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Effect of Accelerated Weathering on Biocomposites Processed by SMC and Compression Molding

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Abstract The durability of biocomposites utilized for building components has been a subject of recent concern and questioning. To address these concerns, the long-term effects of weathering on biocomposites used as building components were evaluated using an accelerated weatherometer. The biocomposite samples were processed by sheet molding compounding (SMC) panel processing and/or compression molding. The accelerated weatherometer served to expose the samples to ultraviolet radiation (UV), condensation, and water spray at levels pertinent to actual conditions: 48 cycles of UV (340 nm) treatment at 60 °C for 2.5 h was followed by water spray for 0.5 h, and then condensation at 45 °C for 24 h. Twelve cycles were repeated in each test, and the total duration for the complete test was 2016 h. Measurements for color, surface roughness test weight change, and dynamical mechanical analysis were taken at regular intervals of time. It was found that the surface roughness increased, as the color changed, and storage modulus decreased with increases in the exposure time of the samples to accelerated weathering conditions, compared to their properties at the beginning of the test.

Keywords Biocomposites · Accelerated weathering · Weathering · Durability · SMC line · Surface roughness · Color change · QUV

Introduction

Biocomposites have always been looked at with suspicion with regards to their durability as building components. It is known that the thermal as well as mechanical properties of wood composites and natural fiber-based composites fade with time. Many research groups have examined the moisture absorption or water uptake of biocomposites [1–9] and although some research has been carried out on the durability of wood composites [10–19], the weathering of biocomposites has not been adequately addressed. To address some of the concerns regarding the durability of biocomposites, it is necessary to evaluate the effect of long-term weathering on biocomposites.

Since the 1990s, many researchers have actively examined the durability of wood-fiber/plastic composites in various applications. Fungal attacks on wood composites have been studied by different lab and field tests. Matuana et al. [10] investigated the durability of polyvinyl chloride (PVC)/ wood-fiber composite samples subjected to a cyclic UV light/spray weathering tests over a period of 1200 h. The samples were analyzed by Fourier transform-infrared spectrophotometry (FTIR), colorimetry, contact angle measurement,

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and surface roughness measurement. They observed that the wood fibers act as sensitizers and reinforcements in the PVC matrix and accelerated the photodegradation of the polymer matrix. They also observed greater discoloration in the composite samples compared to neat plastic. Therefore, it is expected that the natural fiber will be the first component of the biocomposite to undergo weathering effects.

A number of studies attest to the fact that increased wettability may be an important contributor to the degradation of wood structures and articles. For example, Kalnins and Feist [11] exposed western red-cedar panels to outdoor weathering and measured the wettability of the panels with water using contact angle analysis, and found that the contact angle decreased as the exposure time increased, leading to greater wettability. Feist [12] performed outdoor study of various finish systems on aspen siding and found that acrylic latex paints are best protection for weathering. Thus, it is clear from these studies that in order to increase the resistances of biocomposites against the weather elements, their external surfaces need to be protected for preservation of their bulk properties.

Ultraviolet weathering performance of rigid PVC filled with different concentrations of wood flour was studied by Matuana and Kamdem [13]. The extruded and compression molded samples were subjected to cyclic exposure to UV and for 300 h and analyzed by the following techniques: FTIR spectrophotometry, colorimetry, contact angle measurement, tensile test and notched Izod impact test. It was found that incorporation of wood fibers in the PVC matrix led to an increased degradation of the matrix material and also that the exposed PVC plastic samples had lower impact strength and lower elongation at break compared to original plastics. However, all of the composites retained their impact strength, tensile strength, tensile modulus as well as elongation at break. This study points to a very important fact the optimal interaction between the fiber and the matrix is not only important for the bulk properties of the biocomposites, but also for conserving the integrity of the biocomposites by maximizing fiber-matrix adhesion.

Podgorski et al. [14] developed an artificial weathering method to assess the durability of exterior wood coatings and wood in a short period of time. The optimized cycle they developed contained a condensation period of 24 h, UVA at 340 nm for 2.5 h and water spray for 0.5 h. The total duration of exposure was 2016 h. This optimized cycle was tested on different wood substrates, wood coatings, and also examined for reproducibility. However, such analysis techniques have not been used for natural fiber-based biocomposites so far.

Chow and Bajwa studied the weathering effects on the decay resistance of creosote treated oak [15]. They used a standard soil block culture method to test decay resistance of naturally and artificially aged oaks infected with brown and white rot fungi. They found that naturally aged samples were more vulnerable to fungal attack as compared to artificially aged ones. Nzokou and Kamdem studied the weathering of African paduak and red maple, both of which are hardwoods. The wood samples were artificially weathered for 1000 h, and changes in color, roughness and contact angle were measured and recorded at regular intervals of exposure [16]. They observed that the color change for both species was very fast during the first 24 h of exposure. With longer exposure times, the roughness of both wood types increased, and the contact angle decreased due to a decrease in lignin and extractive content of the wood surface. Feist [17] and coworkers evaluated the long-term effect of solvent borne and waterborne water repellent preservative treatments on the performance of various paint systems applied to different wood substrates. Six substrates were subjected to 9 years of outdoor exposure and evaluated for degradation, finish and decay. They found that the performance of substrates treated with waterborne preservatives was slightly better than those treated with solvent-borne preservatives.

Stark and Matuana [18] studied the performance of photostabilized HDPE/wood flour composites after accelerated weathering exposure of 2000 h. They found that both colorants and UVA are better photostabilizers than hindered amine light stabilizers for HDPE/wood composites. The flexural properties of neat HDPE dropped significantly after weathering, but those of photostabilized HDPE/wood composites remained same until 2000 h of exposure. Gassan and Bledzki [19] determined the thermal degradation of untreated and alkali-treated jute and flax fibers. The fibers were exposed to temperatures between 170 and 210 °C for a maximum of 120 min. The exposed fibers were mechanically tested in a yarn tensile test to measure the influence on tenacity. In all cases both fibers showed none or only a slight decrease in tenacity and degree of polymerization at temperatures below to 170 °C. For temperatures above 170 °C the tenacity as well as the degree of polymerization decreased rapidly, and depended on both exposure time and temperature. In general, a higher temperature or longer time of exposure led to an increase in the level of depolymerization and to a drop in tenacity. Because of chain scission due to this thermal treatment, an increase in

degree of crystallinity with a maximum of 20% was found. These previous studies clearly suggest that although several analytical tools have been used for find weathering behavior of wood and wood-based composites, such effort has not been seen for biocomposites. The weathering studies are of particular interest for biocomposites because their most promising aspect seems to be that they can replace glass fibers based composites in many different applications, some of which are exterior applications. Our group is interested in using the unsaturated polyester resin (UPE)-based biocomposites for housing panel applications, and one of the fundamental aspect that needs to be analyzed before any commercial scale up, is the weathering of these biocomposites. Thus, we performed weathering studies on some of our promising bioplastics and biocomposites, by selecting a prototype weathering cycle which has been successfully used for wood-based composites.

The weathering of biocomposites can be carried out in an accelerated weathering chamber, where the samples can be exposed to harsh weather conditions including harmful UV, condensation, humidity, elevated temperatures, and rain simulating water spray. At regular intervals of time, the samples can be evaluated for physical properties like color, surface roughness, weight change, and mechanical and thermal properties like, tensile and flexural strength, modulus of elasticity, impact strength, storage modulus, and coefficient of thermal expansion, for example.

It is expected that increasing the exposure times would simulate conditions of accelerated weathering, so the surface roughness should increase, while color should turn lighter, and thermal as well as mechanical properties should decrease, compared to their properties at the beginning of the test. Such weathering experiments can give an insight about the amount of damage the samples can undergo in accelerated weathering conditions, and can also help to set guidelines about the life time of the products performing at the acceptable levels. However, such tests cannot be compared to real time, and no correlation exists to convert the test time in the chamber to actual time in the real world. With this perspective, we performed durability studies on the biocomposites.

Experimental

The biocomposites were made using sheet molding compounding (SMC) and compression molding. The details of raw materials and processing are available elsewhere [20]. Briefly, a resin mixture of 60% UPE, 30% calcium carbonate, 0.03% cobalt naphthanate, 0.5% methyl ethyl ketone peroxide was formulated. The resin mixture was transferred to the upper and lower resin pots of a modified SMC line. The line was run at a speed of 0.3 in/s. A combination of K-tron twin-screw feeder and vibratory feeder dispensed pre-cut natural fibers onto the SMC line. The modified feeder setup distributed fiber evenly and consistently. The finished product was cut into 1 ft long segments and was placed flat in a sealed polyethylene container and stored in freezer. The sheet material was compression molded for making samples for testing and characterizations. The prepreg samples were placed between two aluminum plates pre-coated with teflon sheets. The plates were pressed in a compression molding press (Carver Lab Press) at around 80 psi for 2 h at 100 °C followed by 2 h at 150 °C. The resulting composite is then cut into desired shapes for various tests. For making the bioresin sample, a degassed UPE-bioresin solution was poured into degassed silicone molds and cured in a conventional oven at the same curing conditions.

The biocomposite samples were subjected to moisture absorption, accelerated weathering and flammability tests. Figure 1 shows samples of biocomposites after 2000 h of exposure to weathering testing. The 7 samples tested were as follows: bioplastic samples: containing 10, 20 or 30% of bioplastic (GFTSOPEP3, composed of grafted soybean poylol and UPE); compression molded biocomposite samples: untreated and acrylonitrile treated industrial hemp fiber mat (hemp mat) in a UPE matrix; biocomposite sheet molding compound panel process (BCSMCP) molded biocomposite samples: silane treated big blue stem grass (BBSG)-$CaCO_3$-UPE and silane treated BBSG and green flax core-$CaCO_3$-UPE.

Moisture Absorption Test

Moisture absorption test was carried out to find out the moisture uptake by the composites and control. Moisture absorption tests determine the rate of absorption of materials and also showcase the equilibrium moisture content of the samples. The samples were dried until their weight stabilized, the weights were recorded, and then they were placed in a humidity chamber operating at 30 °C and 90% relative humidity. At regular intervals, they were taken out of the chamber, wiped dry, and weighed again. After weighing the samples, they were reinserted in the humidity chamber. Measurements were taken once a week until the material reached a steady state (no longer absorbing moisture).

Fig. 1 Weathered samples, on left, a hemp mat-unsaturated polyester resin (UPE) biocomposite, on right, a big blue stem grass (BBSG)-GFC-UPE biocomposites

Weatherability Test

Biocomposite samples were placed in an accelerated weatherometer (QUV, at Department of Forestry, MSU) for weathering tests. The accelerated weatherometer was set to the following cycle to expose the samples to UV, condensation, and water spray: 48 cycles of UV treatment (340 nm) at 60 °C for 2.5 h followed by water spray for 0.5 h, and then condensation at 45 °C for 24 h. Twelve cycles were repeated in the test, and the total duration for the test was 2016 h. The measurements for color, surface roughness test weight change, and dynamical mechanical analysis were taken at regular intervals of time.

Sample Preparation

Samples of biocomposites were cut into the dimensions of 76.2 mm $\times$ 31.75 mm $\times$ 4 mm. The samples were conditioned at 65% RH and 25 °C after machining and polishing. Thirteen specimens of each sample were used for these experiments.

Weatherometer (QUV)

The samples were subjected to weathering in a QUV accelerated weathering tester Model QUV/Spray (Accelerated Weathering Tester, Q-Panel, Cleveland, OH, USA), which allowed for water spray as well as condensation. The samples were subjected to accelerated weathering by exposure to fluorescent ultraviolet light radiation at a wavelength of 340 nm and temperature of 60 °C for 2.5 h, followed by a spray of water for 0.5 h, followed by condensation at 45 °C for 24 h. The average irradiance was set to 0.85 W/m^2 at a wavelength of 310 nm and the temperature of the spray was set to 25 °C. The exposure times for the samples in this study were 0, 500, 1000, 1500, and 2000 h. The measurements for color, surface roughness test weight change, and dynamical mechanical analysis were taken at regular intervals of time.

Color Measurements

The color of the biocomposite samples was determined in accordance with the ISO-2470 standard, using a reflectometer (Datacolor international, Lawrenceville, NJ, USA) with CIELAB system. The CIELAB system is characterized by three parameters, L*, a*, and b*. The L* axis represents the lightness, whereas, a* and b* axes are the chromaticity coordinates. In the CIELAB co-ordinates, +a* is for the red, – a* for green, +b* for yellow, – b* for blue and L* varies from 100 (white) to zero (black). L*, a*, and b* color coordinates of each specimen were measured before and after the exposure to weathering conditions. These values were then used to calculate the color change, ΔE* and the color saturation, C* as a function of the weathering exposure duration.

Surface Roughness Measurement

A surface profilometer system (HommelWerke, Germany) was used to evaluate modifications on the biocomposites' surface before and after weathering. The system was equipped with a 25 mm long stylus, which traverses the surface and its vertical displacement is converted into an electrical signal. The signal is amplified before it is converted into a set of digital information. The digital information is transmitted to the computer and the surface roughness parameters calculated from this information. The stylus travel speed was set at 0.5 mm^{-1} across the biocomposites sample with a span of 25.6 mm. The maximum range

was set at 800 μm and an average of five measurements was taken from each sample. Each sample was evaluated before and after the exposure to weathering.

Several surface-texture parameters were obtained from this method: R_a, R_z, R_{max}, R_k, R_{pk}, and R_{vk}. R_a is the average surface roughness and it represents the deviation from the mean peak. R_a is often used to define surface roughness, but it does not differentiate between the peaks and the valleys of a surface profile. R_z is the mean of the peak-to-valley height, R_{max} is the maximum of the peak-to-valley height and R_a, R_z, and R_{max} were all measured to characterize the physical changes of the biocomposite sample surfaces.

Weight Change

The weights of the samples were measured before and after the weathering exposure. The samples were dried until their weight stabilized, and then their weight was recorded unto four significant figures.

Results and Discussions

The biocomposites were exposed to moisture absorption tests, accelerated weathering and flammability tests to assess their durability. The results of these tests are discussed in the following sections.

Moisture Absorption

The samples of bioplastics and biocomposites were subjected to controlled moisture absorption analysis in a humidity chamber. The percent weight gained by the samples was plotted against square root of time. The test was continued until the curve leveled off, and the equilibrium moisture content was achieved. Figures 2–4 show the moisture absorption characteristics of the bioplastic samples made from grafted
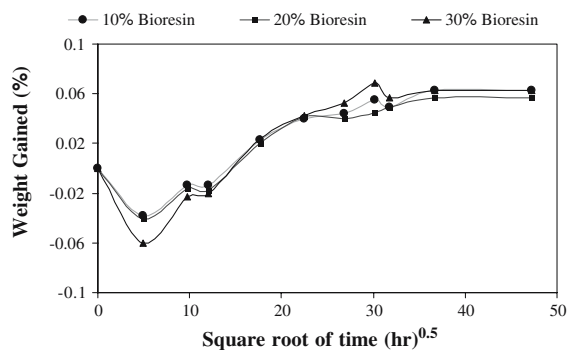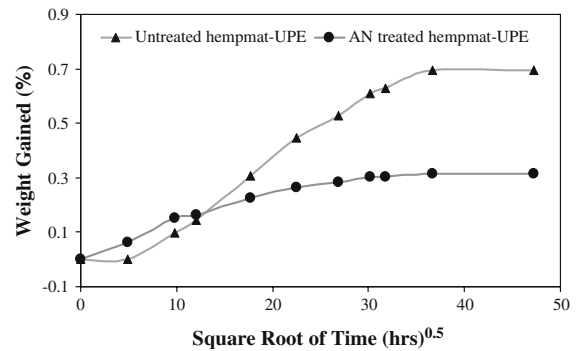
Fig. 2 Moisture absorption of bioresins

Fig. 3 Moisture absorption of biocomposites of hemp mat

soybean polyol, compression molded hemp mat samples, and biocomposites manufactured using SMC.

From Fig. 2, it was seen that the bioplastics samples made using 10, 20, and 30% GFTSOPEP3, lost weight in the beginning of the experiment until 100 h, and then started gaining weight. The equilibrium moisture content for these samples was about 0.006% moisture. This shows very high hydrophobicity of the samples made using bioresins, because under the same conditions, UPE control would have the equilibrium moisture content of about 1%. However, the initial weight loss of these bioplastics samples was not understood. Possible explanations for this cause are the leaching out of bioresin from the plastic samples, or the presence of any unreacted bioresin in the plastic. To investigate these claims, thermal analysis of the samples was done after their initial exposure to humidity chamber.

Figure 3 shows the moisture absorption characteristics of biocomposite samples made with untreated and acrylonitrile treated hemp mat in a UPE matrix. The samples started gaining weight right from the beginning of the experiment, and continued doing so until equilibrium was reached. This tendency was due to the hydrophilic nature of the fibers due to the presence of many OH groups in the cellulosic backbone of biofibers so water molecules get hydrogen bonded to the hydroxyl groups within the fiber cell wall of the biofibers. The equilibrium moisture content for the samples with untreated hemp mat was 0.7%, while that for the one with acrylonitrile treated hemp mat was about 0.3% moisture. Thus, it was observed that in addition to increment in mechanical and thermal properties, acrylonitrile treatment leads to less moisture absorption, giving rise to a more stable composite.

In Fig. 4 the plot of weight gain percent versus time is seen for silane treated BBSG-CaCO$_3$-UPE and silane treated BBSG and green flax core-CaCO$_3$-UPE, both of which were processed by BCSMCP. It was seen that these biocomposites too started gaining weight
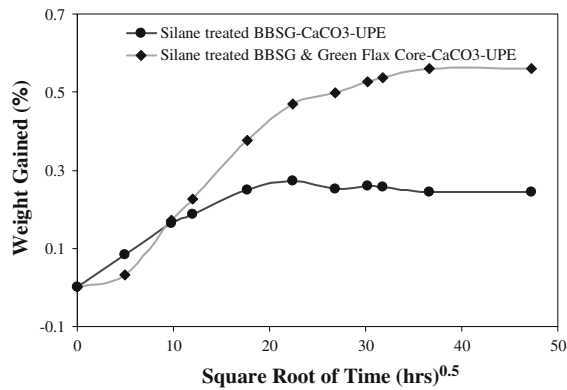
Fig. 4 Moisture absorption of sheet molding compounding (SMC) manufactured biocomposites

right from the beginning of the experiment, and continued doing so until the equilibrium was reached. This weight gain has been observed by many authors, and was due to hydrophilic nature of the fibers due to the presence of many OH groups in the cellulosic backbone of biofibers [10–19]. The equilibrium moisture content for the samples with silane treated BBSG was 0.28%, while that for the one with silane treated BBSG and green flax core was about 0.55% moisture. Here, the equilibrium moisture content of silane treated BBSG and green flax core was more than that of silane treated BBSG. Green flax core, which constitutes 50% fiber and 50% core, is more hydrophilic than grass because of the presence of powdered core. This led to higher weight increase in the hybrid biocomposite containing grass and green flax.

Thermal Analysis of Bioplastics

The bioplastics which lost weight in the initial period of moisture absorption test were thermally investigated by TGA and DSC. These samples were at room temperature before the test. Figures 5 and 6 show the plots from TGA analysis and DSC analysis of the bioplastics
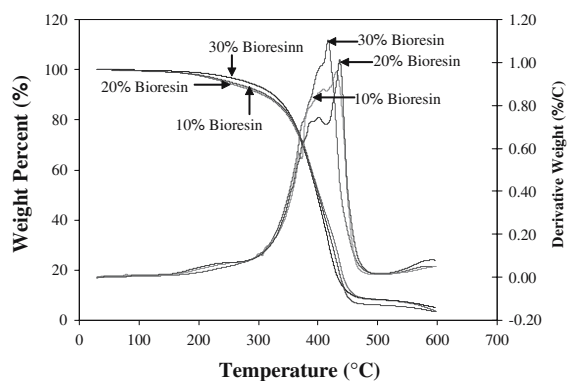

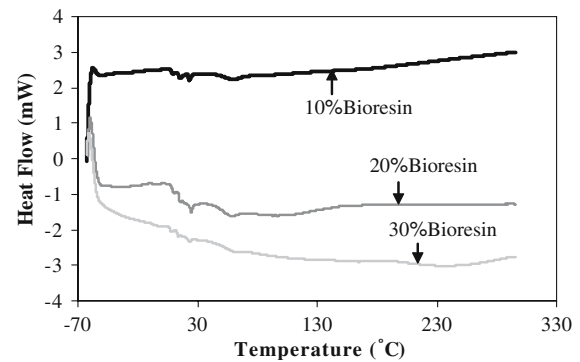**Fig. 5** TGA of bioplastics

Fig. 6 DSC of bioplastics

and Table 1 shows the maximum degradation temperature of the bioplastics examined by TGA. It was observed that on increasing the amount of bioresin in the bioplastic, the maximum degradation temperature decreased. For a bioplastic with 10% GFTSOPEP3, the maximum degradation temperature was 346 °C; for a bioplastic with 20 or 30% GFTSOPEP3, the maximum degradation temperature was 341 and 333 °C, respectively. The initial decomposition temperature of the bioplastics was measured from the TGA plots (shown in Fig. 5). The initial decomposition temperature decreases with an increase of bioresin concentration. The reduction of the initial decomposition temperature is indicative of the existence of unreacted constituents. Generally, thermoset polymers having higher cross-link density show higher maximum decomposition temperature.

Figure 6 shows the hest flow curves from – 60 to 300 °C, obtained from DSC. There were no exothermic peaks in the DSC curves of any of the bioplastic samples. This indicated the absence of any unreacted bioresin in the bioplastic samples.

Accelerated Weathering

The accelerated weathering of the biocomposite samples was done to study the effect of harsh weather elements on the properties of biocomposites. The

Table 1 Maximum degradation temperature of the bioplastics

Sample	Maximum decomposition temperature (°C)
A	346.15
B	341.23
C	332.66

Legend: A = 10% Bioresin, B = 20% Bioresin, and C = 30% Bioresin

exposed samples were evaluated by color test, surface roughness, weight change, and dynamical mechanical analysis. The results from these analyses are presented below.

Color Change

Figures 7–10 show the change in various color parameters of the biocomposite samples with exposure to accelerated weathering.

In the CIELAB system, there are three parameters for color, L*, a*, and b*. The L* axis represents the lightness, whereas, a* and b* axes are the chromaticity coordinates. While +a* is for the red, – a* is for green, +b* for yellow, – b* for blue, and L* varies from 100 (white) to zero (black). The changes in the values of L, a, and b were used to calculate dE*, which is the cumulative color change. The values of dL increased from 0 at beginning of the experiment to 50 for samples exposed for 85 days. This was because the samples were changing color from greenish brown to white after being exposed to UV, rain, condensation and humidity. The combination of water, oxygen and UV irradiation promotes the change of color of these biocomposite samples. The change in L was less pronounced for samples containing BBSG and green flax core which were processed in SMC.

The values of dA decreased from 0 for all samples. The values of dB changed from 0 to positive in case of hemp mat composites, but changed from 0 to negative in case of BBSG and GFC biocomposites. The overall color change of the biocomposites, dE, increased from 0 to 50 for all biocomposites. Here again, the dE values of biocomposites with hemp mat were higher than those of samples containing BBSG and green flax core which were processed in SMC. The color change of untreated hemp mat-based biocomposites was slightly
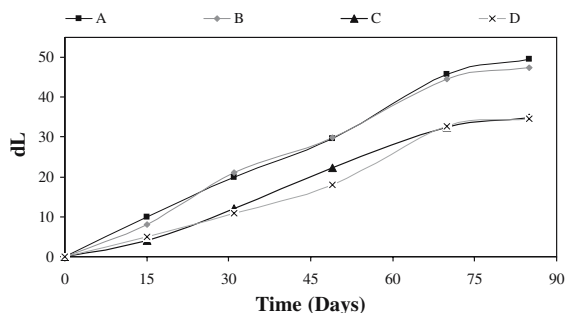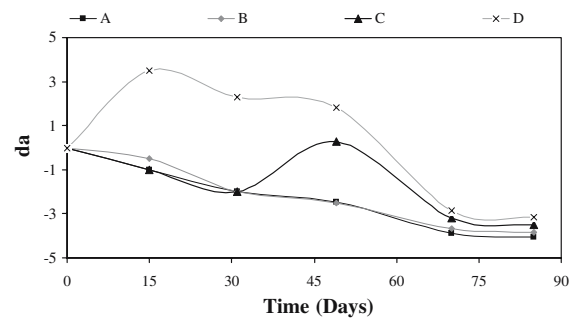

Fig. 8 Change in color parameter 'a' over time for biocomposites. Legend: A = Untreated hemp mat-unsaturated polyester resin (UPE), B = Acrylonitrile treated hemp mat-UPE, C = Silane treated big blue stem grass (BBSG)-CaCO$_3$-UPE, D = Silane treated BBSG and Green flax core-CaCO$_3$-UPE
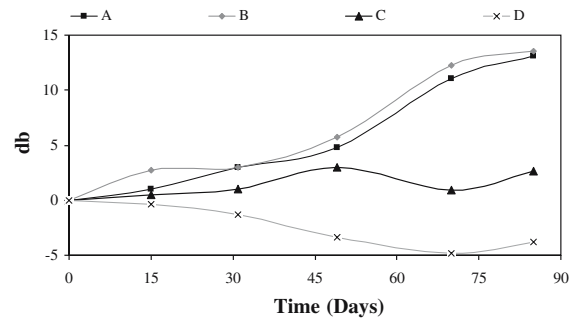

Fig. 9 Change in color parameter 'b' over time for biocomposites. Legend: A = Untreated hemp mat-unsaturated polyester resin (UPE), B = Acrylonitrile treated hemp mat-UPE, C = Silane treated big blue stem grass (BBSG)-CaCO$_3$-UPE, D = Silane treated BBSG and Green flax core-CaCO$_3$-UPE

higher than that of the acrylonitrile treated hemp mat-based biocomposite.

Weight Change

Figure 11 shows the plot of percentage weight gain with exposure time for biocomposite samples. All of
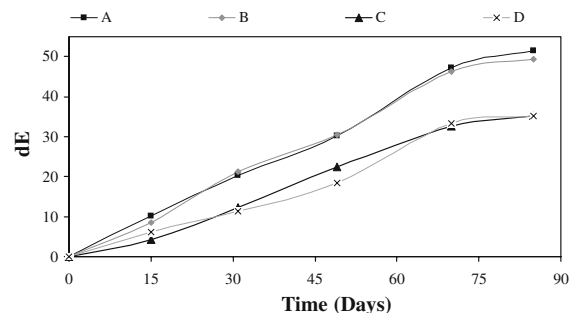

Fig. 7 Change in color parameter 'L' over time for biocomposites. Legend: A = Untreated hemp mat-unsaturated polyester resin (UPE), B = Acrylonitrile treated hemp mat-UPE, C = Silane treated big blue stem grass (BBSG)-CaCO$_3$-UPE, D = Silane treated BBSG and green flax core-CaCO$_3$-UPE

Fig. 10 Change in color parameter 'E' over time for biocomposites. Legend: A = Untreated hemp mat-unsaturated polyester resin (UPE), B = Acrylonitrile treated hemp mat-UPE, C = Silane treated big blue stem grass (BBSG)-CaCO$_3$-UPE, D = Silane treated BBSG and Green flax core-CaCO$_3$-UPE
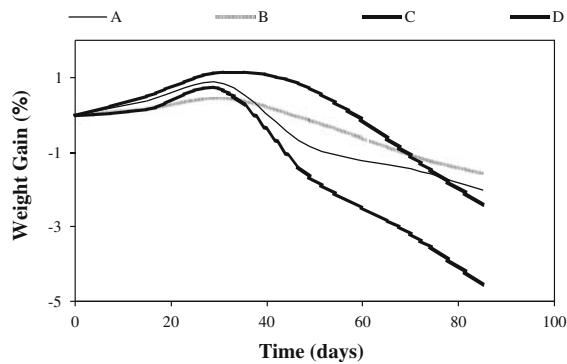
Fig. 11 Change in weight over time for biocomposites. Legend: A = Untreated hemp mat-unsaturated polyester resin (UPE), B = Acrylonitrile treated hemp mat-UPE, C = Silane treated big blue stem grass (BBSG)-CaCO$_3$-UPE, D = Silane treated BBSG and Green flax core-CaCO$_3$-UPE

Fig. 12 Change in roughness parameter R_a over time for biocomposites. Legend: A = Untreated hemp mat-unsaturated polyester resin (UPE), B = Acrylonitrile treated hemp mat-UPE, C = Silane treated big blue stem grass (BBSG)-CaCO$_3$-UPE, D = Silane treated BBSG and Green flax core-CaCO$_3$-UPE

Fig. 13 Change in roughness parameter R_z over time for biocomposites. Legend: A = Untreated hemp mat-unsaturated polyester resin (UPE), B = Acrylonitrile treated hemp mat-UPE, C = Silane treated big blue stem grass (BBSG)-CaCO$_3$-UPE, D = Silane treated BBSG and Green flax core-CaCO$_3$-UPE

Fig. 14 Change in roughness parameter R_{max} over time for biocomposites. Legend: A = Untreated hemp mat-unsaturated polyester resin (UPE), B = Acrylonitrile treated hemp mat-UPE, C = Silane treated big blue stem grass (BBSG)-CaCO$_3$-UPE, D = Silane treated BBSG and Green flax core-CaCO$_3$-UPE

the samples were gaining weight in the beginning of the weathering test, until about 30 days into the test. The weight gain was due to hydrophilicity of the biofibers.

After 30 days of exposure, the biocomposite samples started losing weight and continued doing so until the end of the exposure time. This weight loss was due to the biodegradation of the biocomposites, which began after 30 days of exposure to weathering. However this weight loss was less than 2% for samples with untreated hemp mat and silane treated BBSG. The weight loss was less than 5% for biocomposite sample with silane treated BBSG and GFC, while, it was about 1.25% for the sample with acrylonitrile treated hemp mat. Therefore, it was established that acrylonitrile treatment of the hemp fibers makes them more stable compared to untreated hemp-based ones. This could be due to improved adhesion between fibers and the matrix, and better interfacial bonding in a composite made with surface treated fibers. The values of weight loss was highest for the biocomposite containing silane treated BBSG and GFC was again because of presence of core particles which do not have the characteristics as the fibers.

Surface Roughness

Figures 12, 13, and 14 show the comparison of surface roughness parameters of the biocomposite samples as a function of exposure time. In general, the roughness of the composite samples increased with exposure time. Of all surface roughness parameters, the values of R_a were smallest, followed by those of R_z, and finally those of R_{max}. The roughness parameters of the samples with untreated hemp mat were the highest, followed by samples with silane treated BBSG and GFC, followed by sa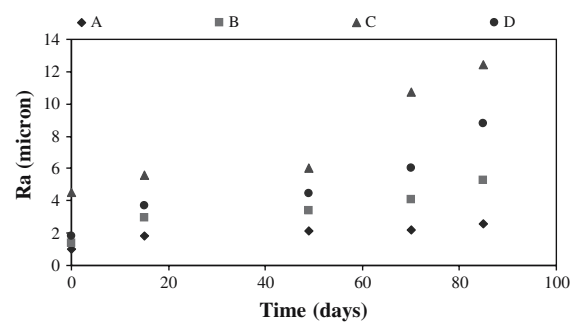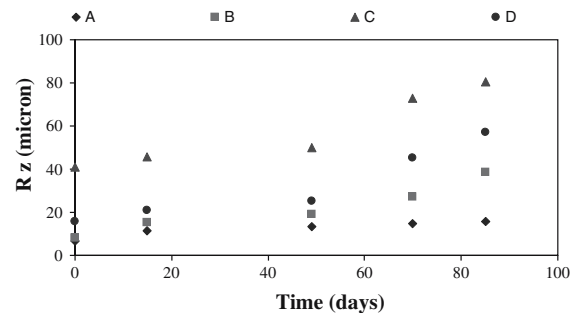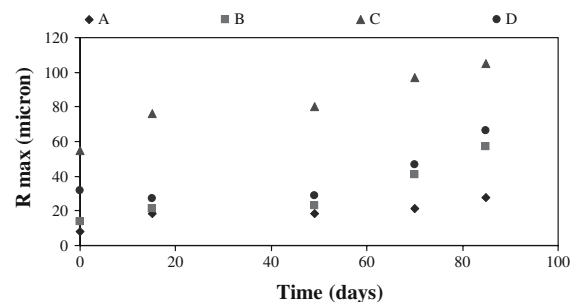mple with acrylonitrile treated hemp mat. The biocomposite samples with silane treated BBSG had the lowest values of surface roughness parameters.

The samples get washed over by water, irradiated by UV, and react with ambient oxygen while in the

accelerated weathering chamber. These conditions lead to breaking of the linkages between the fibers and the matrix, and the biocomposite surface starts crumbling. On increasing the exposure time of weathering, this spreads though the thickness of the composite. The reactions involved in the weather degradation are oxidation, reduction, dehydration, hydrolysis, swelling, shrinking, freezing, and cracking.

The cell wall polymers responsible for the moisture sorption of biofibers are: hemicellulose, accessible cellulose, non-crystalline cellulose, lignin, and crystalline cellulose. The cell wall polymers accountable for the ultraviolet degradation are: lignin, hemicellulose, accessible cellulose non-crystalline cellulose, and crystalline cellulose. While, the cell wall polymers responsible for the thermal degradation properties of biofibers are: hemicellulose, cellulose, and lignin. The strength of the biofibers is controlled by crystalline cellulose, matrix (non-crystalline cellulose + hemicellulose + lignin), and lignin. The biological degradation if cell wall of biofibers is influenced by hemicellulose, accessible cellulose, and non-crystalline cellulose.

Dynamic Mechanical Analysis

Figures 15 and 16 show the storage modules at 40 °C and the T_g of the biocomposites as a function of the exposure time of weathering, respectively, analyzed by DMA. With the physical and chemical changes occurring in the samples in the course of artificial weathering, it was no surprise to see that the values of storage modules at 40 °C and T_g of the biocomposites decreased as the weathering time increased. However, this decrease in modulus was reasonably small, as was seen by other authors earlier [18].

The highest storage modulus was of the sample containing acrylonitrile treated hemp mat-based biocomposite, followed by untreated hemp mat, silane
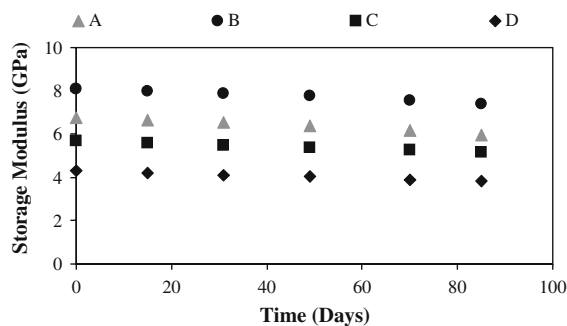

Fig. 15 Change in storage modulus over time for biocomposites. Legend: A = Untreated hemp mat-unsaturated polyester resin (UPE), B = Acrylonitrile treated hemp mat-UPE, C = Silane treated big blue stem grass (BBSG)-CaCO$_3$-UPE, D = Silane treated BBSG and Green flax core-CaCO$_3$-UPE
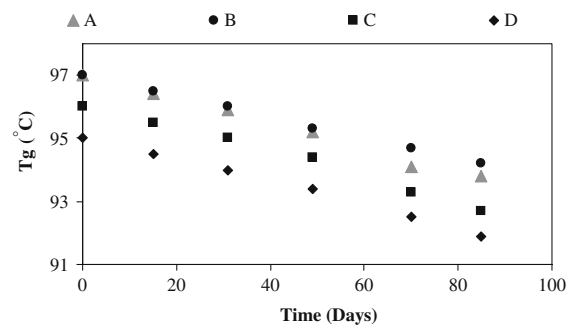

Fig. 16 Change in T_g over time for biocomposites. Legend: A = Untreated hemp mat-unsaturated polyester resin (UPE), B = Acrylonitrile treated hemp mat-UPE, C = Silane treated big blue stem grass (BBSG)-CaCO$_3$-UPE, D = Silane treated BBSG and Green flax core-CaCO$_3$-UPE

treated BBSG, and silane treated BBSG and green flax core. The same trend was observed for glass transition temperatures of biocomposites. The overall decrease in T_g for all samples was less than 3 °C for the entire exposure time. The overall decrease in modulus of surface treated hemp fibers based biocomposites was 8.6% over the entire weathering exposure time, 10% for silane treated BBSG-UPE, 10.3% for untreated hemp mat-UPE, and 11.5% for silane treated BBSG and GFC-based biocomposite. The change in storage modulus was related to change in weight of these samples.

The tendency of biofibers to absorb moisture causes off-gassing (void formation) during compounding. This results in a molded article with a microstructure having variable porosity and resembling that of high-density foam. The pores formed will act as stress concentration points which then lead to an early failure of the composite during loading. Another major drawback of using biofibers as reinforcing agent is the high moisture absorption of the fibers due to hydrogen bonding of water molecules to the hydroxyl groups within the fiber cell wall. This leads to a moisture build-up in the fiber cell wall (fiber swelling) and also reduction in the fiber–matrix interface bonding. This is responsible for changes in the dimensions of biofiber-based composites, particularly in the thickness and the linear expansion due to reversible and irreversible swelling of the composites. As a consequence, the fiber–matrix adhesion is weak and the dimensional stability of biofiber-based composites particularly for outdoor applications will be greatly affected.

Conclusions

In this study the properties of bioplastics and biocomposites following an accelerated weathering expo-

sure have been outlined. It has been observed that the physical, thermal, mechanical and surface properties of the bioplastics and biocomposites change after weathering.

Nature builds lignocellulosic resources from carbon dioxide and water, and it has all the tools to recycle them back to the starting chemicals. Possible ways of degradation include biological, thermal, aqueous, photochemical, chemical, and mechanical means of degradation. In order to produce cellulose fiber-based composites with a long service life, the degradation processes caused by nature need to be retarded. One way of preventing or slowing down the natural degradation process is by modifying the cell wall chemistry of the material which is responsible for many of its properties. This can be accomplished by chemical modification of the fibers. These modifications will help in not only making the biocomposites more weather resistant but also in making their thermo-mechanical properties comparable to glass-based composites.

In order to compare glass-based composites with biocomposites, such studies should be done simultaneously on these composites. Biocomposites offer many advantages over traditional composite materials, and in order to make their use widespread, we need more weathering studies.

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