

Effect of Highly Degraded High-Density Polyethylene (HDPE) on Processing and Mechanical Properties of Wood Flour-HDPE Composites

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ABSTRACT: The influence of highly degraded high-density polyethylene (HDPE) on physical, rheological, and mechanical properties of HDPE-wood flour composites was studied. For this purpose, the virgin HDPE was subjected to accelerated weathering under controlled conditions for 200 and 400 h. The virgin and exposed HDPE and pine wood flour were compounded to produce wood flour-HDPE composites. The results showed that the accelerated weathering highly degraded HDPE. Degradation created polar functional carbonyl groups and also produced extensive cross-linking in HDPE and consequently poor processibility. The interruptions in the flow characteristics of the degraded HDPE potentially caused processing hurdles when using them for extrusion or injection molding manufacturing as only small part (10%) of virgin HDPE could be replaced by highly degraded HDPE for wood flour-HDPE composite manufacturing. The mechanical properties of composites containing highly degraded HDPEs were similar to the composites with virgin HDPE and in some cases they exhibited superior properties, with the exception being with the impact strength. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

KEYWORDS: crosslinking; Composites; degradation

Received 7 April 2012; accepted 14 January 2013; published online 00 Month 2013

DOI: 10.1002/app.39021

INTRODUCTION

Plastic waste is one of the major components of global municipal solid waste (MSW) accounting for 12.3% of the annual 243 million tons generated in the USA during 2009.¹ Most importantly, only 7.1% of 29.8 million tons of plastic waste was recycled.¹ Problems with separating and contaminants have limited recycled plastics in many processing environments, but continued efforts to improve cleaning and separation techniques have made recycled plastics a more viable alternative to virgin plastics. HDPE comprises 17.8% of 30 million tons plastic waste generated in the USA during 2008.²

The utilization of recycled plastics in wood plastic composites (WPCs) is a feasible market for recycled plastics. Many current WPC manufacturers utilize postindustrial recycled plastics,³ while a few also use postconsumer plastics waste streams. WPCs can commonly accept a wide range of polymer types and grades, making them an ideal candidate for recycled plastics.

The use of recycled and waste plastics has been studied by several researchers and different results have been reported.^{4–12} Because recycled plastics may be obtained from different sources that may be exposed to different storage and reprocessing con-

ditions, they may show different performances depending on their degradation level.¹³

Plastic degradation is a problem that frequently occurs when a polymer is submitted to a process, repeated processes, or service (such as long-term exposure to sunlight that reflects weathering). Some researchers have shown the influence of repeated melt blending on WPCs^{13–16} however; the influence of weathered plastics on WPC product and processing performance has not been addressed so far.

During weathering, polymers are exposed to UV light, heat, and moisture, causing thermo-and/or photo-oxidation to occur. This photochemical degradation changes the chemical, rheological, thermal, physical, and mechanical properties of most thermoplastic polymers.¹⁷ The degradation level depends on irradiation power of UV light, exposure duration, moisture content, temperature, and also the type of polymer.¹⁷ Although several researches have been done to study the effect of weathering on degradation of HDPE,^{18–21} the effect of such changes on physical and mechanical properties of WPCs has been limited in the literature. For this reason the aim of this study was to find the influence of degraded HDPE under weathering exposure on processing and mechanical properties of wood flour-HDPE composites.

In this research the influence of accelerated weathering of plastics on physical and mechanical properties of resultant WPCs has been considered. Among the various plastics in MSW, high-density polyethylene (HDPE) was selected because it is widely used in WPCs manufacturing and comprises a main part of recycled plastics. HDPE comprises 17.8% of 30 million tons plastic waste generated in the USA during 2008.²

EXPERIMENTAL

Materials

The copolymer HDPE was grade HP54-60 FLAKE and was supplied from Bamberger Polymer (NY). The density and melt flow index (MFI; temperature = 190°C, load = 2.160 kg) of HDPE were 0.954 g/cm³ and 0.500 g/10 min, respectively. A commercial grade 60 mesh pine (*Pinus strobus*) wood flour was supplied from American Wood Fibers (WI, USA).

Preparing the HDPE Sheet

An 18 mm twin-screw corotating parallel extruder (A Leistritz laboratory extruder) was used to prepare HDPE sheets of 2 mm thickness. The temperature in the extruder was varied from 160 to 165°C and the temperature of the sheet die was set at 155°C. The hot sheets were cooled and then the specimens (6 × 11 cm²) for accelerating test were cut from them. Also 10 tensile samples were prepared to study the effect of weathering on tensile properties of HDPE.

Accelerating Ageing

The accelerating ageing test was carried out in a UV test chamber (Atlas, UV2000) using UVB 313 fluorescent bulbs. The tests are intended to reproduce the weathering effects that occur when material are exposed to sunlight, moisture and temperature. The HDPE sheets and tensile samples were put in sample holders and subjected to alternating UV light (20 h at 80°C) and moisture condensation (4 h at 50°C) according to cycle 5 of ASTM D154-06.²² The samples were submitted to ageing for 200 and 400 h.

Analytical Measurement

Fourier transform infrared (FTIR) spectrometry was used to identify the chemical changes in and degradation (photooxidation) in the HDPE structure before and after weathering exposure. FTIR spectra were recorded using a NICOLET-670 FTIR spectrometer in the transmission mode with 32 scans and 8 cm⁻¹ resolution over the spectral range 4000–400 cm⁻¹.

Differential scanning calorimetry (DSC) was carried out using 7–8 mg of the ground HDPE materials with a Mettler Toledo DSC-822 analyzer (Tokyo, Japan). All the samples were heated from 40 to 170°C at the rate of 10°C/min in nitrogen atmosphere, held at 170°C for 5 min, then cooled down to 40°C at 10°C/min. This procedure was done twice and the second run was used for analysis. The degrees of crystallinity (X) were calculated from the measured heat of fusion (ΔH) calculated from the following equation:

$$X (\%) = \frac{\Delta H_f}{\Delta H_f^c} \times 100 \quad (1)$$

where ΔH_f is the heat of fusion of the virgin HDPE and exposed HDPEs. ΔH_f^c (293 J/g) is the heat of fusion of 100% crystalline HDPE.²³

Table I. Composition of Evaluated Formulations (wt %)

Formulations	Virgin HDPE (%)	Wood flour (%)	Exposed HDPE (%)	
			200 h	400 h
A	60	40	0	0
B1	55	40	5	0
B2	50	40	10	0
B3	40	40	20	0
B4	30	40	30	0
C1	55	40	0	5
C2	50	40	0	10
C3	40	40	0	20
C4	30	40	0	30

The degree of cross-linking was evaluated through the measurement of the gel content in exposed HDPE. The gel contents (insoluble fraction) of virgin and exposed HDPE were measured based on the procedures outlined in ASTM D2765-01.²⁴ The samples were ground into powder in a Wiley mill to size between 30 and 60 mesh. The powder samples were weighted and then immersed in hot xylene, which is an accepted solvent of the noncrosslinked fraction of HDPE. Butylated hydroxyl toluene was used as an antioxidant to inhibit further cross-linking of the samples.

Capillary rheometer (Rheometric Scientific Acer 2000) equipped with a 2 mm diameter capillary die with a L-to-D ratio of 15 and a flat entry was used to study the shear viscosity of virgin and exposed HDPE. All measurements were done at 190°C.

Compounding and Preparing the Composites

Virgin and exposed HDPE and pine wood flour were compounded into a laboratory torque rheometer (Haake Rheomix, Karlsruhe, Germany) and melt processed at 170°C while the rotor speed was set at 20 rpm, and continuous torque was recorded for 10 min. The composition of the mixture is presented in Table I.

The melt compounds were removed from the rheometer and cooled to room temperature and were then granulated. The milled material was injected molded in a Sumitomo machine (Model SE500) to produce a dog bone-shaped tensile specimen and flexural bar specimen. The mold nozzle temperature was 205°C and mold temperature was 95°C.

Mechanical Properties of the Composites

Tensile properties including tensile modulus and strength of virgin and exposed plastic and also the composites were measured according to ASTM D638-10 specifications²⁵ by using an INSTRON-4466 universal machine. Three-point loading flexural test was done according to ASTM D790-10²⁶ and flexural modulus and strength of the composites were calculated. Both tests were performed by using a screw-driven universal test set-up. At least six replicates of each formulation were tested for each test.

Notched impact tests were carried out according to ASTM D256-10 specifications²⁷ with an Izod testing machine. At least

Table II. Gel Content, Tensile Strength, and DSC Properties of HDPEs

HDPE	Gel content (%)	Melting temperature (°C)	Heat of fusion (J/g)	Crystallinity (%)	Tensile strength (MPa)
Virgin	0.1	132.5	171.1	58.4	22.8 (0.2)
200 h exposure	63.6	130.7	143.4	48.9	18.5 (0.6)
400 h exposure	58.7	132.2	155.1	52.9	10.1 (1.0)

The numbers in parenthesis are standard errors.

six replicates of each formulation were tested for each test. Before the tests, all samples were conditioned for 48 h in an environmentally controlled room maintained at $(23 \pm 2)^\circ\text{C}$ and $(50 \pm 5)\%$ relative humidity.

RESULTS AND DISCUSSION

Table II presents the effect of accelerated weathering on gel content of HDPE. The gel content strongly increased after 200-h exposure time and then slightly decreased after 400 h. The gel content (insoluble fraction) can be attributed to the cross-linking that occurs during the degradation process with a higher gel content indicating a higher level of cross-linking. Cross-linking prevents the mobility of molecular chains causing an interruptive melt-flow behavior. It can also change the nature of HDPE from thermoplastic to thermoset. Figure 1 shows the injection molded specimens of virgin and exposed HDPE at the same processing conditions. The exposed HDPE did not exhibit a typical thermoplastic melt flow and failed to fill the mold.

DSC curves of virgin and exposed HDPEs are shown in Figure 2(a). The effect of exposure time on thermal properties of HDPE is also shown in Table II. It can be seen that the melting temperature remain constant during weathering exposure. Table II also shows that there is a drop in the heat of fusion after exposure. Figure 2(b) shows the DSC cooling curves of virgin and exposed HDPE. A small shoulder at 83°C , broader curves and a

reduction in the crystallinity temperature can be seen for both exposed HDPEs. These results are attributed to chain scission and secondary crystallization of the short molecular due to UV degradation. Similar results were reported by Valadez-Gonzalez et al.¹⁸ and Gulmine et al.¹⁹ for HDPE. Table II shows that the exposed HDPEs exhibit lower crystallinity, and higher decrease was observed for HDPE exposure at 200 h. Reduction in crystallinity can be related to cross-linking which was took place in exposure HDPEs because the crystallinity of the solid polymer decreases with increase in the cross-linking.²⁸ Also oxidation damage can 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 resulting in a breakdown of crystallization.¹⁶ Valadez-Gonzalez et al.¹⁸ reported higher crystallinity for exposed HDPE to UVB 313

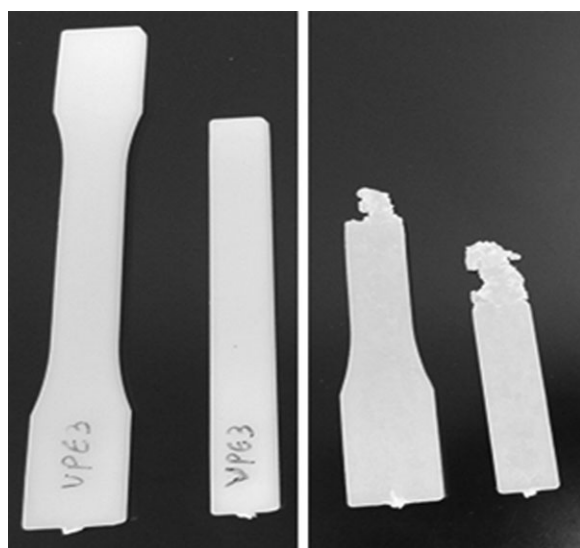


Figure 1. Injection molded specimens of virgin HDPE (left) and exposed HDPE after 200 h (right).

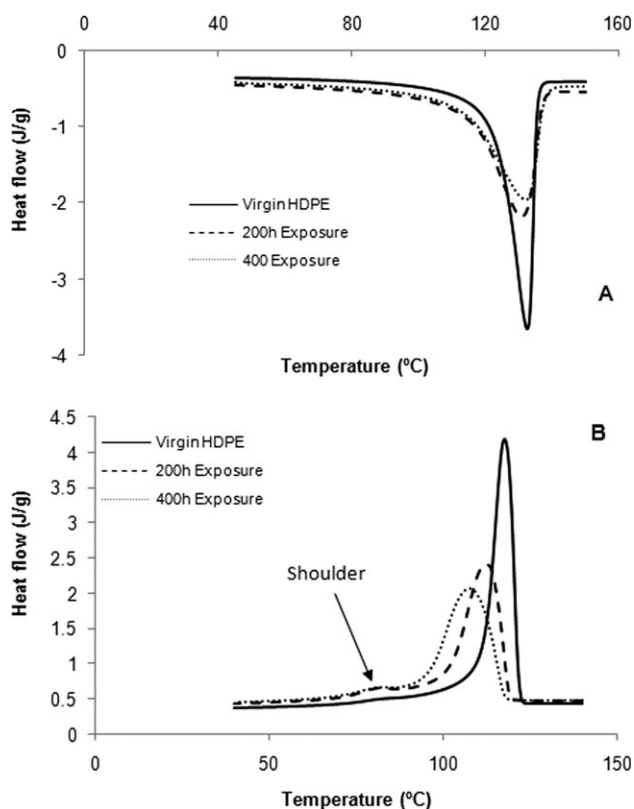


Figure 2. DSC thermograms of virgin and exposed HDPE: (a) heating curve, (b) cooling curve.

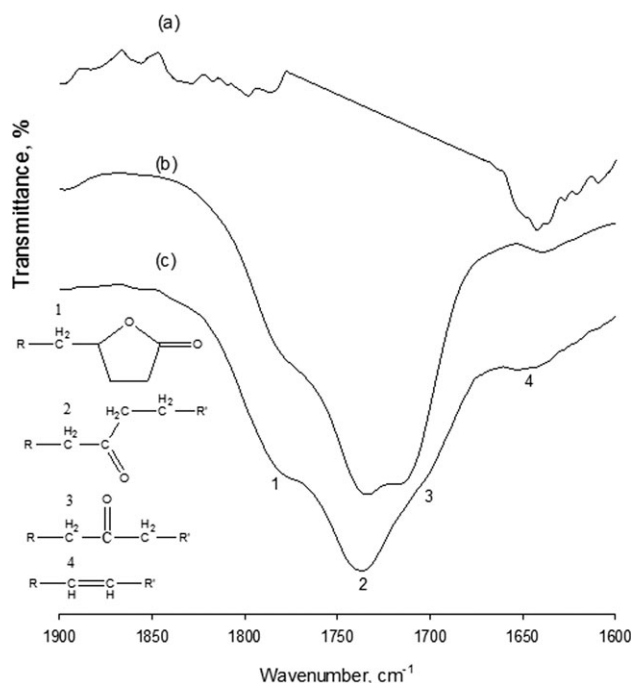


Figure 3. FTIR spectra of virgin HDPE (a) and exposed HDPEs after 200 h (b) and 400 h (c) at carbonyl region.

lamps during 600 h accelerated weathering test. The difference between these results and our result can be related to higher temperature (80°C) that we used. Temperature has very strong influence on the results of weathering by stimulating the effect of UV.²⁹ Previous studies on polyethylene found a small increase by 1°C caused 8% increase in reaction rate of weathering.³⁰ At higher temperature of weathering (in accelerated exposure), cross-linking begins to predominate, while chain scission may be an important mode of polyethylene degradation.¹⁶

The FTIR spectra of the HDPEs indicate that some peaks appeared or disappeared, and the intensity of others increased or decreased with increasing exposure time. The changes in HDPE after accelerated weathering have been studied by following carbonyl and vinyl group formation in HDPE. The new peak stretching at 1700–1780 cm^{-1} is attributed to carbonyl region (Figure 3). It can be seen that a sharp peak at 1736 cm^{-1} and two shoulder peaks around 1720 cm^{-1} and 1780 cm^{-1} are formed in carbonyl region which can be assigned to C=O stretching vibrations in esters, ketone and γ -lactones, respectively.^{18,31} The formation of carbonyl region during accelerated weathering has been reported by other researchers.^{18–20,31,32} Carbonyl groups are postulated to be the main responsible for the photo-chemical-induced degradation reactions of UV-exposed polymers.²⁹ In order to quantify the rate of degradation, the carbonyl index was measured according to the method described by Gulmine et al.¹⁹ The carbonyl index was 1.29 and 1.50 for the specimens exposed to 200 and 400 h of accelerated weathering, respectively. With a higher exposure time, a higher carbonyl index was found indicating more degradation of the HDPE specimens. Similar results have been reported by Gulmine et al.,¹⁹ Stark and Matuana²⁹ and Hoekstra et al.³³ for

HDPE. The increase in carbonyl index is proportional to the number of chain scissions that takes place in HDPE after accelerated weathering.¹⁶

Since increase in carbonyl index is a witness of chain scission in exposed HDPE, so it was expected that the vinyl group concentration increases after accelerated weathering. Indeed the formation of vinyl groups is also an indication of polymer chain scission.³⁴ Increase in vinyl group concentration during natural and accelerated weathering has been reported by several authors.^{21,29,31,32} Figure 4 shows a stretching band around 920 cm^{-1} in virgin HDPE which can be assigned to end-chain vinyl ($-\text{CH}=\text{CH}_2$). The other researchers has been reported the formation this peak around 910 cm^{-1} in UV exposed HDPE.^{21,29,31,32} After 200 h exposure, the intensity of peak around 920 cm^{-1} slightly decreased and it almost disappeared at 400h exposure time. Figure 3 also shows a bands at 1642 cm^{-1} in unexposed HDPE which is attributed to middle bond vibration in vinyl group ($-\text{R}'\text{CH}=\text{CHR}$).^{21,35} The intensity of this also decreased in HDPE exposed to 200 h accelerated weathering. Higher decrease in intensity was observed for higher exposure time (400 h). The decrease in vinyl group can be attributed the formation of considerable cross linking in exposed HDPE. The vinyl groups were consumed by cross linking reactions. Gulmine and Akcelrud³² also reported lower vinyl indices for crosslinked polyethylene. Stark and Matuana²⁹ and Fabiyi et al.³⁵ indicated that with longer exposure time, vinyl concentrations began to decrease in neat HDPE, HDPE- and PP- based WPC composites. It needs to mention that the formation polar functional group (such as carbonyl groups) can significantly improve the compatibility between HDPE and wood flour. Li

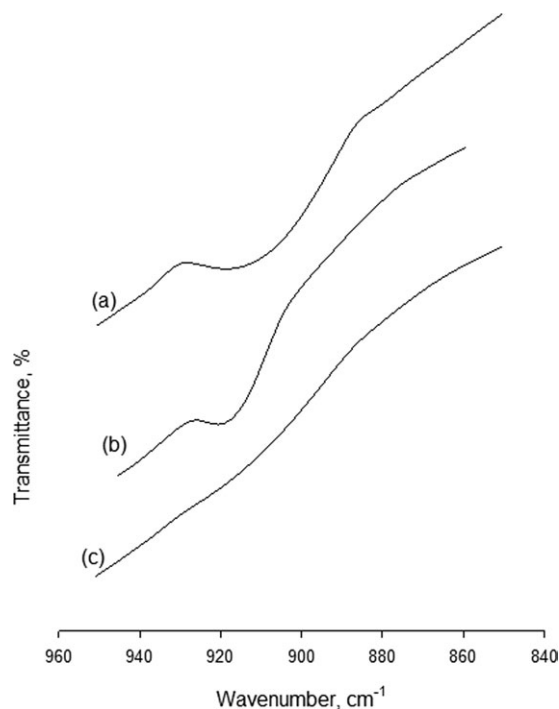


Figure 4. FTIR spectra of virgin HDPE (a) and exposed HDPEs after 200 h (b) and 400 h (c) at 920 cm^{-1} .

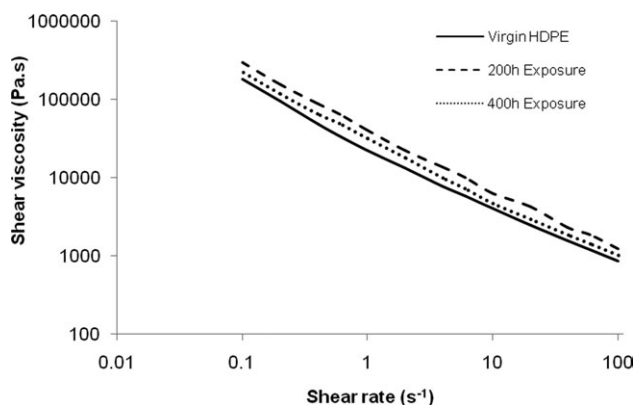


Figure 5. Shear viscosity vs. shear rate curves for virgin and exposed HDPE.

et al.³⁶ showed a markedly improve in interfacial interaction between sericite and HDPE in UV irradiated HDPE/sericite composites. They indicated that no cross-linking is induced in HDPE in short time UV exposure.

Figure 5 shows the shear viscosity vs. shear rate curves for virgin and exposed HDPE utilizing capillary rheometry. The viscosity of the exposed HDPE after 200- and 400-h exposure time is slightly higher than that of virgin HDPE. Although the viscosity exhibits only a small increase, a significant difference was observed at extruded surface of HDPEs after accelerating weathering. The virgin HDPE exhibited a continuously smooth surface while the exposed HDPE had a noncontinuous rough or torn surface.

The strain–stress curves of virgin and exposed HDPEs are shown in Figure 6. The reduction of displacement prior to failure also corresponds to a much more brittle material behavior, which is also indicative of degradation of exposed HDPE. By cross-linking the restriction imposed on elongational behavior of the polymer increases. This restriction is due to smaller length of segments available for stretching and lesser the probability of chain slippage resulting in decrease in elongation at break.³⁷ An obvious decrease in tensile strength due to the accelerated weathering procedure is shown in Figure 6. From

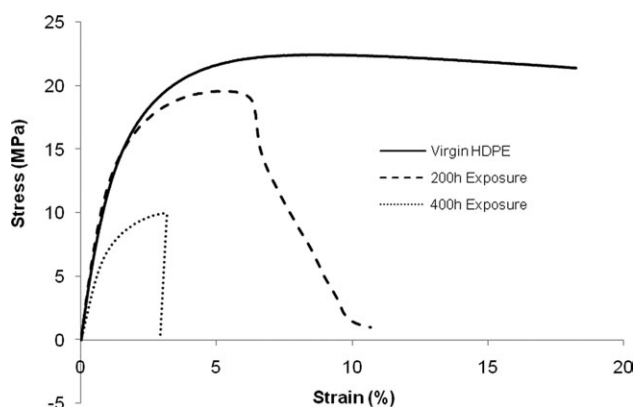


Figure 6. The stress–strain curves of studied materials.

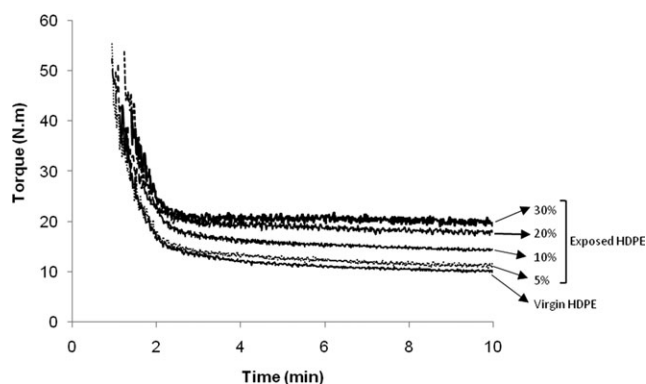


Figure 7. Effect of exposed HDPE (after 200 h) on torques of wood flour-HDPE blends.

the results, tensile strength of HDPE was decreased 18.9% and 55.7% after 200- and 400-h weathering, respectively.

Figure 7 demonstrates the influence of exposed HDPE at 200 h on mixing behavior of a wood flour-HDPE blend. Adding exposed HDPE increased the stabilized torque of the blended materials. The increased torque with degradation is likely due to the increase in viscosity, as observed in the capillary rheometry results. Similar results were observed for exposed HDPE at 400 h.

Figure 8 shows the images of the flexural and tensile samples (containing 200-h exposed HDPE) prepared by injection molding. By increasing the exposed HDPE content to 20% or higher, the mold could not be filled by the wood flour-HDPE blends. The lack of mold filling was accentuated with higher degradation (400 h) HDPE. This phenomenon indicates the poor processibility of highly degraded HDPE. Although the processing characteristics were reduced with the exposed HDPE, the flexure and tensile performance was relatively consistent within the test matrix.

Flexural modulus and strength of the wood-HDPE composites are presented in Table III. Statistical analysis showed that

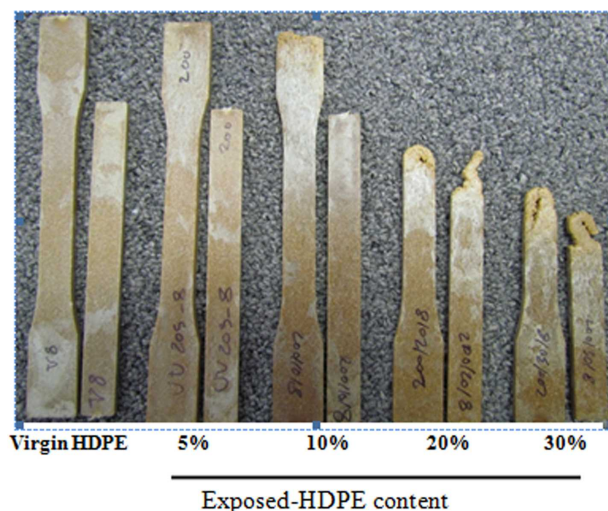


Figure 8. The flexural and tensile samples (containing different content of HDPE exposed at 200 h) prepared by injection molding. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

Table III. Mechanical Properties of the Composites Containing Degraded HDPE

Composites samples code	Flexural properties (MPa)		Tensile properties (MPa)		Notched impact strength (J/m ²)
	Modulus	Strength	Modulus	Strength	
A	2267.1 (40.0)	34.1 (0.4)	204.4 (5.7)	23.3 (0.2)	3869.2 (143.0)
B1	2209.2 (54.4)	36.1 (0.7)	201.6 (5.5)	24.7 (0.2)	3603.4 (194.7)
B2	2329.0 (76.0)	36.2 (0.6)	183.8 (2.5)	23.1 (0.2)	3195.1 (267.6)
C1	2357.3 (67.3)	37.1 (0.3)	210.4 (6.5)	24.9 (0.1)	3697.4 (231.9)
C2	2337.3 (44.2)	40.7 (0.6)	191.7 (3.4)	23.3 (0.3)	2806.1 (185.8)

The numbers in parenthesis are standard errors.

degradation of the HDPE (at 200 and 400 h) had no significant effect on flexural modulus of the composites. Adding the degraded HDPE showed a slight, but significant increase in the flexural strength of the composite, with the composites containing 10% exposed HDPE after 400 h exposure exhibited the maximum flexural strength.

Table III also shows the effect of exposed HDPE on tensile properties of the composites. With adding 5% exposed HDPE, tensile strength of composites significantly increased, but adding 10% exposed HDPE significantly decrease the tensile strength as much as the tensile strength of composites containing virgin HDPE. Tensile modulus also was significantly changed with addition of degraded HDPE. The composites containing 10% exposed HDPE exhibited minimum tensile modulus.

The influence of exposed HDPE on notched impact strength of the composite is given in Table III. Adding degraded HDPE decreased the impact strength of the composites and minimum impact strength was observed for composites containing 10% exposed HDPE after 400 h. Lower impact strength has been reported by several researchers in composites containing recycled HDPE^{4,5} and polypropylene.^{12,15} Highly cross-link area in degraded HDPE causes poor processibility and likely some non-molten regions (due to the thermoset nature of crosslinked HDPE) in virgin HDPE matrix within the composites, since crosslinked HDPE does not melt.³⁰ This non-molten area can be location of stress concentration which will affect on composite properties, especially on impact strength.

CONCLUSIONS

The physical, chemical mechanical, and rheological properties of highly degraded HDPE in accelerated weathering are quite different from virgin HDPE. Degradation created polar functional carbonyl group such as C=O, C—O, and C(=O)O and also produced extensive cross-linking in HDPE. Cross-linking prevents the mobility of molecular chains causing an interruptive melt-flow behavior. The interruptions in the flow characteristics of the degraded HDPE potentially caused processing hurdles when using them for extrusion or injection molding manufacturing as only small part (10%) of virgin HDPE could be replaced by highly degraded HDPE for wood flour-HDPE composite manufacturing. The mechanical properties of composites containing highly degraded HDPEs were similar to the composites with virgin HDPE and in some cases they exhibited

superior properties, with the exception being with the impact strength.

REFERENCES

1. U.S. Environmental Protection Agency, 2010. Municipal solid waste in the United States: 2009 Facts and figures (EPA530-R-10-012). Available at: <http://www.epa.gov/wastes/nonhaz/municipal/pubs/msw2009rpt.pdf>.
2. U.S. Environmental Protection Agency, 2009, Municipal Solid Waste Generation, Recycling, and Disposal in the United States Detailed Tables and Figures for 2008, Available at: <http://www.epa.gov/wastes/nonhaz/municipal/pubs/msw2008data.pdf>.
3. Winandy, J. E.; Stark, N. M.; Clemons, C. M. Consideration in recycling of wood plastic composites, 5th Global Wood and Natural Fibre Composites Symposium. **2004**. April 27–28, Kassel, Germany.
4. Yam, K. L.; Gogai, B. K.; Lai, C. C.; Selke, S. E. *Polym. Eng. Sci.* **1990**, *30*, 693.
5. Kamdem, D. P.; Jiang, H.; Cui, W.; Freed, J.; Matuana, L. M. *Compos. Part A: Appl. Sci.* **2004**, *35*, 347.
6. Kazemi-Najafi, S.; Hamidinia, E.; Tajvidi, M. *J. Appl. Polym. Sci.* **2006**, *100*, 3641.
7. Jayaraman, K.; Bhattacharyya, D. *Resour. Conser. Recycl.* **2004**, *41*, 307.
8. La Mantia, F. P.; Morreale, M. *Polym. Eng. Sci.* **2006**, *46*, 1131.
9. Adhikary, K. B.; Pang, S.; Staiger, M. P. *Compos. Part B* **2008**, *39*, 807.
10. Cui, A.; Lee, S.; Noruziaan, B.; Cheung, M.; Tao, J. *Compos. Part A: Appl. Sci.* **2008**, *39*, 655.
11. Jayaraman, K.; Halliwell, R. *Compos. Part B* **2009**, *40*, 645.
12. Bourmaud, A.; Duigou, A. L.; Baley, C. *Polym. Degrad. Stabil.* **2011**, *96*, 1732.
13. Kazemi-Najafi, S.; Mostafazadeh-Marznaki, M.; Charmahali, M.; Tajvidi, M. *J. Compos. Mater.* **2009**, *43*, 2543.
14. Englund, K. R.; Villechevolle, V. *J. Appl. Polym. Sci.* **2010**, *120*, 1034.
15. Kazemi-Najafi, S.; Mostafazadeh-Marznaki, M.; Charmahali, M. *J. Polym. Environ.* **2010**, *18*, 720.
16. Ghahri, S.; Kazemi-Najafi, S.; Mohebbi, B.; Tajvidi, M. *J. Appl. Polym. Sci.* **2012**, *124*, 1074.

17. Wypych, G.; Handbook of Material Weathering, 3rd ed.; Chem Tec Publishing: Toronto-New York, **2003**.
18. Pages, P.; Carrasco, F.; Saurina, J.; Colom, X. *J. Appl. Polym. Sci.* **1996**, *60*, 153.
19. Valadez-Gonzalez, A.; Cervantes-Uc, J. M.; Veleza, L. *Polym. Degrad. Stabil.* **1999**, *63*, 253.
20. Gulminea, J. V.; Janissekb, P. R.; Heisek, H. M.; Akcelrudd, L. *Polym. Degrad. Stabil.* **2003**, *79*, 385.
21. Carrasco, F.; Pages, P.; Pascual, S.; Colom, X. *Eur. Polym. J.* **2001**, *37*, 1457.
22. Annual Book of ASTM Standards; ASTM Standard G154 – 06; West Conshohocken, PA; **2006**.
23. Alamo, R. G.; Mandelkern, L. *Macromolecules* **1989**, *22*, 1273.
24. Annual Book of ASTM Standards; ASTM Standard D2765-01 (Reapproved 2006); West Conshohocken, PA; **2006**.
25. Annual Book of ASTM Standards; ASTM Standard D638 – 10; West Conshohocken, PA; **2010**.
26. Annual Book of ASTM Standards; ASTM Standard D790 – 10; West Conshohocken, PA; **2010**.
27. Annual Book of ASTM Standards; ASTM Standard D256-10; West Conshohocken, PA; **2010**.
28. Tamboli, S. M.; Mhaske, S. T.; Kale, D. D. *Indian J. Chem. Technol.* **2004**, *11*, 853.
29. Stark, N. M.; Matuana, L. M. *Polym. Degrad. Stabil.* **2004**, *86*, 1.
30. Satoto, R.; Subowo, W. S.; Yusiasih, R.; Takane, Y.; Watanabe, Y.; Hatakeyama, T. *Polym. Degrad. Stabil.* **1997**, *56*, 275.
31. Tidjani, A. *Polym. Degrad. Stabil.* **2000**, *68*, 465
32. Gulmine, J. V.; Akcelrud, L. *Polym. Test.* **2006**, *25*, 932.
33. Hoekstra, H. D.; Spoomaker, J. L.; Breen, J.; Audouin, L.; Verdu, J. *Polym. Degrad. Stabil.* **1995**, *49*, 251.
34. Jabarin, S.A.; Lotgren, E.A. *J Appl Polym Sci* **1994**, *53*, 411
35. Fabiyi, J. S.; McDonald, A. G.; Wolcott, M. P.; Griffiths, P. R. *Polym. Degrad. Stabil.* **2008**, *93*, 1405.
36. Li, S.; Chen, Q.; Wu, S.; Shen, J. *Polym. Adv. Technol.* **2011**, *22*, 2517.
37. Khonakdar, H. A.; Morshedian, J.; Wagenknecht, U.; Jafari, S. H. *Polymer* **2003**, *44*, 4301.