

Effect of Water Absorption, Freezing and Thawing, and Photo-Aging on Flexural Properties of Extruded HDPE/Rice Husk Composites

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ABSTRACT: Durability of lingo-cellulosic fiber composites under environmental conditions such as moisture, freezing and thawing, and UV exposure needs to be determined prior to the use of these composite materials in outdoor applications. Dimensional stability and changes in the flexural strength and stiffness of extruded rice husk filled high-density polyethylene composites with and without processing additives such as compatibilizers and processing aid were examined after exposing the composites to water, conditions of freeze–thaw cycles, and UV light. Water absorption results indicated a decrease in the rate of penetration of water in the composites in the presence of compatibilizers. The reduction in strength and stiffness after water absorption was lower for composites with compatibilizers than for the composites without any additives. Freezing and thawing

experiments also showed the dimensional changes and degradation of strength and stiffness were less in composites with compatibilizers. Presence of processing aid in the composite showed a similar or enhanced water absorption and loss of mechanical properties, compared with those of the composite without processing additives. Although the composites showed a discoloration of the surface after the UV exposure time (745 h) studied, it was found that within this period of UV exposure the flexural strength and stiffness of the composites did not show significant change. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3619–3625, 2006

Key words: aging; composites; extrusion; mechanical properties; polyethylene

INTRODUCTION

Lignocellulosic composite materials are widely used in almost every field wherein conventional composite materials are used and this includes building, automotive, packaging and similar applications. This is because of their inherent advantages such as low cost, renewability, biodegradability, low specific gravity, abundance, high specific strength, and nonabrasiveness.^{1–5} Researchers have already exploited various types of lignocellulosic fibers, including wood fiber, hemp, sisal, flax, jute, etc.^{6–11} The need for materials that are harmless to human body and have the ability to provide characteristic properties for specific applications is increasing because of lack of resources and increasing level of environmental pollution. Underutilized agricultural waste materials and/or by-products of agricultural product processing are rich resources of lignocellulosic materials and some of the examples include rice, wheat, and corn straw, corn-

cobs, rice husk, etc. Researchers are also interested to demonstrate the potential of these agricultural by-products for making useful industrial products such as composites to alleviate the major cause of environmental pollution.^{12–18}

In North America, recyclable wood/natural fiber-thermoplastic composites, especially wood–plastic composites, are experiencing a tremendous boom in building and construction industry. In the last two decades, enormous research and development efforts are afoot to boost the performance properties of the composite profiles while maintaining the esthetic properties. However, these composites are sensitive to changes in the environment and their mechanical properties may vary considerably with environmental conditions. The most important issue is the durability of the composites in outdoor environments such as humidity, temperature, sunlight, and/or microorganisms, as these materials always encountered variations in the exposed environment during their service life. Several researchers have reported the effect of moisture, temperature, and biological agents on the degradation behavior of natural fiber/wood–plastic composites and the respective deterioration in the mechanical properties.^{19–30} However, very few reports are available on the freeze–thaw durability of the com-

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posites, which is important in determining the service life of the composites in the colder regions of the world.^{31–34}

In earlier publications we have already demonstrated the use of rice husk for developing thermoplastic composite materials.^{35,36} Effect of different coupling agents on the mechanical properties of the rice husk filled composites and the effect of processability on various processing additives have already been reported in the above-mentioned publications. It is important to determine the durability of these composites under various environmental conditions before using them in outdoor applications. The objective of this research work was to study the effect of water absorption, freeze–thaw cycling, and UV radiation on the flexural strength and stiffness, and dimensional stability of extruded rice husk filled high-density polyethylene composites as a function of different processing additives.

EXPERIMENTAL

Materials

The polymer matrix used in this study was high-density polyethylene (HDPE) with a density of 0.954 g/cc and a melt flow index of 0.2 g/10 min. Rice husk obtained from CBI building products was used as the filler, without any modification. Density of rice husk used was 1.2 g/cc and contained about 80% of 60 mesh size particles and 20% 30 mesh size particles. Compatibilizers used in this study were (a) terpolymer based on ethylene-(acrylic ester)-(maleic anhy-

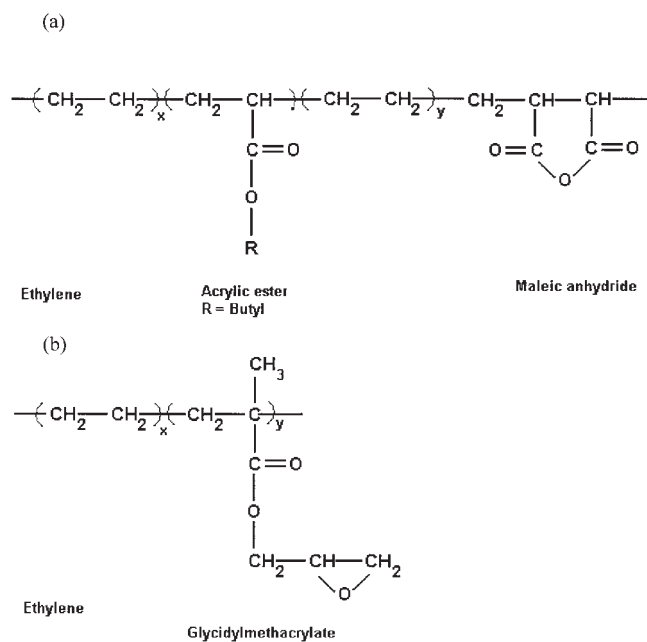


Figure 1 Structure of coupling agents (a) C1 and (b) C2.

TABLE I
Formulation of Composites

Sample code	Processing aid (wt %)	Compatibilizer, C1 (wt %)	Compatibilizer, C2 (wt %)
A	—	—	—
B	—	2.5	—
C	—	—	2.5
D	2	—	—
E	0.6	—	0.7

Base recipe: 65 wt % rice husk and 35% HDPE.
C1, a terpolymer; C2, a copolymer.

dride), with a molecular weight (Mw) of 120,000 g/mol and a maleic anhydride content of 3.1 wt % (abbreviated as C1), and (b) a polymer based on ethylene and glycidylmethacrylate, with a Mw of 100,000 g/mol and a glycidyl methacrylate content of 8 wt % (abbreviated as C2). Polymer and compatibilizers were obtained from Arkema, Canada. Structure of the coupling agents are shown in Figure 1. Processing aid used was Struktol TPW 104 (Zinc stearate based) and was obtained from Struktol.

Test specimen preparation by extrusion

Formulation of the composites used in the study is summarized in Table I. Compounds were formulated based on 65 wt % of rice husk and 35 wt % of PE (composite A) with different processing additives. The amount of processing additives used in the formulation was based on the total weight of the composites and was subtracted from the HDPE content. Melt-blending of HDPE, rice husk, and other additives was carried out in a high-intensity thermokinetic mixer (manufactured by Werner and Pfleiderer Gelimat) at a tip speed of 3200 rpm (23 m/s) and was discharged at a preset temperature of 185°C. The residence time of the material inside the mixer was about 1–2 min. The melt-blended compounds were cooled to room temperature and granulated using a C. W. Brabender Granulator (model S 10⁻⁹). The granulated compounds were then extruded into strips using a 3/4" single screw extruder with a die dimension of 3 × 8 mm². L/D ratio and compression ratio of the extruder was 25 : 1 and 3 : 1 respectively. The respective temperatures for the four different processing zones from the hopper to horizontal die of the extruder were set as 160/165/170/123°C, and the screw speed rate was maintained at 4 rpm.

Water absorption

The flexural samples were immersed in water at room temperature and the samples were taken out periodically and weighed immediately, after wiping out the water on the surface of the sample, using a precise

four-digit balance. All the samples were dried until constant weight was attained with the four-digit balance, before being immersed in water. The percentage of water absorption at any time, t , was calculated using the following equation:

$$\text{Water absorption (\%)} = \frac{W(t) - W_{(0)}}{W_{(0)}} \times 100 \quad (1)$$

where $W(t)$ is the weight of the sample at time t , and $W_{(0)}$ is the initial weight of the sample (at $t = 0$). Water absorption of the samples was determined until there was not much change in the weight of the sample. Water absorption of the control sample remained unchanged around 65–67 days of absorption. To compare the properties of the composites, all the samples were taken out after same period of immersion. Percentage of maximum water absorption, change in thickness, and flexural properties were measured after water absorption. The values reported were averages of four samples.

Freeze–thaw cyclic tests

The flexural test specimens were subjected to freezing and thawing with modification of the ASTM standard (ASTM D 1662). Before the cyclic experiment, the samples were immersed in water for 24-h intervals until the weight gain was less than 1% and then subjected to 12 freeze–thaw cycles. Each cycle consisted of 48 h and was as follows:

- Freezing at -21°C , 24 h
- Thawing at room temperature, 2 h
- Immersion in water at room temperature, 22 h

Dimensional changes, weight gain, and flexural properties of the composites were measured after 12 cycles of freezing and thawing.

Accelerated UV weathering tests

Accelerated artificial UV weathering tests were conducted by exposing the samples under UV-B light at a distance of 15 cm at a wavelength of 312 nm. The intensity of UV-B lamp was measured by a radiometer and was about 8 mW/cm^2 (Labcor Inc.) The weathering schedule involved continuous light irradiation. The samples were aged under UV for a period of 1 month and tested for the color change and flexural properties.

Testing of extruded profiles

Test specimens for flexural strength measurements were cut from the profiles as per the requirement.

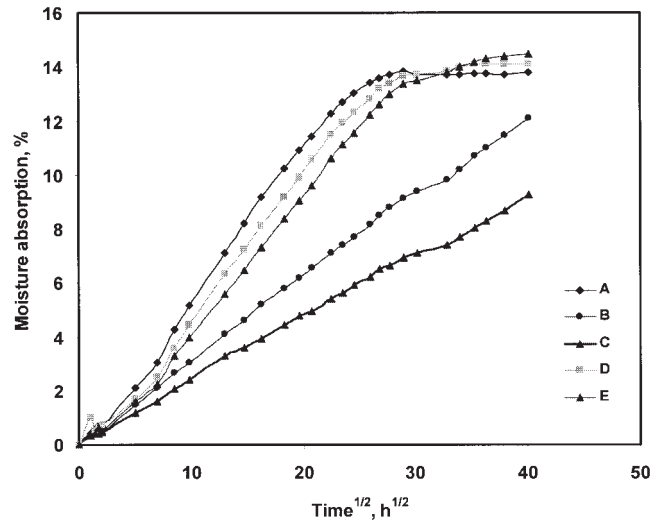


Figure 2 Water absorption curves of composites A–E.

Flexural properties before and after aging were measured in accordance with the procedure in ASTM D 790 in the three point bending mode at a cross head speed of 12.5 mm/min and a span width of 50.8 mm, using a standard computerized testing machine (Sintech Model 20).

Color measurement

The surface color of unweathered and weathered samples was determined according to the procedure outlined in ASTM D 2244.22. A Minolta CR-200 spectrometer was used to measure color according to the CIELAB color system. In the CIELAB coordinates, $+a^*$ is for red, $-a^*$ for green, $+b^*$ for yellow, $-b^*$ for blue, and L^* varies from white (100) to black (0). L^* , a^* , and b^* color coordinates of each sample before and after exposure to UV were measured and the color change ΔE was calculated using the following equation:

$$\Delta E = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$$

where subscripts 1 and 2 denote the values before and after UV exposure.

RESULTS AND DISCUSSION

Water absorption curves of rice husk–HDPE composites with and without processing additives (A–E) are shown in Figure 2. The water absorption curve for the control sample (composite without any additive, composite A) follows a linear relationship between initial moisture absorption and time ($t^{1/2}$), followed by saturation with the immersion time, which conforms to Fick’s behavior of moisture diffusion. The water absorption of the composite is mainly due to the pres-

TABLE II
Initial Slope, Percentage of Maximum Water Absorption,
and Thickness Change of Composites after
1608 h of Water Immersion

Sample code	Initial slope	Maximum water absorption (%)	Thickness change (%)
A	0.573	13.79	9.1
B	0.312	12.09	8.2
C	0.240	9.28	6.3
D	0.512	14.1	9.9
E	0.471	14.45	8.9

ence of the lignocellulosic rice husk, since the nonpolar HDPE absorbs little or no water. Composite A exhibited a high uptake of water (13.8%) after 67 days (1608 h) of water immersion and is attributed to the high content of the rice husk present in the composite. Klason et al. demonstrated that water absorption in lignocellulosic thermoplastic composites is proportional to the filler loading, as the absorption by thermoplastics such as PP and PE could be neglected.¹⁹ Because of the hydrophilic nature of rice husk, these composites can take up a high amount of water, as the water tends to retain in the interfibrillar space of the cellulosic structure of rice husk as well as flaws at the interface and micro voids present in the composites.

It is clear from the figure that addition of both compatibilizers decreases the initial rate of water absorption (observed from the slope shown in Table II), which does not reach the equilibrium condition after 1608 h of water absorption. This indicates that the flaws and gaps at the interface of the rice husk and HDPE are the predominant contributors of moisture diffusion in the composite without compatibilizer. A study by Bledzki and Gassan identified the capillary action of water absorption via the fiber matrix interface of the jute fiber–epoxy composites.²² However, it seems that as the period of immersion increased, water molecules may be able to penetrate the interface and decrease the interfacial interaction. The maximum content of water absorbed by the composite after 1608 h of water immersion and the change in the thickness of the composites (shown in Table II) are also decreased by the modification of the interface between rice husk and HDPE. Similar results were reported by Ishak et al., who reported that incorporation of a coupling agent in EFB-HDPE composite improved the water resistance of the composite, which was attributed to the formation of an interfacial layer which prevents the direct diffusion of the moisture into the composite.²³ The lower water absorption rate and the decreased dimensional change of the composites in the presence of both compatibilizers (Table II) may be attributed to the efficiency of these polymers to increase the interfacial interaction between the matrix and rice husk through their functional groups.

This leads to a reduction in the flaws and gaps at the interface, which otherwise contribute to the moisture absorption. The improved water resistance may also be due to the reduction in the number of hydroxyl groups available for hydrogen bonding with water molecules absorbed, which are already used by the functional group of the compatibilizer for improving the interaction of rice husk and HDPE. The resistance to water penetration into the composite is higher for the composite with C2 than for the composite with C1 and may be due to the difference in the interfacial structure formed between rice husk and HDPE. Unlike C1, C2 does not contain any acrylate pendants on the polymer backbone and results in a flexible polyethylene backbone of the coupling agent that can interact and entangle well with the HDPE matrix and may lead to a better interaction between rice husk and HDPE.

On the other hand, incorporation of processing aid follows a trend similar to that of the control sample (Fig. 2, D). The amount of water absorbed after 1608 h of water immersion and the change in the thickness of the composite with the processing aid are slightly higher than (Table II) those of the control sample. Presence of processing aid in the composite plasticizes the matrix and decreases the interaction between rice husk and HDPE, instead of improving the interaction between the rice husk and HDPE. This may accelerate the water uptake of the composite and leads to dimensional changes. Moisture absorption curve of the composites with 1.1 : 1 ratio of compatibilizers to that of processing aid showed an absorption curve similar to that of the control (A) and composite D. Initial slope, maximum water absorption, and the thickness change after 1608 h of water absorption (Table II) indicate that in spite of the presence of compatibilizer, the composites showed a trend similar to that of the control sample. This showed the outweighing plasticizing and weakening effect of the interfacial interaction produced by the processing aid compared with that of compatibilizers.

Effects of aging on flexural strength and stiffness

Effect of water absorption on the flexural strength and stiffness of the rice husk–HDPE composites with and without processing additives are shown in Figure 3(a,b). As expected, the figures showed that irrespective of the presence of compatibilizers, water absorption resulted in the degradation of performance, both the strength and stiffness, of the composites. This indicates that efficiency of stress transfer from the matrix to the filler deteriorated after the composites were subjected to prolonged water immersion. This may be due to (a) internal stress developed inside the composite because of the water-swollen rice husk, (b) degradation in the interfacial adhesion formed between

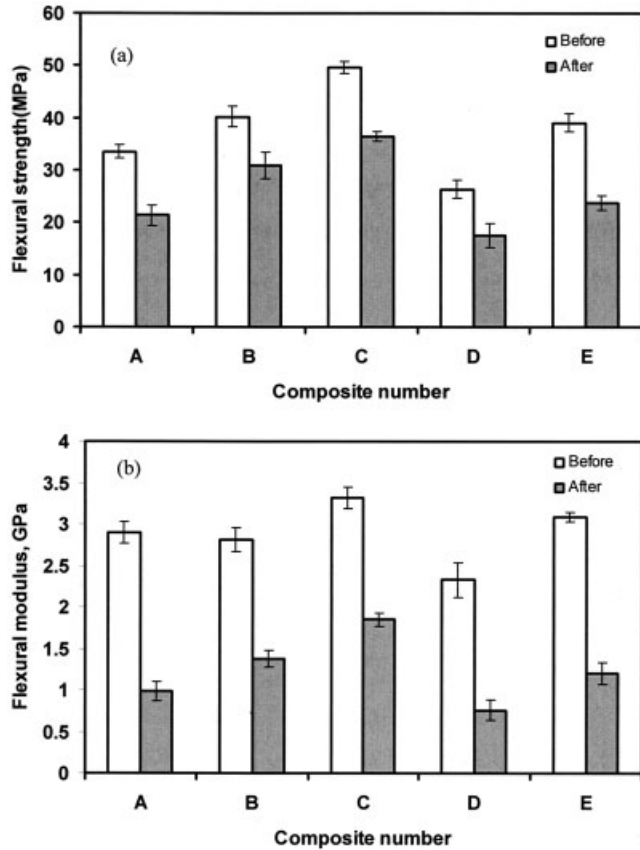


Figure 3 (a) Flexural strength and (b) modulus of composites A–E before and after water absorption.

rice husk and HDPE, and (c) degradation of the rice husk as a result of long-term water absorption. The percentage loss in strength and modulus of the control sample is 36 and 66% respectively, whereas composites with compatibilizers (C1 and C2) showed a decrease in strength by 23 and 26% and a decrease in modulus by 51 and 44%. Interface modification by the functional groups of the compatibilizers slowed down the water absorption (Fig. 2), and also prevents the degradation of the mechanical properties of the composites to some extent. As expected from the observed water absorption behavior, presence of processing aid in the composites did not prevent the degradation of mechanical properties. Loss of strength and modulus of the composites with processing aid is 33 and 67% respectively, which is more or less similar to that of the control sample. A similar loss was observed for the composite E (39 and 61%), which also indicates that the effect produced by the plasticizer used was significant when compared with that by the compatibilizer. It was observed that, in all cases, loss in modulus was higher when compared with the loss in strength. This was similar to the earlier reports available in literature.^{20,25,26}

TABLE III
Weight and Dimensional Changes of the Composites after 12 Freeze–Thaw Cycles

Sample code	Weight change (%)	Thickness change (%)	Width change (%)
A	9.6	6.68	2.1
B	3.5	2.6	0.8
C	3.3	3.5	0.6
D	7.4	5	1.5
E	6.2	4.9	1.4

Freeze–thaw cyclic tests

Test results showed that the overall dimensional stability of the rice husk filled HDPE composites was enhanced by the incorporation of the compatibilizers, irrespective of the chemical structure of the compatibilizers (Table III). This may be attributed to the dimensional stability offered by the composites because of the enhanced interfacial interaction between the rice husk and matrix by the compatibilizers. On the other hand, presence of processing aid did not show significant effect on the dimensional changes of the composites.

The percentage loss in flexural strength and modulus of rice husk filled HDPE composites with and without processing additives exposed to 12 freeze–thaw cycles are shown in Figure 4. Flexural strength and stiffness of the composites were decreased after 12 cycles of freezing and thawing experiments and is thought to be mainly due to the degradation caused by the moisture absorption, as majority of the freeze–thaw cyclic testing consists of changes in moisture content of the samples. Similar results were reported by Pilarski and Matuana³⁴; they studied the effect of freeze–thaw cyclic experiments and modified cycling (by omitting either water or freezing) experiments on

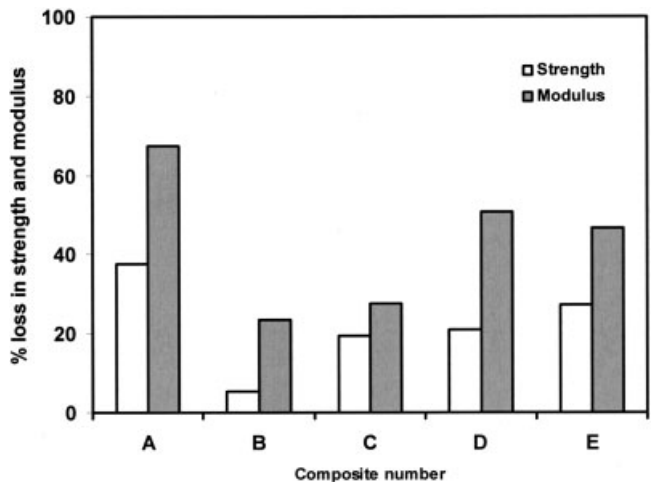


Figure 4 Loss in flexural strength and modulus of composites A–E after 12 freeze–thaw cycles.

TABLE IV
Changes in Color Coordinates of the Composites after UV Exposure

Sample code	After 240 h				After 745 h			
	Δa	Δb	ΔL	ΔE	Δa	Δb	ΔL	ΔE
A	-0.95	0.14	1.57	1.69	-1.37	-0.09	2.42	3.87
B	-1.04	0.13	1.71	2.0	-1.59	-0.04	2.96	5.62
C	-1.05	0.12	1.81	2.19	-1.4	0.25	2.68	4.59
D	-0.95	0.26	2.76	4.36	-1.38	-0.67	3.68	7.95
E	-0.78	0.78	2.00	2.62	-1.02	0.8	2.61	4.23

wood flour filled PVC composites and reported that degradation in properties was mainly because of the interfacial degradation due to moisture absorption during the experiment. Modulus of the composites showed a larger decrease when compared with strength values. The strength and stiffness of control sample decreased by 38 and 67% respectively, and is similar to the loss after 1608 h of water absorption. This indicates that the water is absorbed initially at the interface and leads to degradation of the interface, which in turn leads to degradation of mechanical properties. However, the reduction in strength and stiffness of the composites with compatibilizers C1 is 5 and 23% and those of C2 is 19 and 28%, respectively, which are not similar to the loss after 1608 h of water absorption. In the presence of compatibilizers, penetration of water into the composites through the interface is restricted because of the modified interface formed and absorption of water during the cyclic experiment is expected to be lower and may be the reason for the improved resistance to degradation of mechanical properties. This is also evident from the smaller weight and dimensional changes associated with the composites with compatibilizers. The strength and stiffness of the composite D decreased by 21 and 51% and that of E decreased by 27 and 46% respectively, which is contrary to the observations found in the water absorption behavior and may need further study to have better understanding.

Accelerated UV weathering

Photodegradation of the composites was determined from the discoloration of the surface of the composites. The values of Δa , Δb , ΔL , and ΔE at two different exposure times for rice husk filled HDPE composites are given in Table IV. The values indicate that the surface of the composites with and without processing additives exposed to UV radiation underwent color changes. The calculated total value of ΔE increased with exposure time and a similar trend is observed in ΔL and is found to be the most important parameter influencing the total ΔE within this exposure time, though the determination of ΔE includes the three

color parameters. It seems that neither compatibilizer nor processing aid prevents the surface discoloration.

Flexural strength and stiffness of the rice husk filled HDPE composites with and without processing additives before and after 745 h of UV exposure are shown in Figure 5(a,b). The composite strength and modulus after this exposed time are not significantly different from those of the unexposed composite samples. Similar findings were reported earlier also.^{28,30} It was reported by Stark and Matuana that wood flour composites experienced little degradation within a short exposure period, but exhibited a significant loss in

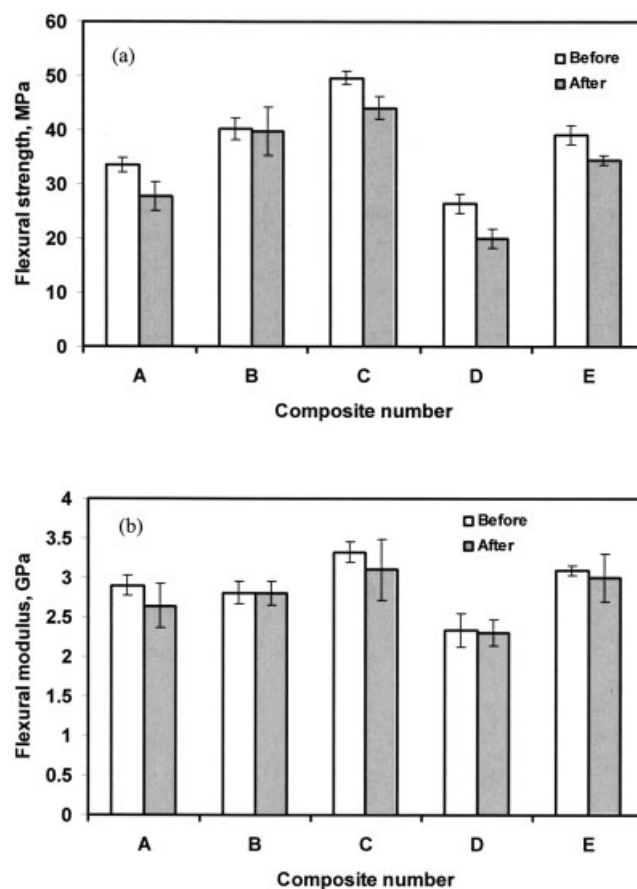


Figure 5 (a) Flexural strength and (b) modulus of composites A–E before and after UV exposure.

strength and stiffness after a prolonged exposure (2000 h) under UV.³⁰ The composite with the processing aid showed 24% loss in flexural strength and exhibited maximum degradation among the composites. Composites with compatibilizer C1 showed almost same strength (% loss -1.2) and stiffness (% loss -0.5) values after UV exposure and showed the least degradation among the composites.

CONCLUSIONS

It is seen that although the exposure to water, and freezing and thawing conditions affects the dimensional stability and degrades the flexural strength and stiffness of the rice husk filled HDPE composites, presence of compatibilizers reduces the changes in dimensions and strength and stiffness of the composites to some extent. Exposure to water caused a pronounced degradation in the strength and stiffness of the composites and the loss in modulus was higher when compared with strength values. It was found that the main degradation effect during the freezing-thawing cyclic experiments was due to the water penetration into the composites. UV exposure for a period of 745 h did not show significant degradation in the strength and stiffness values of the composites. In all cases, composites with processing aid show a trend similar to that of the control sample, one without any processing additives.

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References

1. Woodhams, R. T.; Thomas, G.; Rodgers, D. K. *Polym Eng Sci* 1984, 24, 1166.
2. Sain, M. M.; Kokta, B. V. *J Appl Polym Sci* 1994, 54, 1545.
3. Sain, M. M.; Balatinez, J.; Law, S. *J Appl Polym Sci* 2000, 77, 260.
4. Andreas, M.; Hartmut, W. *Kunstst Plast Europe* 2001, 91, 25.
5. Sain, M.; Law, S.; Suhara, F.; Boullioux, A. *Proceedings of International Symposium, France, March 2003*.
6. Sain, M. M.; Kokta, B. V. *Polym Plast Technol Eng* 1994, 33, 89.
7. Gassan, J.; Bledzki, A. K. *Compos A* 1997, 28, 993.
8. Li, Y.; Mai, Y.-W.; Ye, L. *Compos Sci Technol* 2000, 60, 2037.
9. Vande Velde, K.; Keikens, P. *Polym Test* 2001, 20, 885.
10. Prasad, B. M.; Sain, M. M. *Mater Res Innov* 2003, 7, 231.
11. Sain, M.; Li, H. *Polym Plast Technol Eng* 2003, 42, 853.
12. White, N. M.; Ansell, M. P. *J Mater Sci* 1993, 18, 1549.
13. Hornsby, P. R.; Hinrichsen, E.; Trivedi, K. *J Mater Sci* 1997, 32, 1009.
14. Tsai, W. T.; Chang, C. Y.; Lee, S. L. *Bioresour Technol* 1998, 64, 211.
15. Ishak, Z. A.; Yow, B. N.; Ng, B. L.; Khalil, H. P. S. A.; Rozman, H. D. *J Appl Polym Sci* 2001, 81, 742.
16. Wang, D.; Sun, X. S. *Ind Crops Prod* 2002, 15, 43.
17. Premalal, H. G. B.; Ismail, H.; Baharin, A. *Polym Test* 2002, 21, 833.
18. Han-Sang, Y.; Dae-Jun, K.; Hung-Joong, K. *Bioresour Technol* 2003, 86, 117.
19. Klason, C.; Kubat, J.; Stromvall, H. E. *Int J Polym Mater* 1984, 10, 159.
20. Balatinez, J. J.; Park, B. D. *J Thermoplast Compos Mater* 1997, 10, 476.
21. Morries, P. I.; Cooper, P. *Forest Prod J* 1998, 48, 86.
22. Bledzki, A. K.; Gassan, J. *Prog Polym Sci* 1999, 24, 221.
23. Mohd Ishak, Z. A.; Aminullah, A.; Ismail, H.; Rozman, D. *J Appl Polym Sci* 1998, 68, 2189.
24. Mankowski, M.; Morrell, J. J. *Wood Fiber Sci* 2000, 32, 340.
25. Rangaraj, S. V.; Smith, L. V. *J Thermoplast Compos Mater* 2000, 13, 140.
26. Stark, N. M. *J Thermoplast Compos Mater* 2001, 14, 421.
27. Matuana, L. M.; Kamdem, D. P.; Zhang, J. *J Appl Polym Sci* 2001, 80, 1943.
28. Matuana, L. M.; Kamdem, D. P. *Polym Eng Sci* 2002, 42, 1657.
29. Lin, Q.; Zhou, X.; Dai, G. *J Appl Polym Sci* 2002, 85, 2824.
30. Stark, N. M.; Matuana, L. M. *J Appl Polym Sci* 2003, 90, 2609.
31. Dragomirescu, A.; Waters, J.; Nash, J.; Brissette, D. *Progress in Wood Fiber Plastic Composite Conference, Toronto, May 10-11, 2004*.
32. Kelly, T. P.; Verhey, S. A. *Progress in Wood Fiber Plastic Composite Conference, Toronto, May 10-11, 2004*.
33. Karbari, V. M.; Rivera, J.; Zhang, J. *J Appl Polym Sci* 2002, 86, 2255.
34. Pilarski, J. M.; Matuana, L. M. *J Vinyl Addit Technol* 2005, 11, 1.
35. Panthapulakkal, S.; Sain, M.; Law, S. *Polym Int* 2005, 54, 137.
36. Panthapulakkal, S.; Sain, M.; Law, S. *J Thermoplast Compos Mater* 2005, 18, 445.