

Surface Characterization of Weathered Wood-Plastic Composites Produced from Modified Wood Flour

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Abstract

The effects of weathering on the surface properties of wood-plastic composites (WPC) were examined. High-density polyethylene (HDPE) based WPCs made from modified wood flour (untreated, extractives free, and holocellulose (delignified) fibers) were subjected to accelerated (xenon-arc) weathering. Colorimetry and Fourier-transform infrared spectroscopy were employed to monitor the color change and surface chemistries of the weathered WPC surface. The compositional change that occurred on the WPC surface was determined using pyrolysis GC-MS analysis. The study showed that longer exposure time caused higher oxidation, lower wood lignin and higher plastic content of the weathered WPC surface. From this study, the use of holocellulose fibers improved the weathering performance (color) of WPCs.

Introduction

Fading color and properties change of wood-plastic composites (WPC) during weathering is becoming a great concern both to the manufacturers and consum-

ers. It must be noted that several works have been conducted on weathering and durability issues of WPCs (Stark and Matuana 2004, Fabiyi et al. 2006). Weathering has been reported to cause an increase in surface oxidation (C=O), unsaturation (C=C), while wood lignin content decreased in WPCs (Stark and Matuana 2004, Fabiyi et al. 2006). Lignin has been suggested to be a great contributor to WPC color change during weathering (Fabiyi et al. 2006). There is little or inadequate information, however, about the effects of using extractive-free wood and holocellulose (lignin free) fiber as filler/reinforcement on the weathering of high-density polyethylene (HDPE)-based WPCs.

The use of cellulose or holocellulose fiber for WPC production may be a good alternative to minimize the problem of color change during weathering. The use of pure cellulose fibers over wood fiber in WPCs offers the benefit of higher thermal stability (up to 270°C) in that thermoplastics (e.g., nylon) can be used to obtain materials for structural applications (Sears et al. 2001). Therefore, cellulose fibers would be a suitable reinforcement for HDPE-based WPCs since they are commonly produced at temperatures below 200°C during pulping.

Background information on the chemistry of wood and plastic behavior during weathering may likely foster research toward production of WPCs with improved weathering performance (color). The determination of crystallinity could provide useful information about the plastic behavior during WPC weathering. Chemical changes that occur during weathering affect

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the overall properties of the polymer including melt flow/viscosity, molecular weight, and mechanical strength (Philip et al. 2004). Another reason for studying crystallinity is that it has been reported to be an indicator of polymer chain scission during photodegradation (Stark 2003). The goal of this study was to examine the effect of modifying wood fibers for use in WPCs with enhanced weathering performance. The accelerated weathered WPCs were assessed by several spectroscopic techniques and thermal analysis.

Materials and Methods

Extractive-free wood fiber was prepared from commercial wood flour (pine, 100 mesh, American Wood Fibers) by batch extraction using acetone. Holocellulose (lignin-free wood fiber) was prepared using an acidic-sodium chlorite solution at 70°C according to the method of Wise et al. (1946). The bleached (delignified) wood fiber was recovered by filtration through a polypropylene (PP) screen (100 mesh), then exhaustively washed with deionised water until a conductivity of 1.5 to 2.5 μS was reached (VWR conductivity meter) and then finally rinsed with acetone to aid in drying. The resultant holocellulose fiber (1.5% lignin) was then dried to achieve a yield of 67 percent.

WPCs irrespective of the wood flour (untreated, extractive-free wood, and holocellulose) were composed of 40 percent HDPE (Equistar petrothene, LB 0100-00) and 60 percent wood flour. The materials were weighed and premixed, then compounded and extruded on a 35-mm conical counter-rotating twin-screw extruder (Cincinnati-Milacron) to a profiled dimension of 9.5 by 38 mm. The temperatures of the barrel and die ranged from 150° to 190°C and were held constant throughout each extrusion run. The extruded profiles were machined to give equal exposure of wood and plastic at the WPC surface. Samples for xenon-arc weathering tests (Q-Sun) were cut into 5- by 38- by 102-mm specimens and subjected to accelerated weathering with water spray according to ASTM D6662.

Surface color of weathered WPC specimens (at three locations) was determined in accordance with ASTM 2244 using a StellarNet EPP2000 UV-Vis spectrometer (190 to 850 nm) using a krypton light source (SL1, Stellar Net) and a diffuse reflection fiber optic probe. The spectrometer SpectraWiz software transforms spectral data into CIE LAB color coordinates on the basis of a D65 light source (L^* , a^* , and b^*) (CIE 1986). Color coordinates for each sample, before and after exposure, were measured at three measurements per sample. Relative lightness (ΔL_{rel}) and color change (ΔE_{ab}) were calculated from initial and final values using the following equations:

$$\Delta L_{rel} = \frac{L^*_{final} - L^*_{initial}}{L^*_{initial}} \cdot 100 \quad [1]$$

$$\Delta E_{ab} = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad [2]$$

Surface chemical analysis performed on thin WPC slices (50 μm) (vacuum dried) from three samples were analyzed by Fourier-transform infrared (FTIR) spectroscopy (ThermoNicolet Avatar 370 spectrometer) in the attenuated total reflection (ATR) mode (SmartPerformer, ZnSe crystal). The absorbance spectra were mathematically ATR corrected using Omnic 7.0 software. For the quantitative analysis, the spectra were normalized and curve-fit using IGOR Prof 5.05 software (WaveMetrics, Inc). The area of each band found by curve fitting is mathematically computed by the software. The concentrations of the carbonyl (C=O) groups (degradation products) were estimated based on the Lambert-Beer equation (Equation [3]):

$$A = \epsilon bc \quad [3]$$

The determination of functional groups concentrations was thus limited to carboxylic acid and aldehydes groups. Therefore, there is need to account for other carbonyl groups that are present and wood degradation in weathered WPCs. Thus, carbonyl index (CI) and hydroxyl index (HI) were calculated as the ratio of the peak area (absorption) at 1800 to 1685 cm^{-1} and 3550-3080 cm^{-1} to peak area at 2916 cm^{-1} ($-\text{CH}_2-$ scissoring peak) for HDPE.

Wood-derived compounds (lignin and polysaccharides) were identified and quantified by pyrolysis GC-MS. Less than 100 mg of the sample was collected from the weathered ($\approx 50 \mu\text{m}$ thick) surface using a razor blade, ground, and vacuum dried prior to Py-GC-MS analyses. About 50 μg of each sample (two replicates) was then loaded into a quartz tube and pyrolyzed at 600°C in a SGE Pyrojector II (Ringwood, Australia), coupled to a PolarisQ GC-MS (ThermoFinnigan, San Jose, CA) instrument. Separation of the volatile products was achieved on a ZB-1 capillary column (30 m, 0.25 mm) using a temperature ramp from 40°C (2 min.) to 300°C (10 min.) at 5°C/min. Wood content in the weathered WPC samples was quantified by pyrolysis-GC-MS by developing a calibration curve from the total peak areas under the wood-derived peaks relative to the total peak areas under the polyethylene-derived peaks. Calibration curves were based on tests of a series of WPC formulations of known wood content: untreated and extractive-free pine. Percentage wood content of 0, 10, 20, 40, 60, and 100 percent for HDPE-based WPC produced from untreated and extractive-free pine wood was employed (Schauwecker et al. 2006).

HDPE was extracted from weathered WPC surfaces (500 mg) using 50 mL of 1,2,4-trichlorobenzene (TCB) with microwave (Sanyo, 600-700 W) heating for 2 to 3 minutes. The HDPE solution was filtered through cotton wool and concentrated to dryness leaving a plastic film. The crystallinity of TCB extracted HDPE (5 to 7 mg) from the weathered WPC surface layer was analyzed by differential scanning calorimetry (DSC) according to ASTM D3418 (50 to 160°C at 10°C/min., held isothermally for 10 min., cooled to 50°C at -10°C/min.). The degree of crystallinity was calculated from the heat of fusion corresponding to a perfect PE (293.6 J/g).

Results and Discussion

Relative lightness (ΔL_{rel}) and color change (ΔE_{ab}) of xenon-arc weathered WPCs made from untreated, extractive free, and holocellulose fibers are shown in **Figure 1**. The ΔL_{rel} and ΔE_{ab} for all of the HDPE-based WPCs increased upon weathering until 1,200 hours. The ΔL_{rel} and ΔE_{ab} for WPC produced from untreated and extractive-free pine wood were not significant ($\alpha = 0.05$). WPCs produced from holocellulose fiber had the lowest ΔL_{rel} and ΔE_{ab} compared to pine and extrac-

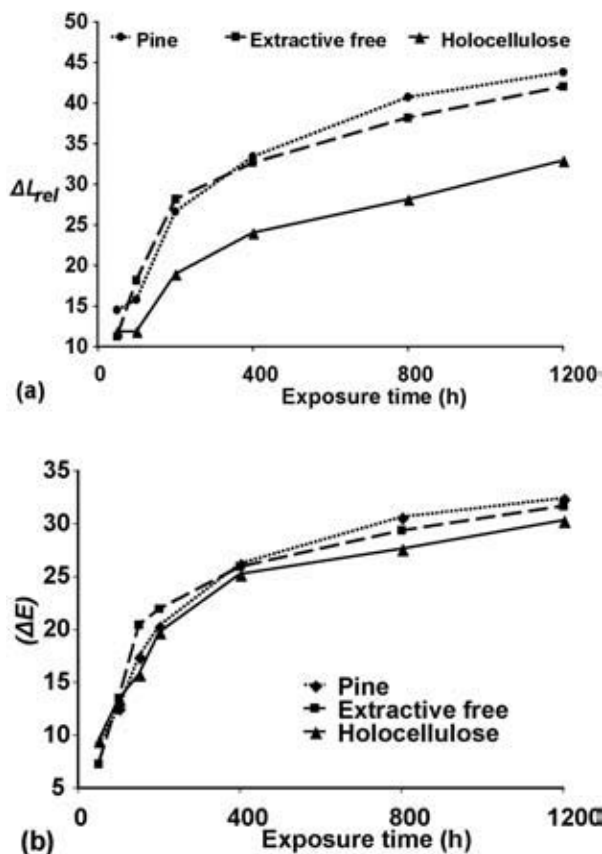


Figure 1. ~ Effect of xenon-arc weathering on (a) ΔL_{rel} and (b) ΔE_{ab} of WPCs made from different modified wood (15 replicates per each WPC sample).

tive-free wood-based WPCs. From these results, it seems that wood lignin as well as wood extractives may contribute to coloration of WPCs. These findings are in agreement with the literature on the weathering of wood (Feist and Hon 1984, Hon 2001). Fabiyi et al. (2006) had previously observed that the higher the delignification in weathered WPCs, the greater the color changes.

FTIR spectroscopy of WPCs revealed that changes in functional groups occurred during xenon-arc weathering (**Fig. 2**). The spectral features assigned to wood (C-O at 1015 and 1050 cm^{-1} and OH at 3080 to 3500 cm^{-1}) regions decreased upon weathering (Faix 1992). In addition, lignin assigned peak (1512 to 1508 cm^{-1}) decreased in intensity as a function of weathering time for pine and extractive-free pine WPC. More importantly, the bands between 1680 and 1800 cm^{-1} assigned to the carbonyl functional groups increased upon weathering which indicates that oxidation occurred with prolonged exposure time (**Fig. 2**) (Mayo 2003). The concentration of carboxylic acids (1715 cm^{-1}) and esters and aldehydes (1735 cm^{-1}), determined using Equation [3], increased upon WPC weathering (**Fig. 3**).

Indices of carbonyl (1680 to 1800 cm^{-1}) and hydroxyl (3080 to 3500 cm^{-1}) were computed for further comparison purposes. The results show that carbonyl index increased while hydroxyl index decreased upon extended exposure time in xenon-arc weathering regimes (**Fig. 4**). The decrease in hydroxyl index indicates that wood was lost upon extended exposure time during weathering.

Pyrolysis gas chromatograms of pine WPCs are shown in **Figure 5**. Molecular fragments from both wood and plastic were obtained from the pyrolyzed samples. The wood-derived compounds were clearly

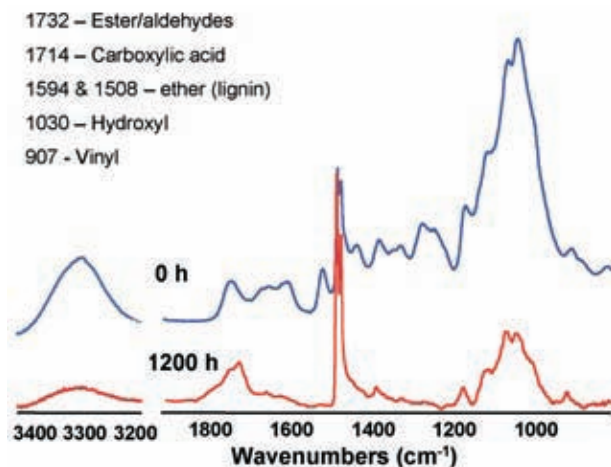


Figure 2. ~ FTIR spectra of control and 1,200 hours xenon-arc weathered pine WPC.

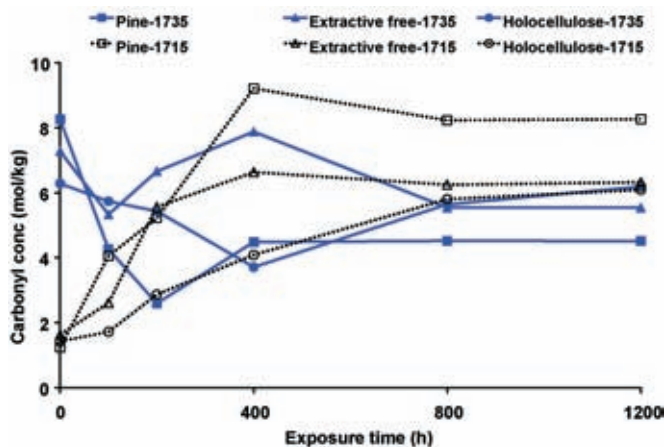


Figure 3. ~ Effect of xenon-arc accelerated weathering on the concentration of carboxylic acids (1715 cm^{-1}) and esters/aldehydes (1735 cm^{-1}) present in WPCs made from the various modified wood fibers.

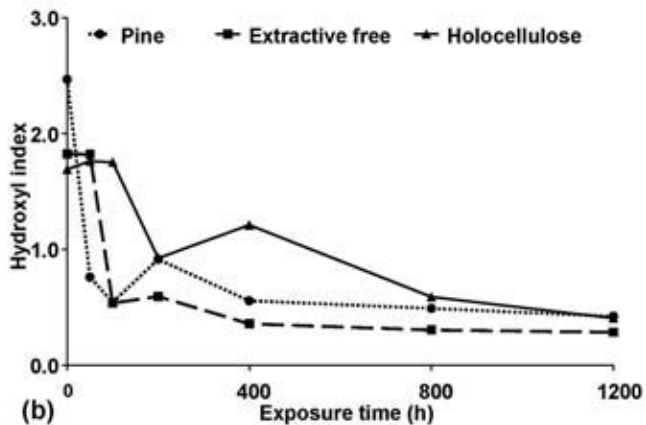
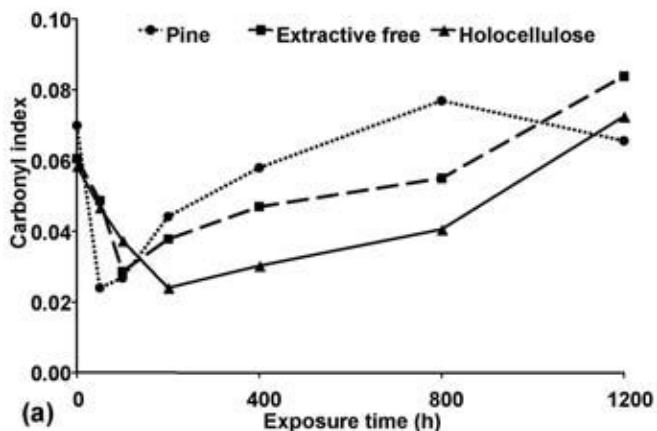


Figure 4. ~ Effect of xenon-arc weathering on (a) carbonyl and (b) hydroxyl index of WPCs made from the various modified wood fibers.

identified from the HDPE-derived compounds (Meier and Faix 1992, Fabiyi et al. 2006, Schauwecker et al. 2006). Wood content decreased from 60 to 38 percent

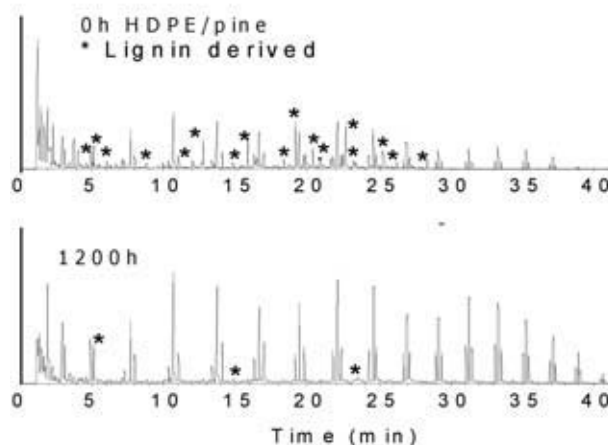


Figure 5. ~ Gas chromatograms of (top) unweathered and (bottom) 1,200 hours xenon-arc weathered HDPE-pine WPC.

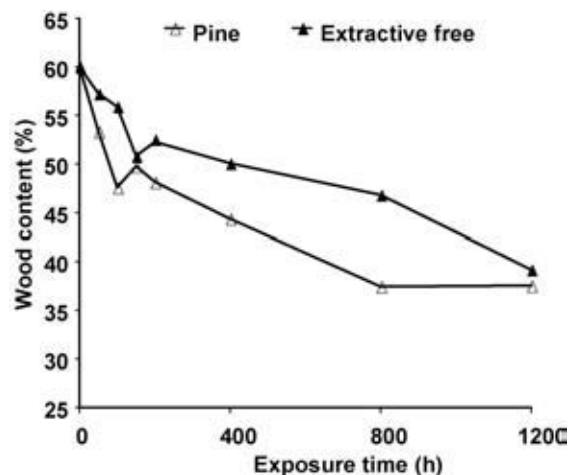


Figure 6. ~ Effect of xenon-arc weathering on wood content of HDPE-based WPC.

and 60 to 39 percent for HDPE/pine and HDPE/extractive-free pine composites, respectively, during xenon-arc weathering (Fig. 6). These data support the evidence from both color measurement and FTIR spectroscopic analysis that there was no difference between the pine and extractive-free pine wood-based WPC.

DSC was employed to determine the percentage crystallinity of HDPE in weathered WPCs. In order to determine the crystallinity of the plastic, its content is required within the WPC to back calculate. An alternative approach is to extract the plastic from the weathered WPC surface. The HDPE in weathered WPCs experienced an increase in percent crystallinity during xenon-arc weathering (Fig. 7). These observations agree with the report of the other study conducted by Stark and Matuana (2004). In the report, the increase in crystallinity was attributed to PE chain scission during photodegradation. Further degrada-

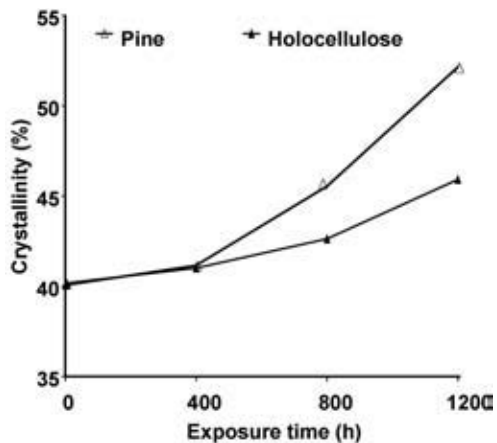


Figure 7. ~ Effect of xenon-arc weathering on HDPE crystallinity of HDPE-based WPC.

tion may be initiated by the free radicals and shorter chain molecules generated during weathering. Chain scission results from via Norrish I and II reactions reduces the density of entanglements in the amorphous phase thereby allowing lower molecular weight PE molecules to crystallize due to higher mobility (Jabarin and Lofgren 1994).

Conclusions

In this study, the effects of weathering on the color and chemical changes of WPCs made from modified wood were examined. The general trend of WPC weathering shows that color changed (lighter) and surface oxidation increased upon longer exposure. During WPC weathering, the wood content at the surface decreased. During WPC weathering, the polymer matrix crystallinity increased upon longer exposure time and this was due to a decrease in HDPE molecular weight. From these results, delignified wood fiber (holocellulose) based WPCs show good color weathering performance for HDPE-based WPCs. Dimensional instability and biodegradation, however, may be associated problems with the use of holocellulose-based WPCs. Therefore, research should focus on producing holocellulose-based WPCs with resistance to water and biodegrading agents.

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