Surface Chemistry and Mechanical Property Changes of Wood-Flour/High-Density-Polyethylene Composites after Accelerated Weathering

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ABSTRACT: Although wood–plastic composites have become more accepted and used in recent years and are promoted as low-maintenance, high-durability building products, they do experience a color change and a loss in mechanical properties with accelerated weathering. In this study, we attempted to characterize the modulus-of-elasticity (MOE) loss of photostabilized high-density polyethylene (HDPE) and composites of wood flour and high-density polyethylene (WF/HDPE) with accelerated weathering. We then examined how weathering changed the surface chemistry of the composites and looked at whether or not the surface changes were related to the MOE loss. By examining surface chemistry changes, we hoped to begin to understand what caused the weathering changes. The materials were left unstabilized or were stabilized with either an ultraviolet absorber or pigment. After 1000 and 2000 h of accelerated weathering, the samples were tested for MOE loss. Fourier transform infrared (FTIR) spectroscopy was employed to monitor carbonyl and vinyl group formation at the surface. Changes in the HDPE crystallinity were also determined with FTIR techniques. It was determined that structural changes in the samples (carbonyl group formation, terminal vinyl group formation, and crystallinity changes) could not be reliably used to predict changes in MOE with a simple linear relationship. This indicated that the effects of crosslinking, chain scission, and crystallinity changes due to ultraviolet exposure and interfacial degradation due to moisture exposure were interrelated factors for the weathering of HDPE and WF/HDPE composites. © 2004 Wiley Periodicals, Inc.* J Appl Polym Sci 94: 2263–2273, 2004

Key words: composites; FT-IR; polyethylene (PE)

INTRODUCTION

Although inorganic fillers currently dominate the thermoplastic industry, wood-derived fillers have become more accepted in recent years and have made significant inroads into specialty markets. Construction, transportation, industrial, and consumer applications for wood–plastic composites are all on the rise. However, building products currently constitute the largest portion of the wood–plastic composite market.[1] Exterior nonstructural or semistructural composite building products such as decking, fencing, siding, and roof tiles are being introduced into the marketplace. For building products alone, approximately 1.1 billion lb (500,000 t) of wood–plastic composites will be used in North America in 2006.[1] Although wood–plastic lumber is promoted as a low-maintenance and high-durability product,[2] ultraviolet (UV) durability is a concern. It has been shown that wood–plastic composites exposed to accelerated weathering experience a color change[3–8] and a loss in mechanical properties.[3–6]

Although the photodegradation of polyethylene has been extensively examined,[9–19] little information is available on the photodegradation of wood-flour-filled high-density polyethylene (WF/HDPE) composites.[3–6,20] Much of the research conducted to date concerns only color fading and mechanical property loss after accelerated weathering.[3–6] Some researchers have examined surface chemistry changes of wood-flour-filled poly(vinyl chloride).[7,8] The crystallinity changes of aspen-fiber-filled polyethylene after weathering have also been studied,[21,22] but information on the surface chemistry changes of WF/HDPE composites after weathering is sparse.[20,22]

It has been postulated that carbonyl groups are the main light-absorbing species responsible for the pho-
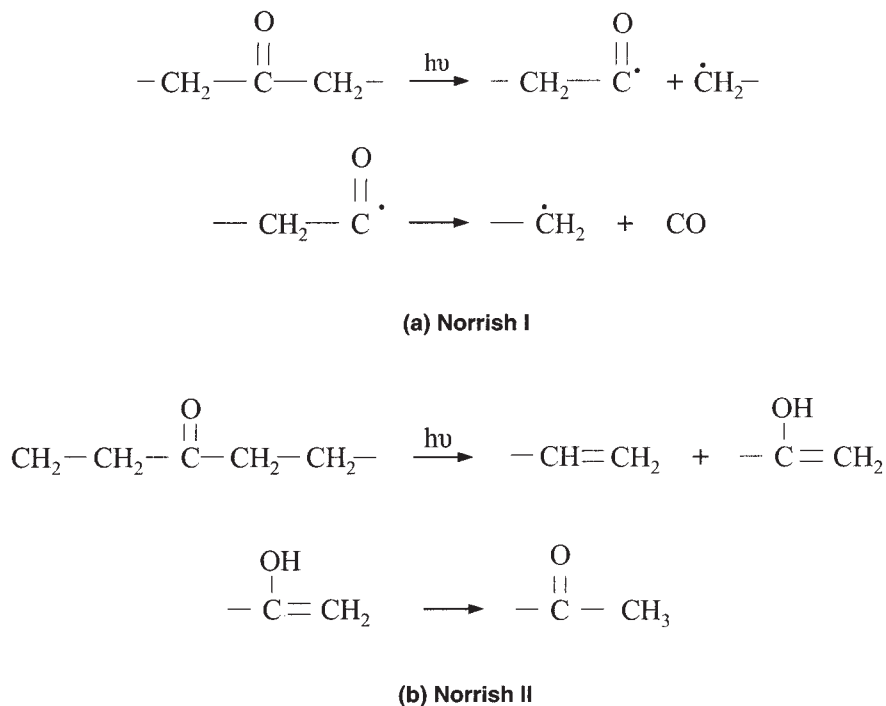
Figure 1 Norrish degradation mechanisms.

tochemical initiation reactions of UV-exposed polyethylene.[9] The degradation reactions proceed from carbonyl group precursors according to Norrish I and II reactions.[9–11] If degradation of the carbonyl groups proceeds according to a Norrish I reaction, the resulting free radicals that form can attack the polymer [Fig. 1(a)]. Free-radical attack may lead to termination via crosslinking or chain scission.[10] If the degradation proceeds according to a Norrish II reaction, carbonyl groups and terminal vinyl groups are produced [Fig. 1(b)], and chain scission occurs. In addition, the carbonyl group that forms is capable of further degradation. During the course of polyethylene photodegradation, the two mechanisms, chain scission and crosslinking, are competing.[9–11] Although chain scission occurs in the amorphous phase of the polymer, imperfect crystalline regions degrade because of crosslinking.[12] Tie molecules, chains traversing the amorphous phase from one crystalline lamella to another, can also be affected during photodegradation.[13] Decreasing the tie-molecule density can increase environmental stress cracking.[23]

The formation of carbonyl groups and vinyl groups indicates main-chain scission.[14–16] An increase in polyethylene crystallinity after weathering also indicates that chain scission has occurred. The shorter chains produced during chain scission are more mobile and are able to crystallize more readily; this results in increased crystallization and associated embrittlement.[9,10] The crystalline component of polyethylene has a higher modulus of elasticity (MOE) than the amorphous component. Therefore, increasing the crystallinity increases the MOE of polyethylene.[24]

Recently, Fourier transform infrared (FTIR) spectroscopy has been used to study the changes in the surface chemistry of polyethylene after weathering. FTIR spectroscopy has also been used to monitor carbonyl group formation,[9,11–16] vinyl group formation,[9,11,12,14] and changes in the crystallinity[19,25,26] of weathered polyethylene.

The mechanical properties of wood–plastic composites are negatively affected by moisture.[27–32] When the composites are exposed to moisture, the hydrophilic fibers swell. Cracks may form in the plastic matrix, which can also contribute to the penetration of water into the composite.[28] Exposing wood–plastic composites to moisture results in a drop in the flexural MOE and strength because of degradation of the wood–plastic interfacial quality.[28–30] The amount of moisture absorbed can be influenced by the concentration of wood flour (WF) and the wood particle size.[28,31]

Photostabilizers are compounds developed to protect polymers and combat UV degradation. These photostabilizers are generally classed according to the degradation mechanism that they hinder. The three main types of photostabilizers are ultraviolet absorbers (UVAs), quenchers, and free-radical scavengers. In addition, pigments, though not technically photostabilizers, are often used as photoblockers to inhibit the photodegradation of plastics.[33]

Much of the available information on photostabilizers covers only the photostabilization of unfilled plas-

TABLE I
Formulations of Neat HDPE and
WF/HDPE Composite Blends

Formulation	Amount of substance (wt %)			
	HDPE	WF	UVA	P
HDPE	100	0	0	0
HDPE/UVA	99.5	0	0.5	0
HDPE/P	99	0	0	1
WF/HDPE	50	50	0	0
WF/HDPE/UVA	49.5	50	0.5	0
WF/HDPE/P	49	50	0	1

tics.[10,11,17,18,33] The hindered amine light stabilizers studied to date have been shown to be ineffective stabilizers for WF/HDPE composites.[3–6] This is possibly due to acid–base interactions between the hindered amine and the wood particles.[6] In a previous study, it was determined that UVAs and pigments are the most effective photostabilizers for WF/HDPE composites, protecting against both color fading and mechanical property loss.[5,6] Others have also shown that pigments are able to prevent some mechanical property loss after accelerated weathering.[3–6]

This study has three main objectives: (1) to characterize the MOE loss of photostabilized high-density polyethylene (HDPE) blends and WF/HDPE composites, (2) to understand how weathering changes the structure and surface chemistry of photostabilized HDPE blends and WF/HDPE composites, and (3) to relate changes in MOE to changes in the surface chemistry. The results of this study will also aid in the understanding of how photostabilizers affect the mechanical properties and surface chemistry changes of WF/HDPE composites after weathering.

EXPERIMENTAL

Materials

The materials used in this study were WF and HDPE. The WF was a 40-mesh (0.420-mm openings) ponderosa pine supplied by American Wood Fibers (Schofield, WI). The HDPE (Fortiflex A60-70-162) was a virgin material with a melt index of 0.72 g/10 min and a density of 0.963 g/cm^3 supplied by Solvay Polymers, Inc. (Houston, TX). A hydroxyphenyl benzotriazole UVA (Tinuvin 328), supplied by Ciba Specialty Chemicals (Tarrytown, NY), and a zinc ferrite pigment in a carrier wax (P; Cedar TI-8536), supplied by Holland Colors Americas, Inc. (Richmond, IN), were used as photostabilizers. The formulations of the neat HDPE and WF/HDPE composite blends are shown in Table I. A 50% WF composite formulation was chosen because it was representative of commercially available lumber products.

Processing

The neat HDPE samples were molded into flexural bar test samples with a Cincinnati Milacron (Batavia, OH) 33-ton injection molder. The mold nozzle temperature was 204°C (400°F), and the injection pressure reached a peak of 12.4 MPa (1800 lb/in.^{2}). The American Society for Testing and Materials (ASTM D 790) mold cavity used for the flexural samples was 120 mm × 3 mm × 12 mm.[34] The WF was dried for 24 h at 105°C (221°F), and then the composites were dry-blended according to the formulations in Table I. Compounding was accomplished with a Davis Standard (Pawcatuck, CT) 32-mm 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/in.^{2}). The pellets were dried at 105°C (221°F) for at least 24 h before injection molding into flexural bar test samples. The injection-molding conditions were the same as those for the neat HDPE manufacture.

Testing and analysis

Weathering

The samples were placed in a xenon arc-type light exposure apparatus, which was operated according to ASTM D 2565.[35] The samples were mounted in four rows on a drum that rotated around the xenon arc bulb at 1 rpm. The samples were rotated every 250 h to ensure that all were exposed to the same irradiance. The weathering cycle consisted of 108-min UV exposure and 12-min simultaneous water spray and light exposure.[35] The samples were removed for analysis after 1000 and 2000 h of weathering and were compared with unexposed samples.

Scanning electron microscopy (SEM)

Molded surfaces were sputter-coated with gold and analyzed with a scanning electron microscope (JSM-840, JEOL USA, Inc., Peabody, MA) at a working distance of approximately 25 mm, a voltage of 15 kV, and a probe current of 6 × 10^{-10} A.

Mechanical properties

The samples were oven-dried at 105°C for 24 h before testing. This ensured the same conditioning for the samples before and after weathering. Flexural tests were carried out according to ASTM D 790[34] on an MTS 810 material test system (MTS Systems Corp., Eden Prairie, MN). The three-point loading system was used with a crosshead speed of 1.3 mm/min corresponding to a strain rate of 0.01 mm/mm/min. The exposed surface was placed away from the center load to place that part of the sample in tension. At

least four replicate specimens were tested for each formulation. The tangent MOE was calculated via the fitting of a line to the initial slope of the stress–strain curve.

FTIR spectroscopy

FTIR spectroscopy was conducted on a Mattson Genesis II spectrophotometer (Thermo Electron Corp., Madison, WI) to provide a detailed analysis of the functional groups present on the surfaces of the samples. Scans were run at a resolution of 4 cm^{-1}. Each sample record consisted of 100 scans recorded in absorbance units from 4000 to 700 cm^{-1}. The spectra were obtained with attenuated total reflectance. The surfaces of the samples were in contact with a ZnSe crystal that had a 45° angle of incidence. At least five replicate specimens were analyzed for each formulation. Both a carbonyl index and a vinyl index were calculated with the following equations:

$$\text{Carbonyl index} = \frac{I_{1715}}{I_{2912}} \times 100 \qquad (1)$$

$$\text{Vinyl index} = \frac{I_{908}}{I_{2912}} \times 100 \qquad (2)$$

where I represents the peak intensity. The peak intensities were normalized with the peak at 2912 cm^{-1}, which corresponds to methyl group vibrations.

The crystallinity of HDPE was determined with the method described by Zerbi et al.[25] The doublet peaks observed at 1474–1464 and 730–720 cm^{-1} corresponded to the polyethylene crystalline content (1474 and 730 cm^{-1}) and amorphous content (1464 and 720 cm^{-1}). The percentage of the crystalline content (X) was calculated as follows:

$$X = 100 - \frac{\dfrac{1 - I_a/I_b}{1.233}}{1 + I_a/I_b} \times 100 \qquad (3)$$

where I_a and I_b can be determined from the bands at 1474 and 1464 cm^{-1} and from the bands at 730 and 720 cm^{-1}, respectively.[25]

Colom et al.[21] examined the crystallinity changes of aspen-fiber-filled HDPE composites with the FTIR method and differential scanning calorimetry (DSC). They determined that the bands at 730 and 720 cm^{-1} were the most appropriate bands to study because a peak from cellulose fibers at 1430 cm^{-1} interfered with the 1474- and 1464-cm^{-1} peaks.[21] In addition, Kaci et al.[19] studied the crystallinity changes of low-density polyethylene (LDPE) films after weathering with FTIR and DSC. They concluded that using the bands at 1474 and 1464 cm^{-1} to determine crystallinity led to unre-

liable results because they were asymmetric.[19] In this study, the crystallinity was calculated with the doublet peaks at 730 and 720 cm^{-1}.

Statistics

To determine the effects of weathering on the properties, we carried out Student two-tailed t-tests at $\alpha = 0.05$ for each blend, testing the data for significant differences within a blend due to weathering. A statistical analysis was performed separately for each HDPE blend or WF/HDPE composite.

One of the objectives of this study was to understand how weathering affected the properties of HDPE blends and WF/HDPE blends. Therefore, comparisons were only performed within each blend between unweathered and weathered samples. Comparisons between unstabilized and stabilized samples were not performed. In the figures, statistically significant differences within each group are represented with separate letters. Means with different letters indicate statistically significant changes after weathering. Other changes were not statistically significant.

To relate the change in the carbonyl index, vinyl index, or crystallinity with changes in MOE after 2000 h of weathering, we performed linear regressions from plots in which the flexural MOE was on the y axis and the carbonyl index, vinyl index, or crystallinity was on the x axis. This was carried out for the HDPE blends and WF/HDPE blends independently. In each case, the samples with and without photostabilizers were included in the analysis.

RESULTS AND DISCUSSION

SEM

Micrographs of the exposed neat HDPE blends and the WF/HDPE composites are shown in Figures 2 and 3, respectively. The surface of the unstabilized neat HDPE without weathering was initially smooth [Fig. 2(a)]. However, after 2000 h of accelerated weathering, surface cracks were readily apparent [Fig. 2(b)]. Adding either UVA or P to HDPE as a photostabilizer prevented surface cracks after 2000 h of accelerated weathering [Fig. 2(c,d), respectively].

The micrograph of the unstabilized and unexposed WF/HDPE composite [Fig. 3(a)] also shows a relatively smooth surface. However, after weathering, two distinct phenomenon occurred for the composite [Fig. 3(b)]: the WF particles rose from the surface, and the HDPE matrix had apparent surface cracks. The addition of UVA or P did not prevent the WF particles from protruding through the sample surface after weathering [Figs. 3(c,d)]. However, the cracks in the HDPE matrix appeared to be less severe for the com-
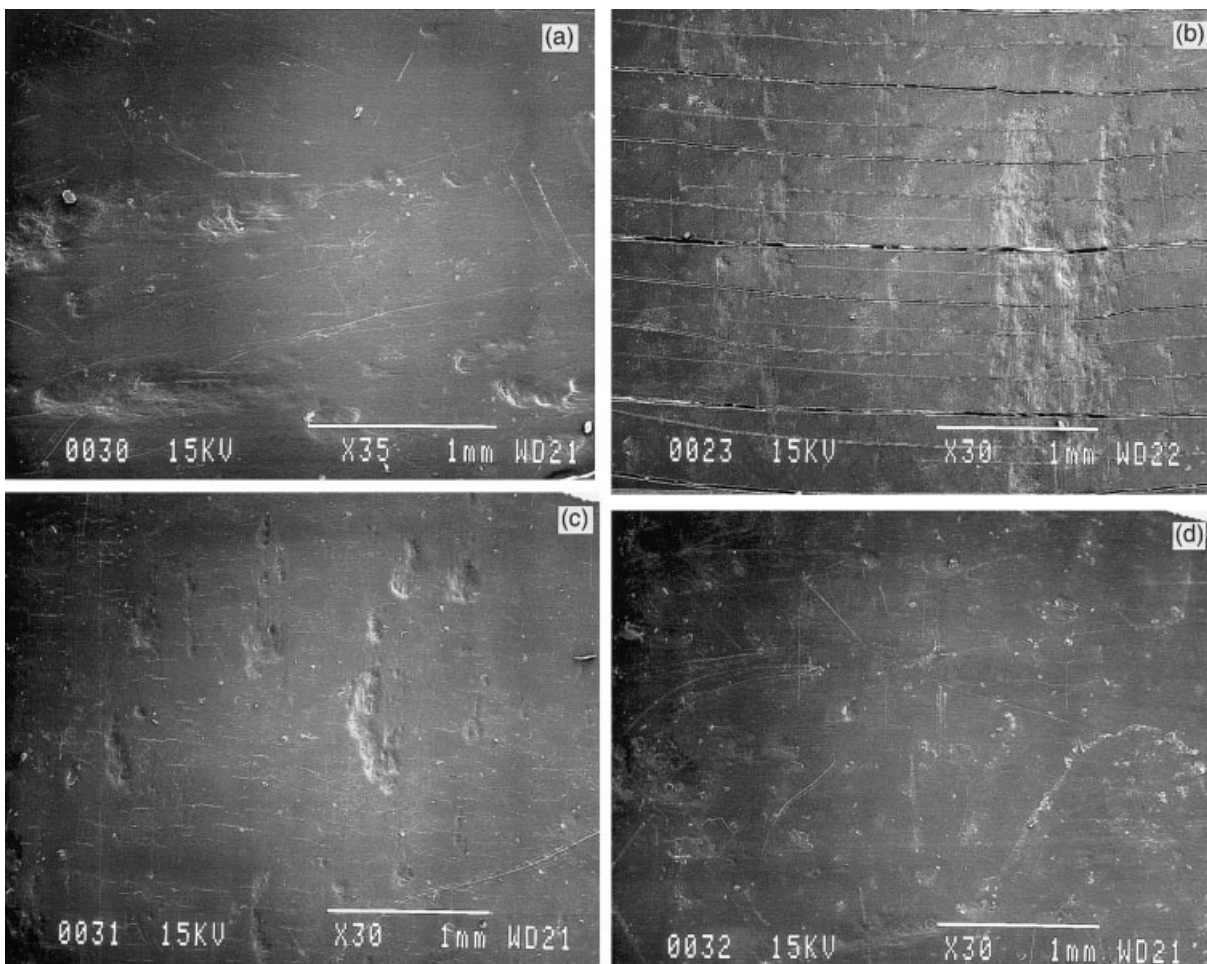
Figure 2 SEM micrographs of neat HDPE: (a) unstabilized without weathering, (b) unstabilized and exposed to 2000 h of weathering, (c) stabilized with UVA and exposed to 2000 h of weathering, and (d) stabilized with P and exposed to 2000 h of weathering.

posites with UVA and P added than for the unstabilized composites [Fig. 3(b)].

Flexural MOE

Figures 4 and 5 illustrate the flexural MOE of unfilled HDPE blends and WF/HDPE composites, respectively. The flexural MOE was calculated with the initial tangential slope of the load–displacement curve. All samples failed on the tensile side during testing.

For unstabilized neat HDPE, the flexural MOE increased significantly upon weathering after 1000 h (Fig. 4). An increase in MOE can be a sign of an increase in crystallinity or crosslinking. After 2000 h of weathering, the MOE decreased to a level that was not significantly different from the initial MOE. The loss of MOE was consistent with the appearance of surface cracks. Environmental stress cracking in polyethylene increases with a decrease in the tie-molecule density.[23]

HDPE stabilized with UVA or P also resulted in an initial increase in the flexural MOE after 1000 h of weathering. However, the addition of UVA prevented the drop in MOE between 1000 and 2000 h of weathering. The addition of P resulted in a significant drop in MOE between the 1000 and 2000 h of exposure, but the MOE after 2000 h was still higher than the initial MOE. The addition of the photostabilizers UVA and P may have delayed the chain-scission process that led to the degradation of MOE. It is expected that further exposure would lead to a drop in MOE for the photostabilized HDPE as well as the formation of surface cracks.

The flexural MOE of unstabilized WF/HDPE decreased slightly but significantly between 0 and 1000 h of weathering and experienced a larger drop between 1000 and 2000 h (Fig. 5). The addition of UVA and P to the WF/HDPE composite resulted in a small increase in MOE between 0 and 1000 h of weathering. The stabilized composites also experienced a drop in MOE between 1000 and 2000 h of weathering. There was a net drop in MOE after 2000 h of weathering for all the
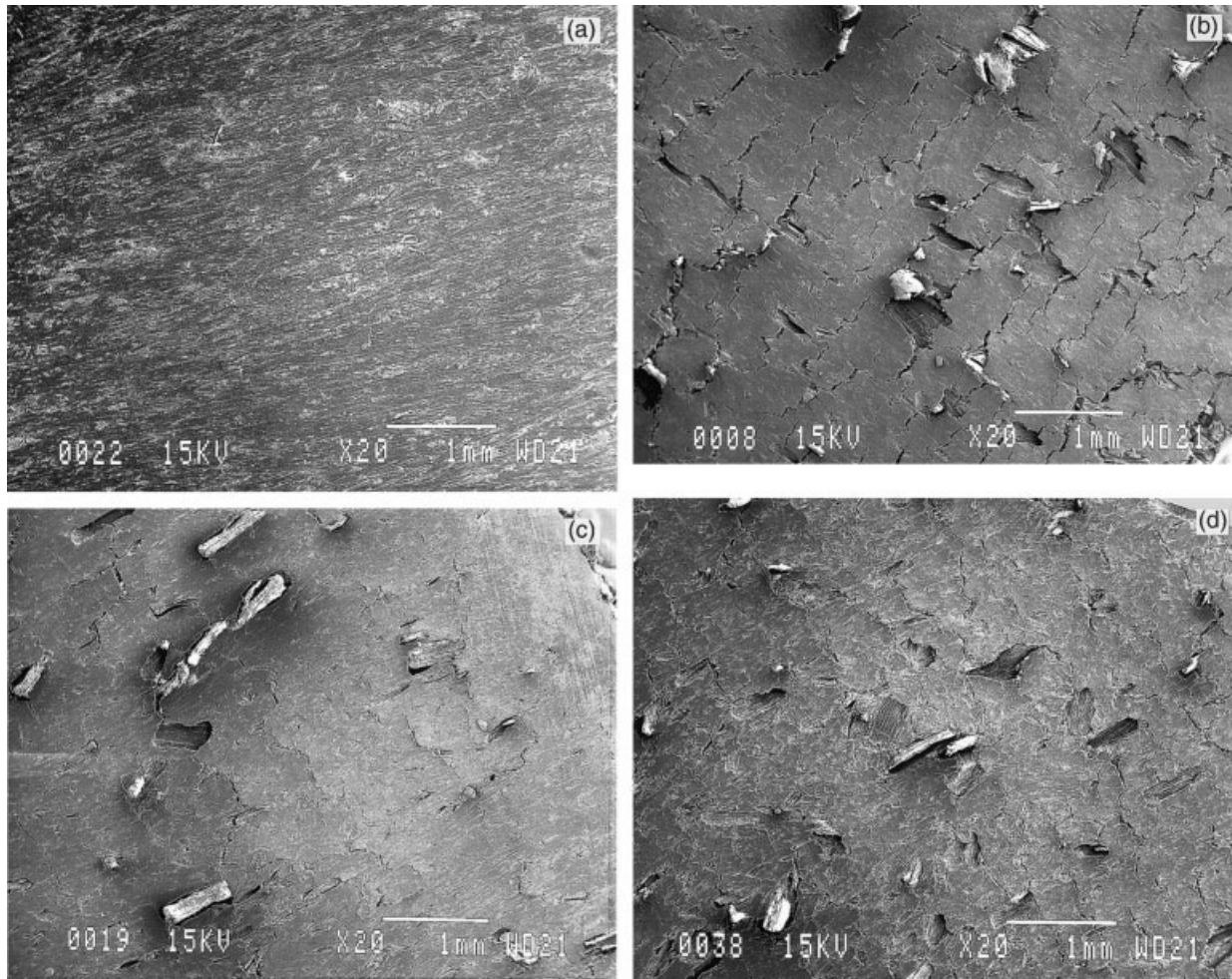
Figure 3 SEM micrographs of WF/HDPE composites: (a) unstabilized without weathering, (b) unstabilized and exposed to 2000 h of weathering, (c) stabilized with UVA and exposed to 2000 h of weathering, and (d) stabilized with P and exposed to 2000 h of weathering.

WF/HDPE blends. However, the loss in MOE was 26% for the unstabilized WF/HDPE and only 18 and 15% for composites with UVA and P stabilizers, re-spectively. Clearly, the photostabilizers UVA and P prevented some loss in MOE of the WF/HDPE com-posites after weathering. Falk et al.[4] also found that
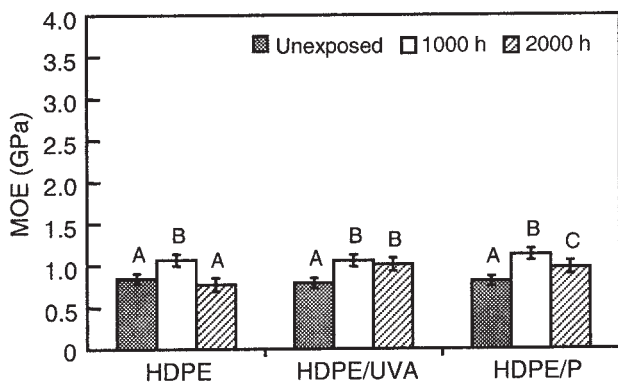

Figure 4 Flexural modulus of neat HDPE blends before and after accelerated weathering. Statistically significant differences within each group are represented with different letters.
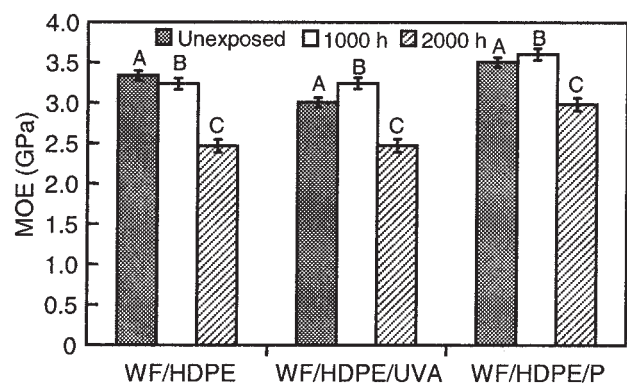

Figure 5 Flexural modulus of WF/HDPE composites before and after accelerated weathering. Statistically significant differences within each group are represented with different letters.

Figure 6 Carbonyl index of HDPE blends before and after accelerated weathering. Statistically significant differences within each group are represented with different letters.

Figure 7 Carbonyl index of WF/HDPE composites before and after accelerated weathering. Statistically significant differences within each group are represented with different letters.
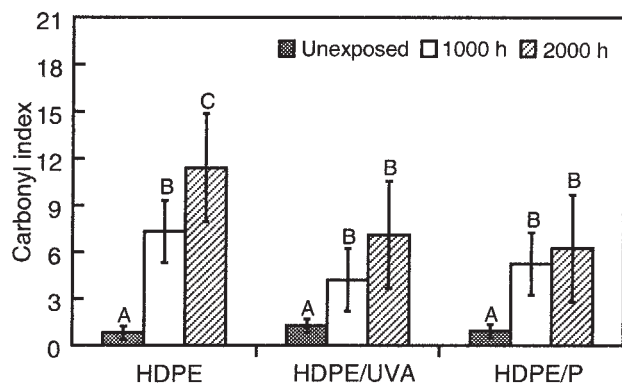
red and black pigments could protect WF/HDPE composites from a loss in MOE after weathering.

FTIR spectroscopy

FTIR spectroscopy was used to determine structural changes in the HDPE and WF/HDPE surface chemistry after weathering. Carbonyl group formation indicated that surface oxidation occurred. The formation of terminal vinyl groups indicated that photodegradation occurred via Norrish II reactions, resulting in chain scission. The method did not differentiate between carbonyl and vinyl functional groups at the HDPE or WF surface. Although increases in crystallinity due to recrystallization of shorter chains suggested that chain scission occurred, decreases in crystallinity due to the breakage of a sufficient number of tie molecules could also be an indication of chain scission.[23] The peaks examined for changes in crystallinity were characteristic of HDPE only. The changes in the carbonyl index are shown in Figures 6 and 7, the changes in the vinyl index are shown in Figures 8 and
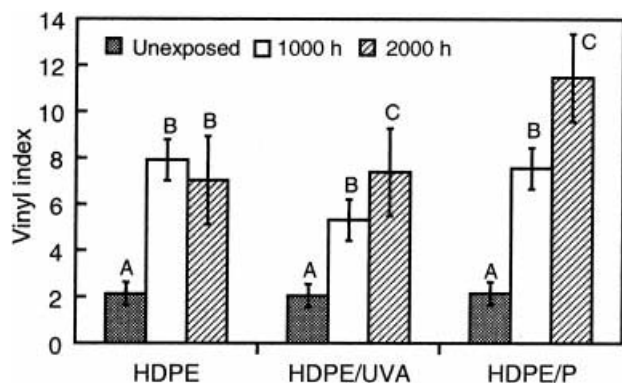
9, and the changes in the crystallinity are shown in Figures 10 and 11.

Carbonyl group formation

After 1000 and 2000 h of weathering, the carbonyl index for unstabilized HDPE increased significantly (Fig. 6). When HDPE was stabilized with either UVA or P, there was still a significant increase in carbonyl formation through 1000 h of weathering. However, between 1000 and 2000 h of weathering, the increase was not statistically significant. Overall, UVA- and P-stabilized samples showed lower carbonyl index values than their unstabilized counterparts, regardless of the exposure time. These results indicate that both UVA and P are effective stabilizers for preventing HDPE oxidation that occurs as a result of UV exposure.

A similar trend in carbonyl group formation was seen for the WF/HDPE composites (Fig. 7). The WF/HDPE composite without any photostabilizer added

Figure 8 Vinyl index of HDPE blends before and after accelerated weathering. Statistically significant differences within each group are represented with different letters.
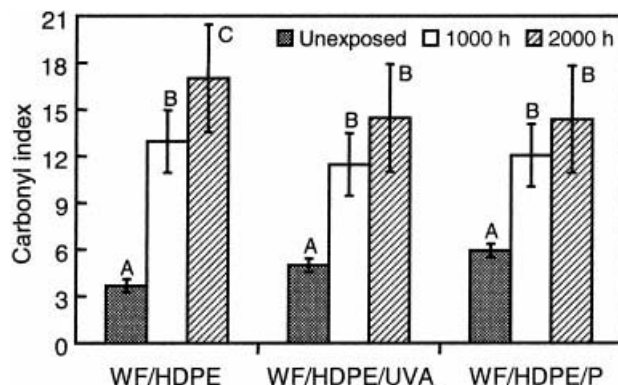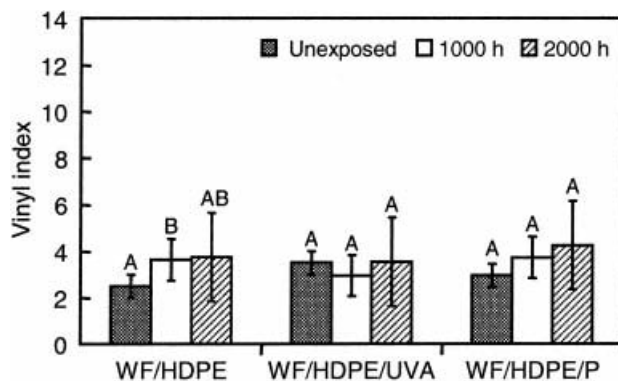

Figure 9 Vinyl index of WF/HDPE composites before and after accelerated weathering. Statistically significant differences within each group are represented with different letters.

Figure 10 Crystallinity of HDPE blends before and after accelerated weathering. Statistically significant differences within each group are represented with different letters.

Figure 11 Crystallinity of WF/HDPE composites before and after accelerated weathering. Statistically significant differences within each group are represented with different letters.
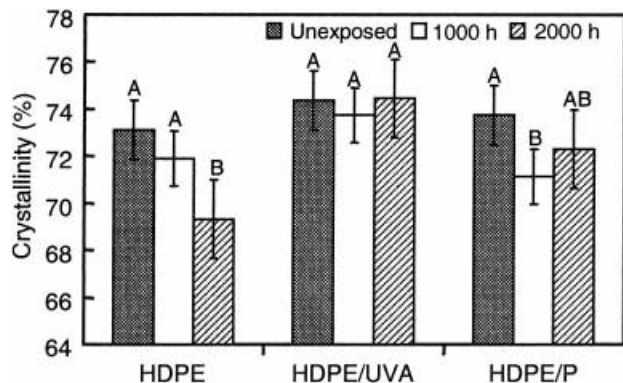
experienced a significant increase in the carbonyl index after the first 1000 h and second 1000 h of weathering. When UVA or P was added to protect the composite, the increase in the carbonyl index was significant only during the first 1000 h of weathering. This confirms that both UVA and P are effective at preventing some oxidation of composites that occurs as a result of UV exposure.

The carbonyl index was consistently higher for WF/HDPE composites than for their HDPE counterparts. This is explained by the fact that carbonyl groups are present in lignin, a component of WF; that is, WF has more chromophores than HDPE. Therefore, the addition of WF to an HDPE matrix is detrimental to weathering because increases in carbonyl groups in the composite in comparison with neat HDPE make it more susceptible to attack by UV light.

Vinyl group formation

The vinyl index appeared to increase for unstabilized neat HDPE after 1000 h of weathering and then did not significantly change between 1000 and 2000 h of weathering (Fig. 8). The formation of vinyl groups during photodegradation via a Norrish II reaction may be followed by a slower formation of secondary carbonyl groups, which could lead to a plateau during later exposure times.[9] When the photostabilizers UVA and P were added to HDPE, a significant increase in the vinyl index also occurred between 1000 and 2000 h of weathering. When the photostabilizer was added, the formation of secondary carbonyl groups could be delayed, and this resulted in a continued formation of vinyl groups. This would explain the lack of change in the vinyl index coupled with the significant increase in the carbonyl index for unstabilized HDPE between 1000 and 2000 h (Fig. 6). The delay of secondary carbonyl group formation also explains the significant increase in the vinyl index between 1000 and 2000 h,
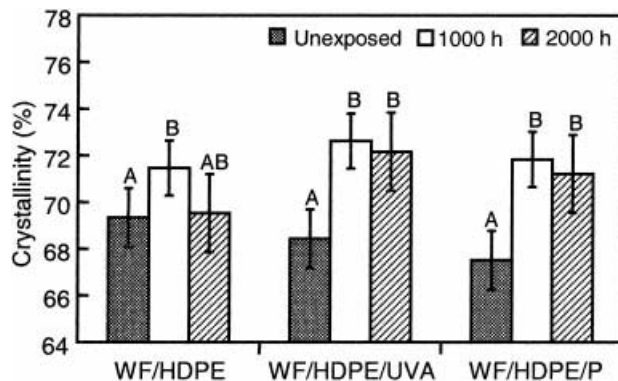
coupled with no significant increase in the carbonyl index for the photostabilized HDPE (Fig. 6).

For the WF/HDPE composites, the vinyl index remained relatively unchanged through 2000 h of weathering, regardless of whether a photostabilizer was added or not (Fig. 9). This, combined with the fact that the carbonyl index increased after weathering, may indicate that the formation in the carbonyl index stemmed primarily from the Norrish I reaction. This may mean that the Norrish II reaction is not as important a mechanism in the photodegradation of WF/HDPE as the Norrish I reaction.

Crystallinity changes

Crystallinity increases are an indication of chain scission because the smaller molecules undergo recrystallization. However, as chain scissions continue to occur, they can affect tie molecules, and this results in a decrease in crystallinity. The crystallinity percentage of unstabilized neat HDPE dropped after 1000 and 2000 h of weathering (Fig. 10). Between 1000 and 2000 h of weathering, this drop was significant. The drop in crystallinity corresponded to the formation of surface cracks (Fig. 2). Therefore, chain scission affected enough tie molecules to result in the degradation of crystallinity and the appearance of surface cracks. After 2000 h of weathering, the net change in crystallinity for HDPE protected with UVA or P was not significant. This confirms that UVA and P both have the ability to delay some chain scission.

For WF/HDPE composites, crystallinity increased after 1000 h of weathering, regardless of the use of stabilizers (Fig. 11). This may be evidence for the domination of chain scission in comparison with crosslinking in WF/HDPE composites. The crystallinity did not significantly change during the second 1000 h of weathering, regardless of the presence of a photostabilizer.

Although a wood fiber can act as a nucleating site for crystallization, it has been found to physically hinder crystal growth, resulting in lower polymer crystallinity. Colom et al.[21] studied the changes in the crystallinity of an HDPE matrix filled with aspen fiber and reported that increasing the fiber content from 10 to 14% decreased crystallinity.[21] A similar effect has also been 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 greater than 20%, crystallinity decreases as the fiber begins to hinder the molecular motion of polypropylene.[36] The addition of 50% WF to the HDPE matrix hinders the ability of HDPE to crystallize.[20] As a result, the crystallinity before weathering is generally higher for the HDPE blends than for the WF/HDPE composites. The increase in the composite crystallinity is probably due to secondary recrystallization.

Structure–property relationships

HDPE blends

First we consider unstabilized neat HDPE. The MOE (Fig. 4), carbonyl index (Fig. 6), and vinyl index (Fig. 8) all increased after 1000 h of weathering. The crystallinity, however, did not significantly change (Fig. 10). Although the increases in the carbonyl index and vinyl index confirmed that some chain scission had occurred, the shorter chains did not recrystallize. Therefore, crosslinking was probably the structural change responsible for the increase in MOE. Initial crosslinking may have hindered the chain mobility, resulting in increased MOE and interrupting the recrystallization process. The carbonyl and vinyl index results clearly showed that chain scission occurred. However, the effects could have been masked by the domination of the crosslinking reaction.

Between 1000 and 2000 h of weathering, there was a significant loss in the MOE and crystallinity, whereas the vinyl index remained the same. Chain scission continued as the carbonyl index increased. Therefore, the number of chain scissions may have been sufficient to begin to affect the tie molecules. Torikai et al.[13] showed that a small amount of oxidation products in polyethylene could cause great damage to the tie molecules, resulting in a breakdown of crystallization. This explains the significant loss in MOE, the drop in crystallinity, and the surface cracking apparent in the micrograph [Fig. 2(b)].

Next we consider stabilized neat HDPE: The addition of UVA or P to HDPE appeared to delay the degradation. The MOE increased after 1000 h of weathering for HDPE blends stabilized with either UVA or P (Fig. 4). As with the unstabilized HDPE, the carbonyl index also increased (Fig. 6) for the stabilized

blends, but the crystallinity did not (Fig. 10). As a result, crosslinking probably occurred in the first 1000 h of weathering for the stabilized HDPE blends. However, a drop in MOE and a drop in crystallinity were not apparent after 2000 h of weathering. This confirmed that the stabilizers aided in protecting against chain scission. Indeed, the carbonyl index did not significantly increase for the stabilized HDPE blends between 1000 and 2000 h of exposure. The number of chain scissions may not be sufficient to affect the tie molecules. The absence of surface cracks after weathering validated this assumption [Fig. 2(c,d)]. The degradation of MOE was effectively delayed, and the degradation would be expected to continue with increased weathering times.

Other researchers have studied the structure–property relationships of polyethylene after weathering and found similar results. Although chain scission may be an important mode of degradation, crosslinking begins to predominate as the temperature increases.[10,15] In accelerated weathering, the temperatures are elevated above the exposure temperatures of natural weathering. Hamid and Amin[12] studied both natural and accelerated weathering of LDPE. They concluded that the crosslinking and chain scission reactions take place simultaneously. Tidjani[14] added that under accelerated weathering, crosslinking reactions occur that reduce the concentration of free radicals taking part in the oxidation process. During the initial stages of weathering, the mechanisms of degradation result in a predominance of crosslinking reactions in comparison with chain scission.[14] A relatively high level of oxidation is necessary to overcome crosslinking.[16]

WF/HDPE composites

The WF/HDPE composite without any stabilizer experienced a small drop in MOE after 1000 h of weathering (Fig. 5). During that time, an increase in the composite carbonyl index (Fig. 7) and a corresponding increase in the HDPE crystallinity occurred (Fig. 11). Although we do not know the reasons for this difference in the degradation mechanism, we believe that the WF particles may physically hinder crosslinking in the composite during the initial stages of accelerated weathering. This would allow more chain scission and a corresponding increase in crystallinity. As a result, secondary crystallization of the shorter chains takes place, and the crystallinity increases. Crosslinking does not appear to be as important in the initial stages of weathering for WF/HDPE composites as it is for HDPE. Between 1000 and 2000 h of weathering, a larger drop in MOE occurred, the composite carbonyl index continued to increase, and the HDPE crystallinity did not significantly change. The increase in the carbonyl index was most likely due to degradation via the Norrish I reaction because the vinyl index did not

TABLE II
Linear Regression Parameters Relating Surface Chemistry Changes to MOE

Formulation	Regression parameter[a]	Vinyl index	Carbonyl index	Crystallinity
HDPE blends	m	0.024	0.0085	−0.0013
	b	0.080	0.90	1.0
	r^2	0.33	0.05	0.00027
WF/HDPE composites	m	−0.30	−0.049	−0.027
	b	4.1	3.6	5.0
	r^2	0.15	0.32	0.015

[a] The regression parameters satisfied $y = mx + b$, where x is the vinyl index, carbonyl index, or crystallinity and y is the MOE.

increase (Fig. 9). At this point, the oxidation was sufficient to affect the tie molecules, and this explains a portion of the loss in MOE.

During the first 1000 h of weathering, the HDPE crystallinity increased, yet the WF/HDPE composite MOE decreased. This was not expected and was most likely due to a degradation of interfacial properties as a result of exposure to moisture. During weathering, the samples cycled through environments of 35°C and 100% relative humidity during the water spray cycle and 40°C and 30% relative humidity during the dry cycle. Moisture has been shown to adversely affect the properties of wood–plastic composites.[27–32] HDPE composites filled with 40% wood fiber and exposed to 30% relative humidity for 2000 h experienced no loss in the flexural MOE. However, composites exposed to a water bath for 2000 h experienced a 39% loss in the flexural MOE.[29] Similarly, 65% wood-filled HDPE lost approximately 40% of its tensile modulus after being saturated with water.[37]

During the initial stages of weathering of WF/HDPE composites, the loss of properties caused by moisture exposure may have canceled out the gain resulting from increasing crystallinity. This would explain the modest loss after 1000 h of weathering. At 2000 h, a substantial decrease in the property values occurred. At this point, the HDPE matrix properties may have been degrading as a result of chain scission, and the composite properties may have been degrading because of moisture effects. For unprotected WF/HDPE composites, this corresponded to a 26% drop in MOE after 2000 h of weathering. The UVA and P provided some protection against MOE loss, resulting in 18 and 15% losses in MOE, respectively. Similarly to the trends with photostabilized HDPE blends, the photostabilizers effectively delayed some degradative properties of the weathering of WF/HDPE blends. However, the photostabilizers may have protected the HDPE matrix only and not influenced the drop in MOE because of moisture.

In addition, WF undergoes photodegradation, which results in the breakdown of lignin to form free radicals.[38] The free radicals may attack the polyethyl-ene chain, resulting in a deleterious effect of adding WF to polyethylene through accelerated chain scission in the polyethylene. Further research needs to be done to ascertain if both the loss of interfacial quality due to moisture sorption and the photodegradation of WF due to UV radiation contribute to the MOE loss of WF/HDPE composites.

To determine if any of the structural changes monitored directly influenced the flexural MOE, we performed three linear regressions. These related the carbonyl index, vinyl index, or crystallinity (x axis) to the flexural MOE (y axis). Table II shows the slope (m) and intercept (b) values of these regressions as well as the coefficient of determination (r^2). The low r^2 values clearly indicate that the carbonyl index, vinyl index, or crystallinity were not linearly related to MOE independently. This confirms that for polyethylene, the changes in the vinyl and carbonyl indices cannot be easily correlated with mechanical property reductions.[9] This appears to also be true for unfilled HDPE composites and WF/HDPE composites. The difficulty of developing a correlation relating structural changes to MOE may lie in the fact that the structural changes are surface phenomena, whereas the experimentally determined MOE is calculated for the whole thickness of a sample. There is probably a gradient in the sample ranging from undegraded material to degraded material.

CONCLUSIONS

Two main structural changes occur in HDPE after weathering. HDPE may undergo crosslinking because of carbonyl degradation via the Norrish I reaction, or HDPE may undergo chain scission because of carbonyl degradation via the Norrish I or II reaction. If chain scission occurs, HDPE can undergo secondary crystallization, which results in increased crystallinity. However, after sufficient photodegradation, the chain scissions become numerous enough to affect the tie molecules, and the crystallinity decreases. Both an increase in the crosslinking and an increase in the crystallinity result in an increase in MOE.

During the initial stages of exposure of HDPE to accelerated weathering, the structure of HDPE changes predominantly through crosslinking. This leads to an increase in MOE. As the exposure continues, chain scission becomes more important, and the photodegradation of the polymer continues to the point at which the tie molecules are affected. This leads to environmental stress cracking and a decrease in MOE. The addition of photostabilizers such as UVAs or pigments prevents a significant loss in crystallinity after 2000 h of exposure, and this in turn delays the appearance of surface cracking and consequent loss in MOE.

During the initial stages of exposure of WF/HDPE composites to accelerated weathering, crosslinking in the matrix does not predominate. It may be that the WF particles physically prevent the formation of crosslinked networks. Instead, the crystallinity of the polymer increases as chain scission occurs. However, the increased HDPE crystallinity does not translate into MOE increases for the WF/HDPE composites. It is suspected that the loss in MOE is due mainly to the effect of moisture. The MOE decreases during the second 1000 h of weathering, possibly because of a combination of chain scission of the tie molecules in the matrix, photodegradation of the WF, and degradation of the interface due to moisture. The addition of photostabilizers prevents a significant loss in crystallinity between 1000 and 2000 h of exposure. However, the MOE decreases during this time for the photostabilized composites, and this further indicates that the MOE loss is due to the degradative effect of moisture on the WF/HDPE interface.

Structural changes in the samples, carbonyl group formation, terminal vinyl group formation, and crystallinity changes cannot be reliably used to predict changes in MOE with a simple linear relationship. This indicates that the effects of crosslinking, chain scission, and crystallinity changes due to UV exposure as well as interfacial degradation due to moisture exposure are all important factors to consider for the weathering of WF/HDPE composites.

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