

Effects of Reprocessing on the Hygroscopic Behavior of Natural Fiber High-Density Polyethylene Composites

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ABSTRACT: Detailed analysis of the effects of recycling process on long-term water absorption, thickness swelling, and water desorption behavior of natural fiber high-density polyethylene composites is reported. Composite materials containing polyethylene and wood flour, rice hulls, or bagasse fibers and 2% compatibilizer were produced at constant fiber loading and were exposed to a simulated recycling process consisting of up to five times grinding and reprocessing under controlled conditions. A wide range of analytical methods including water absorption/desorption tests, thickness swelling tests, density measurement, scanning electron microscopy, image analysis, contact angle, fiber length analysis, Fourier transform infrared spectroscopy, and tensile tests were employed to understand the hygroscopic

behavior of the recycled composites. Water absorption and thickness swelling behaviors were modeled using existing predictive models and a mathematical model was developed for water desorption at constant temperature. Results indicated that generally the recycled composites had considerably lower water absorption and thickness swellings as compared with the original composites which were attributed to changes in physical and chemical properties of the composites induced by the recycling process. Water desorption was found to be faster after recycling. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1258–1267, 2011

Key words: polymer-matrix composites (pmcs); wood; physical properties; recycling

INTRODUCTION

Water absorption plays an important role in the durability of wood/natural fiber plastic composites and, therefore, it has been extensively studied.¹ Because water absorption can influence many properties such as dimensional stability, natural durability, and physical and mechanical properties, better durability and performance of these materials can be achieved if water absorption is restricted. Research has revealed that water absorption in natural fiber plastic composites depends on a good number of formulation and processing characteristics including but not limited to natural fiber or plastic type, processing system, fiber size, and distribution and interfacial quality.^{2–8}

One of the direct consequences of water absorption in natural fiber plastic composites is dimensional instability. Dimensional changes associated with water absorption are the major reason for the permanent reduction of mechanical properties due

to water absorption. That is why recent studies have also focused on the dimensional stability of such composites by primarily considering their thickness swelling behavior.^{9,10} However, it should be noted that dimensional changes comprise both swelling and shrinkage of the product owing to moisture exchange with the environment and, therefore, it is essential that the rate at which natural fiber plastic composites lose moisture be also taken into consideration. Unlike, water absorption, water desorption behavior of natural fiber plastic composites has not been studied yet. Vackova et al. (2009) apparently worked on the water desorption behavior of such composites but data for only water absorption are presented in their report.¹¹

One major advantage of natural fiber plastic composites as compared with the conventional thermo-setting systems is the capability to recycle the product either during the manufacturing process (internal recycling) or later at the end of the service life (external recycling). However, many recycling processes entail extensive grinding as well as high-temperature mixing which could cause degradation in the properties of the constituents and subsequently the composite material. While existing research reports have largely focused on changes in the mechanical properties of the composite materials exposed to recycling or reprocessing cycles,^{12–19}

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presently no information regarding the effects of the recycling process on the water absorption/desorption behavior or dimensional stability of natural fiber plastic composites is available. The present article is a comprehensive investigation on the effects of recycling/reprocessing (internal recycling) on water absorption/desorption and dimensional stability of natural fiber high density polyethylene composites. A wide range of characterization techniques has been employed to achieve better insight into possible reasons behind changes imposed by recycling.

EXPERIMENTAL

Materials and methods

Materials

High density polyethylene (PE) HI-ZEX 1300J (Prime Polymer, Japan) with a melt flow index of 12 g/min (2.16 kg, 190°C) and a density of 0.961 g/cm³ was used. MAPE (Maleic Anhydride Polyethylene) was a proprietary grade supplied by Mitsui Chemicals Inc., Japan, and was used as the compatibilizer. Details on the maleic anhydride content of MAPE cannot be published due to the terms of use set by the supplier. The authors are aware of the importance of MA content of MAPE but this would have negligible effects on the results as it was a constant parameter in all formulations. Three natural fibers were used. Wood flour (WF) was obtained by grinding wood chips of Sugi (Japanese cedar) in a laboratory grinder. The wood chips were obtained from the University of Tokyo Forests located in Tokyo, Japan. Bagasse fibers were supplied by Okinawa Sugar Canes Research Corp. and rice hulls were collected from the University of Tokyo farm in Tokyo. These were also ground by means of the same grinder. All fibers were then screened using a laboratory shaker and the fractions between 20 and 80 mesh screens were collected. The fibers were dried in an air-circulating oven at 103°C for 24 h prior to use.

Composites preparation and recycling process

Three original composite formulations were produced. Composites were made at constant 50% (by weight) fiber content at 190°C in a laboratory internal mixer at 40 rpm. The 50% fiber loading was selected to represent its frequent use in the industry. Two percent MAPE was used in all formulations as compatibilizer. Recycling was performed in two stages; first the materials were ground into a nominal pellet size of 3 mm using a grinder and after drying they were processed again in the same mixer under the same mixing conditions. All original and recycled composites were hot pressed at 180°C to produce sheets of 2 mm nominal thickness. Test

specimens were cut out of these sheets. The recycling process was performed five times.

Characterization

After the first, third, and fifth cycles, samples were removed from the stream and were characterized. Original samples (not recycled) were also tested in the same way. Throughout this paper, the suffix Orig refers to original materials. Suffixes Rec1, Rec3, and Rec5 refer to one time, three time and five time recycled materials, respectively.

Water absorption and thickness swelling tests

Three samples of each formulation were dried and weighed to a precision of 0.001 g. Thicknesses of the specimens were also measured using a digital micrometer to a precision of 0.001 mm. The samples were then placed in distilled water and kept at room temperature for a total duration of seven weeks. At predetermined intervals, specimens were removed from water, wiped, weighed, and placed back into water after thickness measurement. Tests were terminated after both equilibrium moisture content and thickness swelling were reached. Water absorption and thickness swelling were then calculated using eqs. (1) and (2), respectively.

$$WA\% = \frac{(W_t - W_0)}{W_0} * 100 \quad (1)$$

where WA% is the water absorption in percent, W_t is the wet weight at any time t , and W_0 is the oven-dried weight.

$$TS\% = \frac{(T_t - T_0)}{T_0} * 100 \quad (2)$$

where TS% is the thickness swelling in percent, T_t is thickness at any time t , and T_0 is the initial thickness.

Water desorption tests

Saturated water absorption specimens were dried at 105°C in an *AND MX-50* digital moisture analyzer equipped with data acquisition system. Temperature was increased rapidly and kept constant until a desorption rate of less than 0.1%/min (based on wet weight) was reached. Data were recorded on the computer and converted to values based on dry weight of the samples.

Fiber length measurement

A small piece of the material was placed on a slide glass and heated at 180°C in a hot press for a few seconds until the plastic melted. A piece of Teflon film was then placed on top of the sample and the

press was closed for a few more seconds at low manual pressure. This produced a flat film of composite which was then photographed using a Nikon Eclipse E600 POL microscope at 100 \times magnification. The digital images so obtained were analyzed using the Image J image analysis software to determine fiber lengths before and after recycling. One hundred fibers of each formulation were measured.

Tensile tests

Tensile tests were performed using a Shimadzu EZ Test tensile tester (Shimadzu, Tokyo, Japan) at 5 mm/min crosshead speed. Five specimens of each formulation were tested at room temperature.

SEM

After carrying out tensile tests, the fractured surfaces of tensile specimens were immediately platinum coated and directly observed using a Hitachi S-4000 SEM microscope (Hitachi, Tokyo, Japan). To quantify interface quality, the SEM micrographs were analyzed using the Image J software to quantify fractional area of the cross section covered by holes resulting from fiber pull-out. First a binary image was produced and then the fractional area was calculated by the software after defining the threshold.

Contact angle measurement

Contact angles of distilled water drops on composite surfaces were measured using a Drop Master (Kyowa, Japan) device. Measurements were carried out every three seconds for 30 s and average values of contact angle after reaching equilibrium were determined. Five points on each specimen were tested.

FTIR tests

One milligram of finely ground samples of each formulation was mixed with 200 mg of KBr and pressed into transparent KBr disks for transmission FTIR analysis. Prior to producing the KBr disks, the materials were dried in an air-circulating oven at $100 \pm 2^\circ\text{C}$ for 24 h to remove any moisture which would otherwise result in an opaque disk production. FTIR spectra were obtained using a Nicolet MAGNA-IR 860 Spectrometer at a spectral resolution of 4 cm^{-1} over the spectral range of $4000\text{--}400\text{ cm}^{-1}$.

RESULTS AND DISCUSSION

Long term water absorption behavior

Long-term water absorption isotherms of all studied formulations are presented in Figure 1. Figure 1(a) shows that water absorption in wood flour PE com-

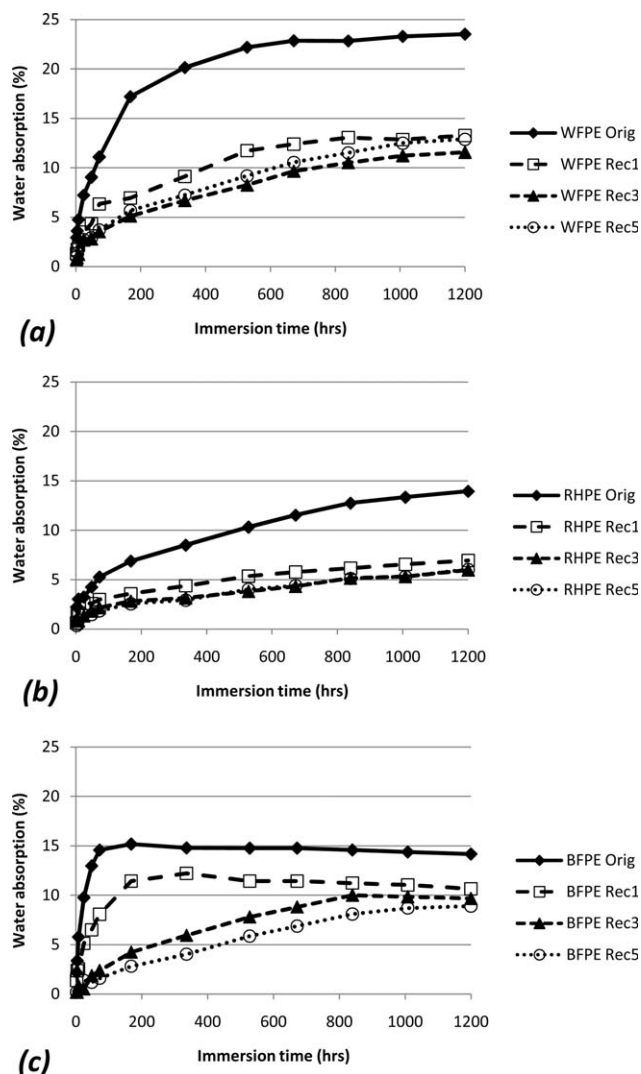


Figure 1 Long-term water absorption behavior of (a) wood flour, (b) rice hulls, and (c) bagasse fiber PE composites.

posites remarkably decreased after only one time recycling. Subsequent recycling cycles also reduced water absorption but were not as effective as the first cycle. Maximum water absorption for the original composites was 23.5% which was reduced to 11.5% after three times recycling. Maximum water absorption after five times recycling was slightly higher and reached 13.3%. Time to reach maximum absorbed water was almost the same for all wood flour formulations irrespective of the number of times they were recycled.

For rice hulls composites, a similar behavior to that of wood flour composites was observed [Fig. 1(b)]. Maximum water absorption for the original rice hulls composite was 13.9% which was considerably smaller than that of original wood flour composite. This was reduced to 6% after five cycles. Generally, rice hulls composites reached considerably lower maximum water absorption values as compared with wood

flour composites. For rice hulls formulations too, all original and recycled composites reached maximum water absorption at relatively the same time.

While similar behaviors were observed for wood flour and rice hulls composites, bagasse fiber PE composites had a very different water absorption behavior. As seen in Figure 1(c), although the general trend of reduced water absorption at higher recycling times is still observed, the original bagasse fiber formulation clearly reached its maximum water absorption much faster than the recycled ones. As the materials were recycled, the rate of water absorption also reduced. Maximum water absorption was found to correspond to the BFPE-Orig formulation (15.2%) whereas the BFPE-Rec5 formulation only absorbed 8.9% water. The BFPE-Rec5 formulation reached saturation in a much slower pace as compared with the other three formulations. On the other hand, while the original bagasse fiber composite absorbed the entire water in only 168 h, this time was increased to 336, 840, and 1200 h for BFPE-Rec1, BFPE-Rec3, and BFPE-Rec5 formulations, respectively. This indicates slower water absorption at higher recycling times.

Comparing the three graphs presented in Figure 1 reveals that five times recycling considerably reduced maximum water absorption in all three original composites. The bagasse fiber composite however underwent the highest reduction in water absorption (58%), whereas those for the wood flour and rice hulls composite were 49 and 43%, respectively. Possible reasons for differences observed between various fibers and formulations will be discussed later.

Water diffusion coefficients

Water absorption values were plotted versus root time/thickness values and the slopes of the linear portion of the curves (m) were determined. Water diffusion coefficients of the composite formulations were then calculated using the following formula.²⁰ This formula has been widely used for natural fiber plastic composites^{2,5,7-9,21} and has been found to predict water absorption rate accurately.

$$D = \pi \left[\frac{mh}{4M_{\infty}} \right]^2 \left[1 + \left(\frac{h}{L} \right) + \left(\frac{h}{n} \right) \right]^2 \quad (3)$$

where D is the water diffusion coefficient corrected for edge effect; m , the slope of linear portion of the water content against root time/thickness curve; M_{∞} , the equilibrium moisture content, which is the value of the water absorbed such that there is no further change in the water absorption with time; h , the thickness; L , the length; and n is the width.

Water diffusion coefficient which shows the rate at which water diffuses into the composite material was slightly influenced by the recycling for wood flour and

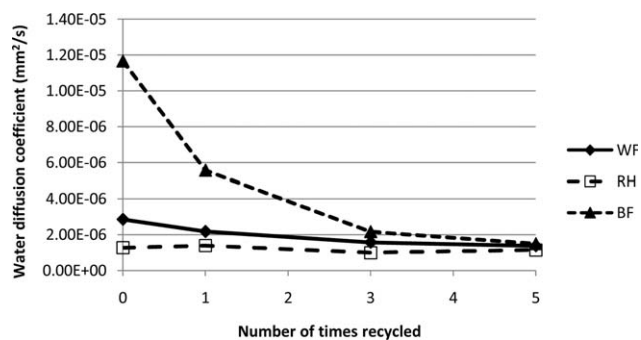


Figure 2 Effect of recycling on water diffusion coefficients for wood flour (WF), rice hulls (RH), and bagasse fibers (BF) composites.

rice hulls composites (Fig. 2). However, for bagasse fiber composites a completely different trend was observed where the water diffusion coefficient considerably reduced as the material was recycled. The high diffusion coefficient calculated for the original bagasse fiber composite is in good agreement with the short time required to absorb maximum water content for this formulation [Fig. 1(c)]. As indicated earlier, the water absorption behavior of bagasse fiber PE composites was different from the other two formulations.

Long-term thickness swelling

Long-term thickness swelling behavior of natural fiber PE composites exposed to the recycling process is presented in Figure 3. For wood flour composites [Fig. 3(a)], the original formulation had the highest thickness swelling at the initial stages of immersion. However, as thickness swelling of this formulation leveled off at around 500 h of immersion, the recycled formulations continued to swell and had slightly higher final thickness swellings. Maximum thickness swellings for the WFPE-Orig, WFPE-Rec1, WFPE-Rec3, and WFPE-Rec5 formulations were 8.1, 8.8, 8.4, and 8.1%, respectively, which were very close to each other. Time to reach maximum thickness swelling was almost the same for all wood flour formulations irrespective of the number of times they were recycled.

Maximum swelling of rice hulls composites [Fig. 3(b)] was considerably smaller than the two other natural fiber types. For this formulation, the highest thickness swelling (3.8%) was observed for RHPE-Orig whereas the lowest one (2.4%) was found to correspond to the RHPE-Rec5 formulation. For rice hulls formulations [Fig. 3(b)], all formulations except RHPE-Rec5 reached maximum thickness swelling at the same time whereas the five times recycled formulation needed a longer time to level off.

It is interesting to note that bagasse fiber PE composites had a completely different swelling behavior. The original bagasse fiber composite reached its maximum thickness swelling (4.8%) in only 72 h of

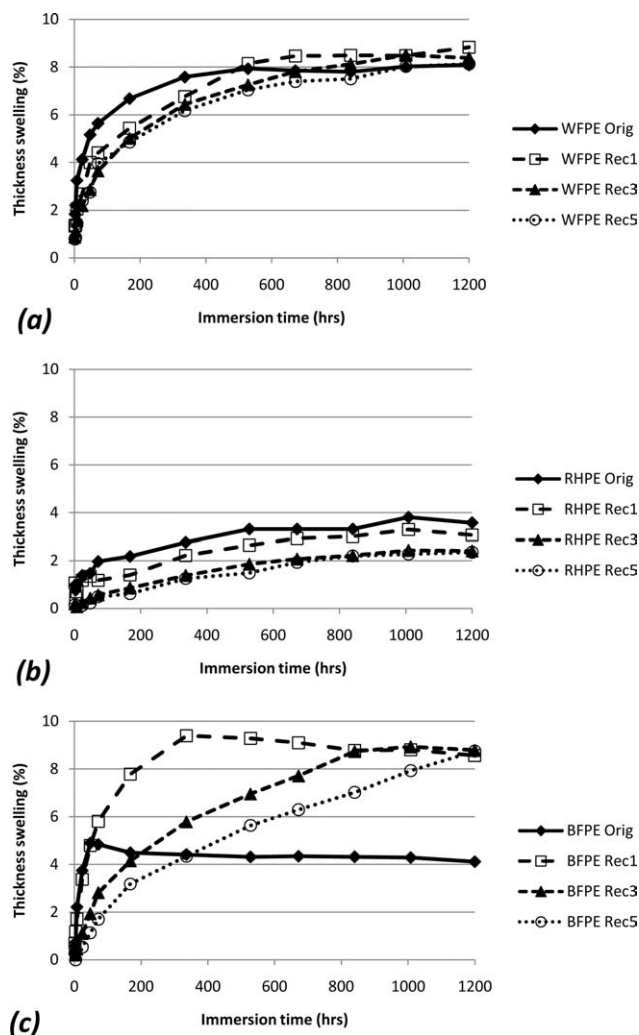


Figure 3 Long-term thickness swelling behavior of natural fiber PE composites: (a) wood flour, (b) rice hull, and (c) bagasse fibers.

immersion and had the lowest final thickness swelling value as well. However, after being recycled one time, a considerable increase in thickness swelling was observed. All recycled formulations eventually reached more or less the same final thickness swelling values (around 8.7%) but the rate at which the recycled bagasse fiber composites swelled was reduced as the materials were recycled more. The five times recycled bagasse fiber composite never reached equilibrium and no level-off was observed even after seven weeks of immersion.

Comparing the three graphs presented in Figure 3 reveals that five times recycling affected thickness swelling of the three original composites in different ways. While slight changes were observed for the original wood flour and rice hulls composites, the thickness swelling of the original bagasse fiber composite was considerably increased upon recycling. Possible reasons for differences observed between various fibers and formulations will be discussed later.

Modeling thickness swelling behavior

Shi and Gardner²² developed a model to quantify swelling rate in composite materials. This model has been successfully used for different natural fiber plastic composites by others as well.^{9,10} In this model, a swelling rate parameter (K_{SR}), determined from the test data, can be used to quantify the swelling rate. The swelling model can be expressed as follows:

$$TS(t) = \left(\frac{T_{\infty}}{T_0 + (T_{\infty} - T_0)e^{-K_{SR}t}} - 1 \right) * 100 \quad (4)$$

where T_{∞} and T_0 are the equilibrium and initial specimen thicknesses, respectively. K_{SR} is a constant called the initial (or intrinsic) relative swelling rate and $TS(t)$ is swelling at any given time t .

Rearranging eq. (4) and taking natural logarithm of both sides gives:

$$\ln\left(\frac{100T_{\infty}}{TS(t) + 100} - T_0\right) = \ln(T_{\infty} - T_0) - K_{SR}t \quad (5)$$

which would give a straight line with the slope of $-K_{SR}$ on a linear scale from which the swelling rate can be calculated by employing a least squares method.

K_{SR} values as determined using eq. (5) are presented in Table I. For wood flour and rice hulls composites, slight decreases in swelling rate can be observed as the materials were recycled. For wood flour composites, the initial decrease in KSR value is followed by a slight increase at five times recycling. However, for bagasse fiber PE composites, a very considerable drop in swelling rate was found indicating that swelling rate in this formulation is greatly reduced by recycling. This observation is in agreement with both the considerably shorter time to reach maximum swelling and higher water diffusion coefficient of the original bagasse fiber composite.

Sum of squares as determined using eq. (6) was used to compare how well the model fitted the experimental data.

$$SS = \sum_{i=1}^n (y_i - \hat{y})^2 \quad (6)$$

where SS is sum of squares, y_i is the observed value, \hat{y} is the predicted value, and n is the number of observations.²² The SS shows the deviation from the model and therefore a lower SS means a better fit.

As seen in Table I, the best fits were observed for rice hulls and bagasse fiber composites, whereas higher SS values were observed for wood flour PE composites. Generally, the model worked better for the recycled formulations than original ones indicating that it can predict thickness swelling behavior more accurately at lower swelling rates.

TABLE I
 K_{SR} Values and Sums of Squares for the Thickness Swelling Model

Number of times recycled	Natural fiber type					
	Wood flour		Rice hulls		Bagasse fiber	
	$K_{SR} (hr^{-1}) \cdot 10^{-3}$	Sum of squares	$K_{SR} (hr^{-1}) \cdot 10^{-3}$	Sum of squares	$K_{SR} (hr^{-1}) \cdot 10^{-3}$	Sum of squares
0	13.6	19.2	7.1	4.1	147	3.2
1	8.3	12.2	3.8	3.7	15.5	4.1
3	6.7	6.7	3.6	1.1	5.3	5.1
5	8.0	8.1	3.4	3.7	3.3	7.9

Water absorption/thickness swelling relationship

It is well known that a major part of the thickness swelling is caused by the absorption of water by the composite material. Thickness swelling is brought about by the swelling of the individual fibers as well as penetration of water into the interface between the two phases and the subsequent damages to this area caused by the absorbed water. However, the mechanism of thickness swelling is not fully known. Evaluation of the relationship between water absorption and thickness swelling can help to understand the mechanism of thickness swelling as well.⁷ As seen in Figure 4, for all wood flour composite formulations, thickness swelling increased nonlinearly as water absorption increased. However, the dependence of thickness swelling on water absorption was not the same for original and recycled wood flour composites where the slope of the relationship was considerably smaller for the former. For rice hulls composites, the nonlinear relationship between water absorption and thickness swelling was transformed to a linear one after recycling. Bagasse fiber PE composites exhibited linear relationships before and after the recycling process but the slopes were considerably higher after recycling. No leveling-off was observed in the relationships indicating that almost all of the thickness swelling was caused by water absorption. The higher slopes in the relationships after recycling clearly indicate that recycled formulations swelled more at any given water absorption.

Water desorption behavior

Water desorption profiles were also remarkably affected by the recycling process. As seen in Figure 5(a–c), for wood flour, rice hulls, and bagasse fiber composites, respectively, generally the recycled composites had lower initial saturation moisture content and lost moisture in a shorter time. For all three natural fiber formulations, only one time reprocessing considerably affected desorption behavior.

An exponential decay function was used to quantify the rate at which moisture in the samples was

lost during desorption process. Considering the following differential equation:

$$\frac{dMC(t)}{dt} = -K_{DR}MC(t) \quad (7)$$

where $MC(t)$ is moisture content (%) at any time t , and K_{DR} is a constant called desorption rate

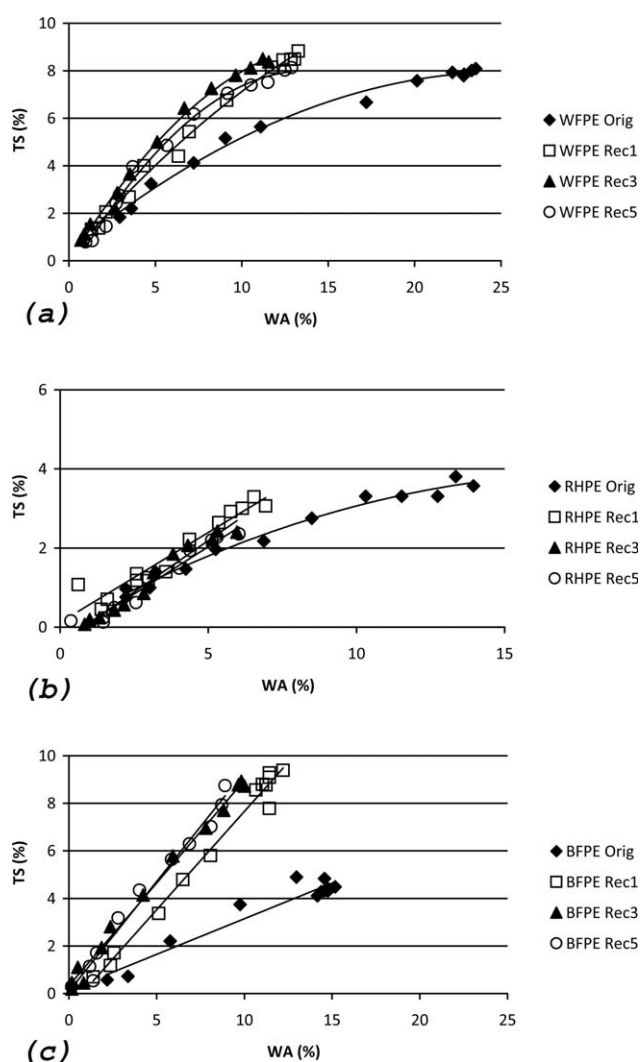


Figure 4 Relationships between water absorption and thickness swelling: (a) wood flour, (b) rice hull, and (c) bagasse fiber composites.

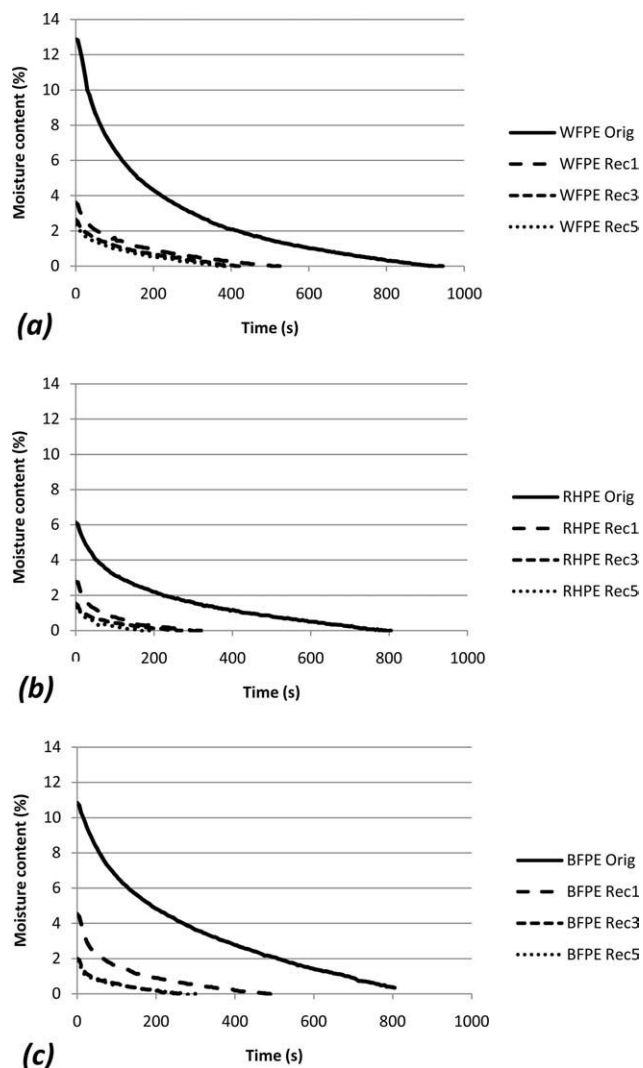


Figure 5 Water desorption behavior (at 105°C) for (a) wood flour, (b) rice hull, and (c) bagasse fiber composites.

constant. Rearranging eq. (7) followed by integration gives

$$MC(t) = MC_0 e^{-K_{DR}t} \quad (8)$$

where MC_0 is the initial moisture content.

The calculated K_{DR} values as well as coefficients of determination (R^2) as obtained by fitting eq. (8) to the

experimental data are presented in Table II. The high R^2 values obtained indicate that the equation fitted the experimental data well and therefore the model predicted moisture desorption process satisfactorily. Generally, K_{DR} values significantly increased as the materials were recycled. However, although all three original formulations had similar desorption rates, they were affected by the recycling process in different manners. For wood flour composites, the K_{DR} was almost doubled after five times recycling, whereas those for rice hulls and bagasse fiber composites were almost five-fold and three-fold, respectively. The high desorption rates calculated are in close agreement with considerably shorter times required for the complete moisture desorption. It is therefore understood that recycling causes increased desorption rates in the studied natural fiber high density polyethylene composites.

Other tests

To study structural changes in composite materials due to the recycling process in more detail, a number of complementary tests were performed. Results from density measurements, fiber length, contact angle, FTIR, and interface quality examination (reported in Table III) can help to explain some of the changes in the water absorption/desorption and thickness swelling behavior due to recycling.

Table III shows that in general all recycled formulations had slightly higher densities as compared with their originals. This is in part due to the reduction in fiber length which has caused denser materials with smaller amounts of voids. Another reason for the lower density of original composites especially in the case of wood flour composites can be the presence of volatile substances (extractives) in the natural fibers. For example, the extractives content (soluble in benzene, ethanol, and hot water) for the wood flour was determined to be around 4% which is relatively high as compared with other wood species.²³ These volatile materials can evaporate and produce voids at the interface which will in turn cause poor interface quality and higher water absorption and thickness swelling. Because volatiles can be mainly lost at subsequent recycling cycles, the increased density

TABLE II
 K_{DR} Values and Coefficients of Determination for the Water Desorption Model

Number of times recycled	Natural fiber type					
	Wood flour		Rice hulls		Bagasse fiber	
	$K_{DR} (s^{-1}) \times 10^{-3}$	R^2	$K_{DR} (s^{-1}) \times 10^{-3}$	R^2	$K_{DR} (s^{-1}) \times 10^{-3}$	R^2
0	4.51	0.98	4.14	0.98	3.41	0.99
1	6.39	0.98	12.79	0.98	7.82	0.97
3	6.84	0.98	11.98	0.98	12.32	0.97
5	7.46	0.98	19.8	0.98	11.85	0.96

TABLE III
Density, Fiber Length, Contact Angle, Hydroxyl Group Concentration and Cross-Sectional Holes Fractions in Composite Formulations

Sample code	Density (g/cm ³)	Fiber length (μm)	Contact angle (°)	—OH concentration	Cross-sectional holes fraction (%)
WFPE Orig	1.01	488	66.6	0.88	5.4
WFPE Rec1	1.11	421	80.6	0.78	3.9
WFPE Rec3	1.12	311	86.7	0.77	1.3
WFPE Rec5	1.10	232	77.3	0.79	0.0
RHPE Orig	1.10	407	77.5	0.80	2.9
RHPE Rec1	1.15	336	65.2	0.79	3.9
RHPE Rec3	1.15	236	72.0	0.85	3.3
RHPE Rec5	1.18	164	77.3	0.73	3.6
BFPE Orig	1.00	524	46.8	0.93	5.0
BFPE Rec1	1.09	313	73.1	0.90	2.5
BFPE Rec3	1.10	203	51.0	0.87	0.8
BFPE Rec5	1.16	125	73.3	0.68	1.8

can contribute to lower water absorption and thickness swelling in recycled composites.

Fiber length remarkably decreased as a result of mechanical attrition in both the grinder and the mixer (Table III). The highest reduction was seen for bagasse fibers and the lowest was observed for wood flour. This difference is mainly attributed to the morphology of these natural fibers as bagasse fibers are mainly long fiber bundles with high aspect ratios, whereas rice hulls and wood flour are mostly shorter and have smaller aspect ratios. Therefore, one of the main reasons for the lower water absorption and thickness swelling of the recycled formulations is their smaller fiber size. The increase in surface area caused by fiber length reduction is most probably compensated for by better encapsulation of the fibers by the matrix. Also fiber–fiber interactions are reduced at smaller fiber sizes provided that no agglomeration occurs. In addition, the considerable reduction in fiber length due to recycling in bagasse fiber composites confirms that at least part of the decrease in water absorption and thickness swelling can be explained by lower fiber length.

Hemicelluloses present in natural fibers are the most hydrophilic constituents in natural fiber plastic composites due to the abundance of hydroxyl groups in them and their amorphous nature.²⁴ However, these materials are also the most sensitive ones to thermal degradation.²⁵ Therefore, the composite materials can become more hydrophobic as they are recycled as a result of the loss of parts of the hemicelluloses. Table III presents the relative hydroxyl group contents in composite formulations as determined by normalizing absorbance at 3408 cm⁻¹ (—OH) to that of 2917 cm⁻¹ (C—H) in the FTIR test. As it can be seen, in most cases, OH concentration decreased at more recycling cycles indicating the less hydrophilic nature of recycled products. This clearly indicates that chemical changes in the natural fiber structure are also responsible for lower hygroscopicity of the recycled materials. The reduction in OH concentration

was also found to be more pronounced for bagasse fiber composites, which is again in agreement with water absorption and thickness swelling findings.

The decreased hygroscopicity of the composite materials as a result of recycling also manifests itself when the contact angle is measured. Data presented in Table III show that contact angle values are generally higher when the materials are recycled. This again bolsters the idea that the composite materials became less hydrophilic by recycling. The effect of recycling on the contact angle was more pronounced for bagasse fiber composites, which is in agreement with the more considerable changes observed in hygroscopic properties of this formulation.

In natural fiber plastic composites, water is absorbed by individual cell walls as well as voids and cracks present in the composite due to poor interface quality or fiber agglomeration.² However, as the natural fibers are mostly fiber bundles rather than individual fibers, examining fractured surfaces to evaluate interface quality is not easy especially at higher fiber loadings. SEM micrographs for original and five times recycled formulations are presented in Figure 6. Better fiber distribution and fewer fiber pull-out locations are evident in this figure. An image analysis method was employed to quantify the surface area covered by holes resulting from fiber pull-out on fractured surfaces of the formulations and the corresponding data are summarized in Table III. According to Table III, considerable improvements in interface quality are observed for wood flour and bagasse fiber composite formulations which are in close agreement with the reduced water absorption and improved dimensional stability in these composites. However, for rice hulls composites, not much change in interface quality was observed even after five times recycling.

Tensile strength values for original and five-time reprocessed formulations are compared with maximum water absorption and thickness swelling values in Figure 7. For water absorption, close

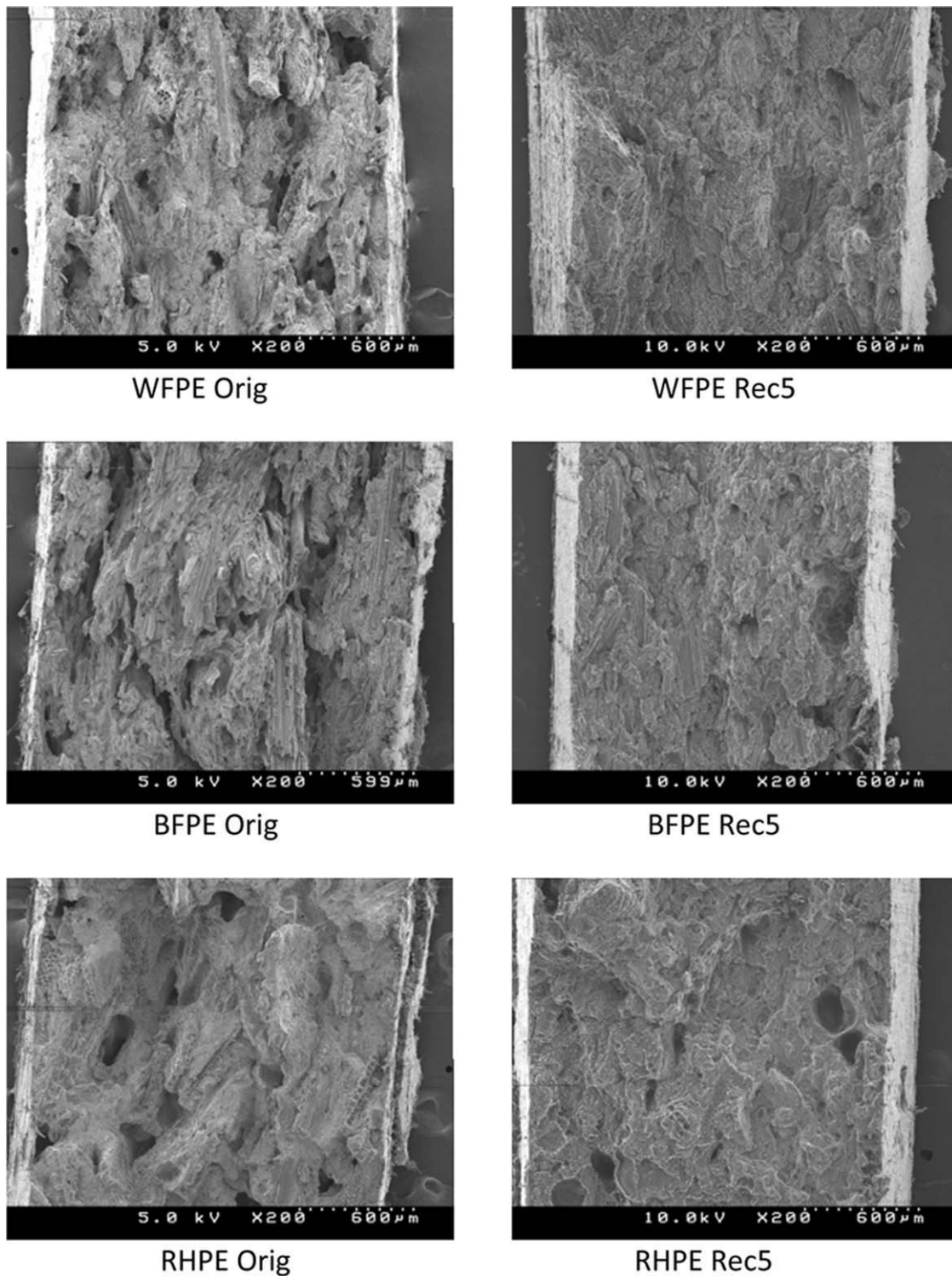


Figure 6 SEM micrographs of fractured surfaces of original and five time recycled formulations.

agreement between water absorption values and tensile strengths was observed so that formulations with higher tensile strengths had lower water absorption. This again indicates the positive effect of reprocessing on the improvement of polymer–fiber interface quality previously discussed while examining fractured surface SEM micrographs. However,

such an observation was not made for thickness swelling where only the rice hulls composite exhibited lower thickness swelling at higher tensile strength. This observation can be explained by the fact that thickness swelling is more influenced by interfacial quality than water absorption, as water can be absorbed by cell walls themselves as well as

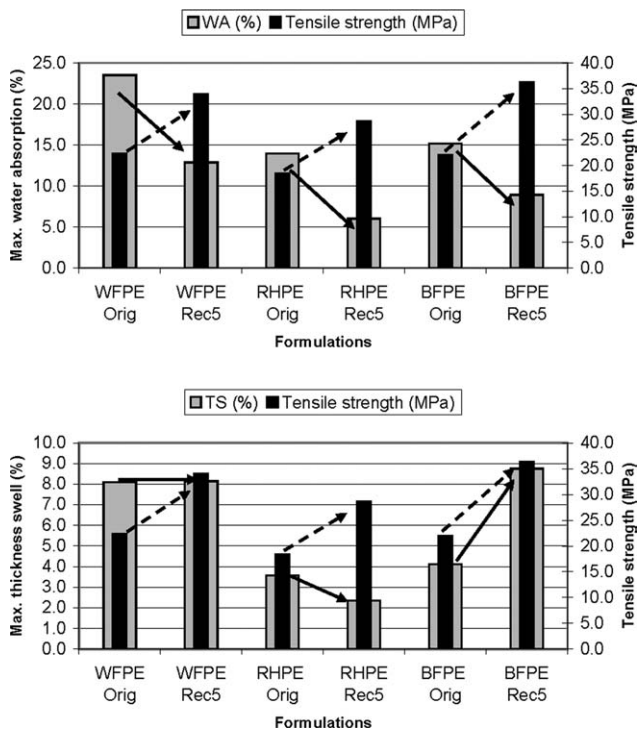


Figure 7 Relationships between tensile strength and maximum water absorption/thickness swelling.

gaps and cracks in the interphase, whereas swelling is only a result of individual fibers expansion due to water absorption.

CONCLUSIONS

Water absorption and thickness swelling behavior of recycled natural fiber plastic composites at a given fiber loading depend on a wide array of factors including interface quality, chemical composition, fiber length and distribution, and density. Because recycling can have different effects on these properties in various formulations, different composite formulations may be influenced by recycling in different manners. The results of the present study confirmed that generally the recycling process enhanced water resistance and dimensional stability in the studied formulations. This is mainly due to better fiber distribution, higher density, lower amounts of voids, better interface quality, and increased hydrophobicity in the recycled formulations. For bagasse fiber formulations, it could be hypothesized that the interactive effects of reduced hydrophobicity, reduced fiber length, and considerable changes in chemical structure due to recycling might have been responsible for different behaviors of these formulations. Bagasse fiber composites also contained some sugar and other water soluble materials which could have

been removed upon one time recycling. This might explain the considerable effects of one time recycling on their hygroscopic properties. Water desorption was found to be faster in the recycled composites which can be attributed to the lower hygroscopicity of natural fiber polyethylene composites as indicated by FTIR and contact angle results. In conclusion, it seems that recycling natural fiber plastic composites is not an issue as far as water absorption and dimensional stability of the composite materials are concerned. However, some other important variables including processing system, temperature, fiber loading, and possible environmental effects on physical properties were not included in the present research and will remain interesting future research topics.

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