Degradation Resistance of Alkali-Treated Eucalyptus Fiber Reinforced High Density Polyethylene Composites as Function of Simulated Sea Water Exposure

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To enhance the resistance of eucalyptus (EU) reinforced high density polyethylene (HDPE) composites to exposure in simulated seawater, the EU fibers were modified by alkali treatment with NaOH to prepare wood-plastic composites (WPCs). The materials were characterized by scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), moisture absorption, mechanical properties, and color change tests. After exposure to the sea water, all composites experienced deterioration of water repellency and mechanical properties, and color change. The NaOH concentration greatly influenced the properties of the EU/HDPE composites both before and after exposure. The alkali-treated EU fibers presented low polarities, which resulted in better interfacial bonding, improved mechanical properties, lower moisture absorption, and lower color change relative to the untreated samples after immersion in simulated sea water. The results showed that the HDPE composite prepared with 3% NaOH treated EU fiber had better degradation resistance compared with the untreated composite. The tensile strength, flexural strength, flexural modulus, and impact strength increased 29.9%, 19.8%, 35.4%, and 39.3%, respectively, in comparison with the untreated composite after 21 d exposure. The improved degradation resistance of the alkali-treated EU/HDPE composites could ensure the expected service life of their products and widen their practical applications.

Keywords: Alkali treatment; Eucalyptus; High density polyethylene; Sea water; Mechanical properties; Color change

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INTRODUCTION

Wood-plastic composites (WPCs) have low cost, low density, good mechanical properties, potential sustainability, and biodegradability. They are widely used in outdoor and indoor fabrication applications, such as decking for fencing, landscaping timbers, furniture, boardwalk, timber bridges, and so on. (Leu *et al.* 2012; Olakanmi and Strydom 2016). There also have been numerous cases of WPCs failures in service; with the exceptions of design and construction errors, and accidental or unexpected usage, many failures are due to the service environment, such as exposure to the light, humidity, freezing, thawing, or biodeterioration. These cases stress the need to ensure suitable and safe performance during its expected working life, and its durability and aesthetic aspects play an important role. The serviceability of WPCs applied in UV radiation (Hou *et al.* 2013), natural weathering (Zukowski *et al.* 2018), aging (Wang *et al.* 2017; Wang *et al.* 2018), mildew corrosion (Shao *et al.* 2019), and some outdoor conditions have already been studied. While it is not surprising that sea water diminishes the mechanical properties of WPCs, there has been little research on the serviceability of WPCs in sea water conditions.

Eucalyptus is one of the most common wood species used for furniture, decking, and other wood products. The hemicellulose and lignin in wood fibers are sensitive to UV radiation and moisture, and the wood fibers have weak interfacial bonding with the matrix of the composites (Cai *et al.* 2015). It may be sensible to proceed with surface modification before the WPCs have been prepared. Alkali treatment with NaOH is commonly used to remove nanocelluloses from natural fibers. It exposes hydroxyl groups and roughens fiber surfaces, leading to improved interfacial bonding (Islam *et al.* 2011). Among the different surface modifications of wood fibers, alkali treatment is one of the most popular and lowest cost methods, and it improves the mechanical properties of WPCs (Liu *et al.* 2016; Li *et al.* 2017).

This study explored the degradation resistance of eucalyptus (EU)/high density polyethylene (HDPE) composites under simulated seawater conditions. An alkali treatment was applied to modify the eucalyptus fibers, and hot compression molding was chosen to promote material shaping. The effects of the different NaOH concentrations on the degradation resistance of EU/HDPE composite in simulated sea water were examined. The morphology, moisture absorption, mechanical properties, Fourier transform infrared spectroscopy (FTIR), and color change analysis were examined. It was expected that improved performance of the EU/HDPE composite will broaden its potential application and facilitate large-scale production.

EXPERIMENTAL

Materials

Eucalyptus (EU) powder was purchased from Weihua Perfumery Plant (Jiangmen, China). High density polyethylene (HDPE) and maleic anhydride polyethylene (MAPE) was purchased from Baoxinnuo Plastic and Chemical Co., Ltd. (Suzhou, China). The size of the EU and HDPE particles was 149 μm (100 mesh). The NaOH (1 M), NaCl, $MgCl_2$, Na_2SO_4, $CaCl_2$, KCl, $NaHCO_3$, KBr, H_3BO_3, $SrCl_2$, and NaF (technical pure) were purchased from Zhiyuan Chemical Additives Co., Ltd. (Tianjin, China).

Preparation of EU/HDPE Composites

The EU powder was soaked in 1%, 3%, and 5% NaOH at a temperature of 100 °C for 1 h (solid: liquid = 1:2, v:v). The alkali-treated fibers were separated by filtration and washed with deionized water until the rinsed solution became neutral. The rinsed fibers were dried at a temperature of 90 °C for 24 h, and the HDPE powder and MAPE were dried at a temperature of 90 °C for 12 h in a DHG-9140A electro-thermostatic drum-wind drying oven (Dongmai Scientific Instrument Co., Ltd., Nanjing, China) before the composite preparation step.

The EU fiber, HDPE, and MAPE were mixed with the mass ratio 100:100:3 in an SBH-5L 3D linkage mixer (Xinbao Mechanical and Electrical Industry Co., Ltd., Nanjing, China) followed by hot compression molding at 155 °C, 3.7 MPa for 9 min. All samples were 120 mm in length, 100 mm in width, and between 5 mm and 8 mm thick. They were processed to obtain the required dimensions for characterization after demolding and cooling. The untreated EU fiber reinforced HDPE composite was the control group and labeled as “untreated”; the different concentrations of alkali treated EU/HDPE composites were labeled as “1% NaOH”, “3% NaOH”, and “5% NaOH”, respectively.

Degradation Testing of EU/HDPE Composites in Simulated Seawater Exposure

The simulated sea water was prepared according to the standard ASTM D1141-1998 (2013), and its chemical components are listed in Table 1. NaOH was used to adjust the solution to pH 8. The degradation test of the samples was carried out in a constant temperature water-bath (35 °C) in the HH-600 thermostatic water tank (Bongxi Instrument Equipment Co., Ltd., Shanghai, China) by total immersion in a stagnant solution without agitation. All samples were subjected to 7 d, 14 d, and 21 d exposure followed by air-drying. Then, the composites were sealed and stored for further characterization analysis.

Table 1. Chemical Components of the Simulated Sea Water

Component	Concentration (g·L^{-1})
NaCl	24.53
$MgCl_2$	5.20
Na_2SO_4	4.09
$CaCl_2$	1.16
KCl	0.695
$NaHCO_3$	0.201
KBr	0.101
H_3BO_3	0.027
$SrCl_2$	0.025
NaF	0.003

Characterization

The morphology of the samples was studied with a HITACHI S-4800 field emission scanning electron microscope (SEM; Tokyo, Japan). The samples were sputter-coated with gold-palladium using an E-1010 ion sputter and operated at 3 kV.

The composites were subjected to 90% relative humidity at a temperature of 23 ± 0.5 °C for 6, 12, 24, 48, 72, or 96 h in an HPX-160BSH-III temperature humidity incubator (CIMO Medical Instrument Manufacturing Co., Ltd., Shanghai, China). The moisture absorption value was calculated from the weight gains after removing excess water on the exterior surface.

The tensile strength, flexural strength, and flexural modulus of samples were measured using a CMT6104 electronic universal testing machine (MST Systems (China) Co., Ltd., Shanghai, China) at a loading speed of 2 mm·min^{-1}. The impact strength of the composites was evaluated using an XJJ-5 beam impact testing machine (Jinjian Testing Instrument Co., Ltd., Chengde, China) at an impact energy of 2 J.

The Fourier transform infrared spectroscopy (FTIR) spectra of the samples were recorded by a Nicolet iS10 FTIR spectrometer (Thermo Fisher Scientific, Shanghai, China) at the range of 4000 cm^{-1} to 400 cm^{-1} and resolutions of 4 cm^{-1} for 16 scans.

The color change of the composites was evaluated using a HP-200 colorimeter according to the CIE 1976 ($L^*a^*b^*$) color system. Lightness (L^*) and chromaticity coordinates (a^* and b^*) were measured for six replicate samples. L^* represents the lightness coordinate and varies from 100 (white) to 0 (dark); a^* represents the red ($+a^*$) to green ($-a^*$) coordinate; b^* represents the yellow ($+b^*$) to blue ($-b^*$) coordinate. The discoloration (ΔE^*) was calculated according to the following equation:

$$\Delta E^{*}=[(\Delta L^{*})^{2}+(\Delta a^{*})^{2}+(\Delta b^{*})^{2}]^{1/2} \quad (1)$$

where $+\Delta L^{*}$ and $-\Delta L^{*}$ represent whitening and darkening, respectively; $+\Delta a^{*}$ and $-\Delta a^{*}$ represent the color shift toward red and green, respectively; $+\Delta b^{*}$ and $-\Delta b^{*}$ represent the color shift toward yellow and blue, respectively. It should be noted that the ΔE^{*} represents the magnitude of the color difference but does not indicate the direction of this difference.

RESULTS AND DISCUSSION

Morphology of EU/HDPE Composites

The SEM images of the untreated and alkali-treated EU fiber-reinforced HDPE composites before and after 21 d of simulated seawater exposure are shown in Fig. 1. Before the exposure, the interface between the EU fiber and HDPE was well jointed and revealed good compatibility, except in the case of the 1% NaOH-treated composite (Fig.1a-1d). With the increase of the NaOH concentration, fewer fibers were exposed and the composites presented smooth and integrated surfaces (Fig. 1c, 1d). Fiber delamination and several fiber fines appeared in the micro-surface of the 1% NaOH-treated sample (Fig. 1b). After the alkali treatment, most of the hemicellulose, lignin, and other soluble materials were removed, and the alkali-treated wood fiber resulted in a rough surface, which allowed the polymer to adhere onto it through mechanical interlocking and improved the interaction between the two phases (Mngomezulu *et al.* 2011). In the lower alkali concentration (≤1%), only a small part of the EU fibers could be bonded with HDPE, and some fibers remained uncovered outside the matrix. After 21 d of simulated sea water exposure, some fibers were pulled out, and fiber breakage (large voids formed by the fibers pulling out of the matrix) was apparent on the fractured surface of the untreated composite (Fig. 1e). Interfacial delamination and small voids emerged on the 1% NaOH sample (Fig. 1f). The surfaces of the 3% NaOH and 5% NaOH composites exhibited well-defined interfaces after 21 d exposure, especially the 3% NaOH sample (Fig. 1g, 1h). The alkali pretreatment could induce dispersion of the fiber bundles into fine fibers, which caused an increase in aspect ratio of the fiber and the effective contact area between the fiber and matrix. Therefore, the alkali treatment of the EU fibers would enhance the adhesive strength between the fiber and HDPE matrix. During the treatment at a high NaOH concentration (≥ 5%), the EU fiber was dispersed into many small pieces, indicating more contact points, but each contact area between the fiber and matrix became smaller. The smaller contact area would be disrupted after 21 d exposure. The fiber pull-outs, fiber breakage, and voids that appeared in the microstructure all indicated the presence of micro-cracks and weak interfacial interaction, which would directly correspond to the degradation of the mechanical properties of the composites.

Moisture Absorption of EU/HDPE Composites

The moisture absorption of the untreated and alkali-treated EU fiber-reinforced HDPE composites before and after 7 d, 14 d, and 21 d simulated sea water exposure are presented in Fig. 2. The moisture absorption in each exposure period, including the untreated sample was similar: with the increased absorbing-time, the moisture content of all composites grew rapidly at first (in 24 h) and then reached saturation gradually. The moisture content before exposure and after 21 d exposure of the untreated and 1%, 3%, and 5% NaOH treated composites increased from 1.41% to 3.23%, 0.99% to 2.4%, 0.83% to

2.24%, and 0.63% to 1.89% when saturated, respectively. The untreated EU/HDPE composite exhibited higher moisture absorption relative to the three alkali-treated composites before exposure and after 7d, 14d, and 21d exposure. And as expected, the order was as follows: untreated > 1% NaOH > 3% NaOH > 5% NaOH. This result demonstrated that the reduction of hemicellulose, lignin, and other hydrophilic components endowed the composite with hydrophobicity, and this behavior increased with NaOH concentration. Under the alkali treatment, the individual fibers were detached from the fiber bundles, and the effective contact area of fibers and matrix was expanded. Hence, the moisture absorption could also indicate the changes in interfacial bonding.

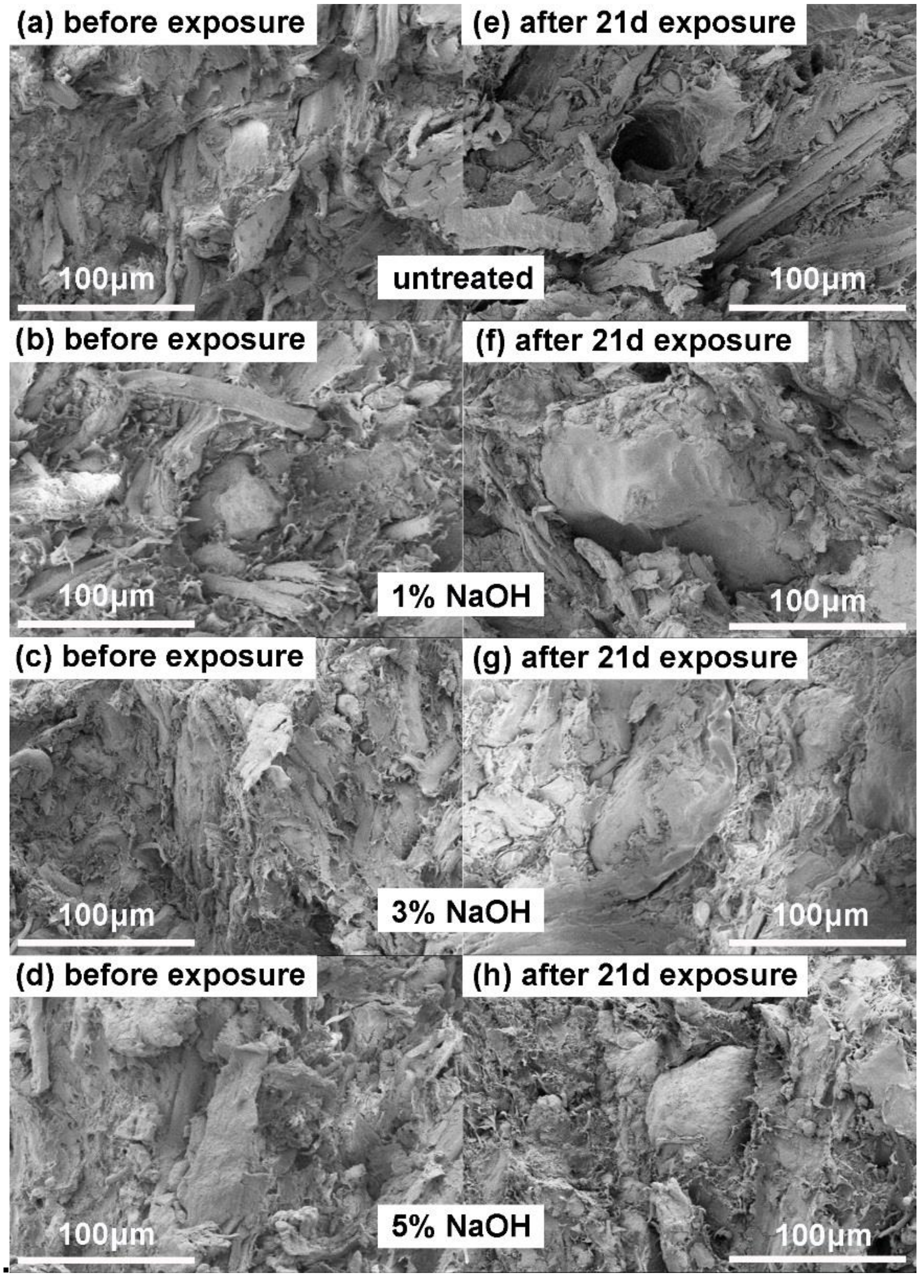

Fig. 1. SEM images of untreated and alkali-treated EU fiber reinforced HDPE composites before and after 21 d of simulated sea water exposure

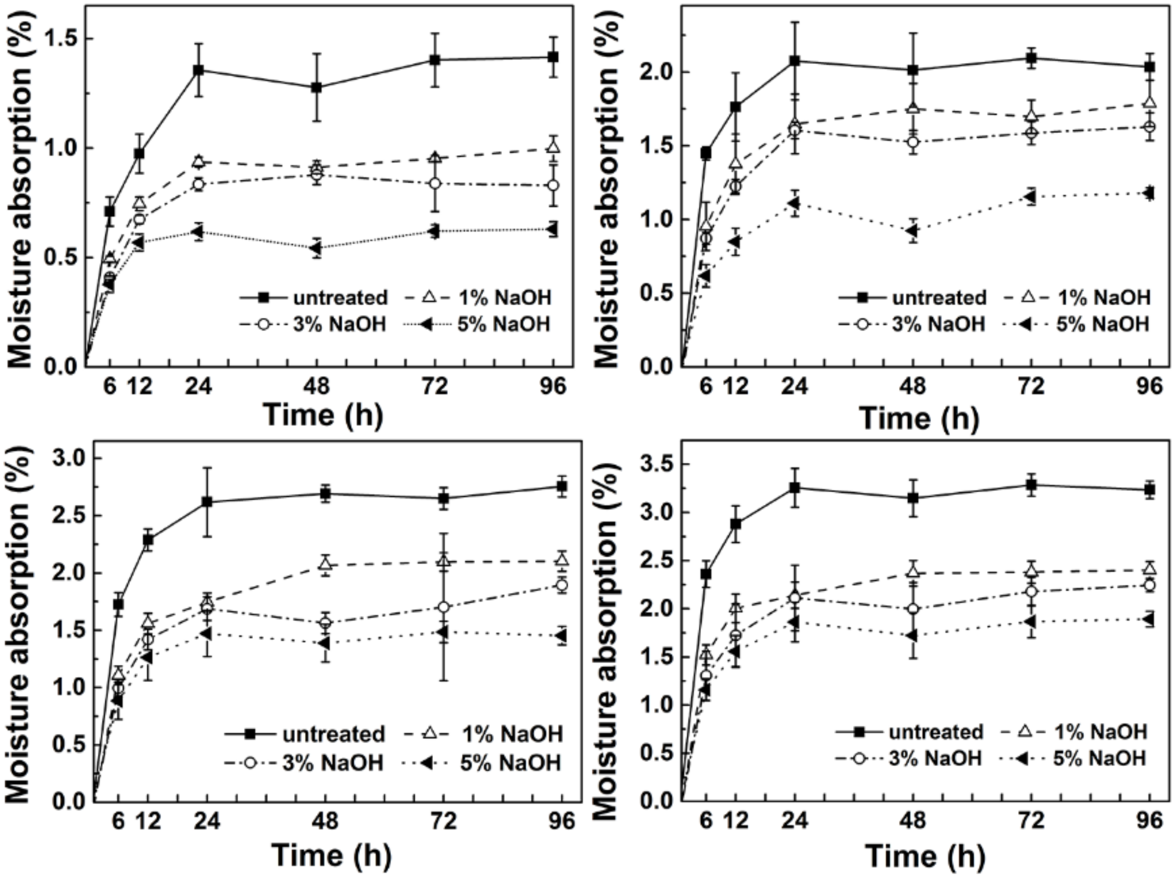

Fig. 2. The moisture content of untreated and alkali-treated EU fiber reinforced HDPE composites (a) before and (b) after 7 d, (c) 14 d, and (d) 21 d of simulated seawater exposure

Mechanical Properties of EU/HDPE Composites

Figure 3 shows the plots of the compiled data for the mechanical properties for the untreated and alkali-treated EU fiber-reinforced HDPE composites before and after 7 d, 14 d, and 21 d of simulated sea water exposure. With the increase of the exposure time, the tensile strength, flexural strength, flexural modulus, and impact strength of the untreated and alkali-treated EU/HDPE composites all tended to decline. The simulated sea water could degrade and destroy the inner structure of the composites. The fractures and voids that formed would limit the stress transferring from the matrix to fibers, which made it easier to accumulate stress, causing stress ruptures. Furthermore, the sea water molecules played a “swelling agent” role in the cellulose network structure, which led to more freedom of movement, damaging the non-deformability of the cellulose. Therefore, longer exposure time of the composites led to more fractures and voids, which brought poorer bonding quality in the two phases and lower rigidity of the fibers.

The different concentrations of alkali treatments all could significantly ameliorate the mechanical properties of the EU/HDPE composites after immersion in the simulated sea water. This behavior could relate to the following two aspects (Luo *et al.* 2016; Shanmugasundaram *et al.* 2018): (1) unwanted substances were removed from the fiber surface, and fiber fibrillation was induced (the bundle of fibers split into filaments) under the alkali treatment, which increased the surface roughness and resulted in a better interlocking of the cellulose chains and a good mechanical bonding between the fiber and matrix; (2) more cellulose was exposed on the fiber surface, which provided more reaction sites for the two phases. In the role of the alkali treatment, the EU fibers were rearranged along the direction of the extension deformation, resulting in higher tensile strength; improvement of the flexural strength and modulus was due to the strengthened fiber-matrix interface; the low impact strength owed to the short fiber pull-out length (Bledzki *et al.* 2012). The alkali treatment endowed the matric with better compatibility, which could lengthen the propagated crack and the sample required a higher energy amount to reach to the critical point of impact fracture.

The mechanical properties of the composites increased with the increase of the NaOH concentration, but those deceased slightly at higher alkali concentrations (5%). This phenomenon occurred in each exposure period. Based on the above analysis, the alkali treatment could strengthen the interfacial bonding and improve the mechanical properties. Higher alkali concentrations would lead to excess delignification of the natural fibers, thus resulting in weaker or damaged fibers, which corresponded with degraded mechanical properties. The optimum mechanical properties were observed with the 3% NaOH treatment before and after exposure. After 21 d of simulated sea water exposure, the tensile strength, flexural strength, flexural modulus, and impact strength of the 3% NaOH treated EU/HDPE composite was 13.81MPa, 24.27MPa, 2.29GPa, and 4.35 KJ·m^{-2}, respectively. These values equated to an increase of 29.9%, 19.8%, 35.4%, and 39.3% in comparison with the untreated composite. The mechanical properties of the 3% NaOH treated sample exposed for 21 d were all higher than the unexposed untreated sample.

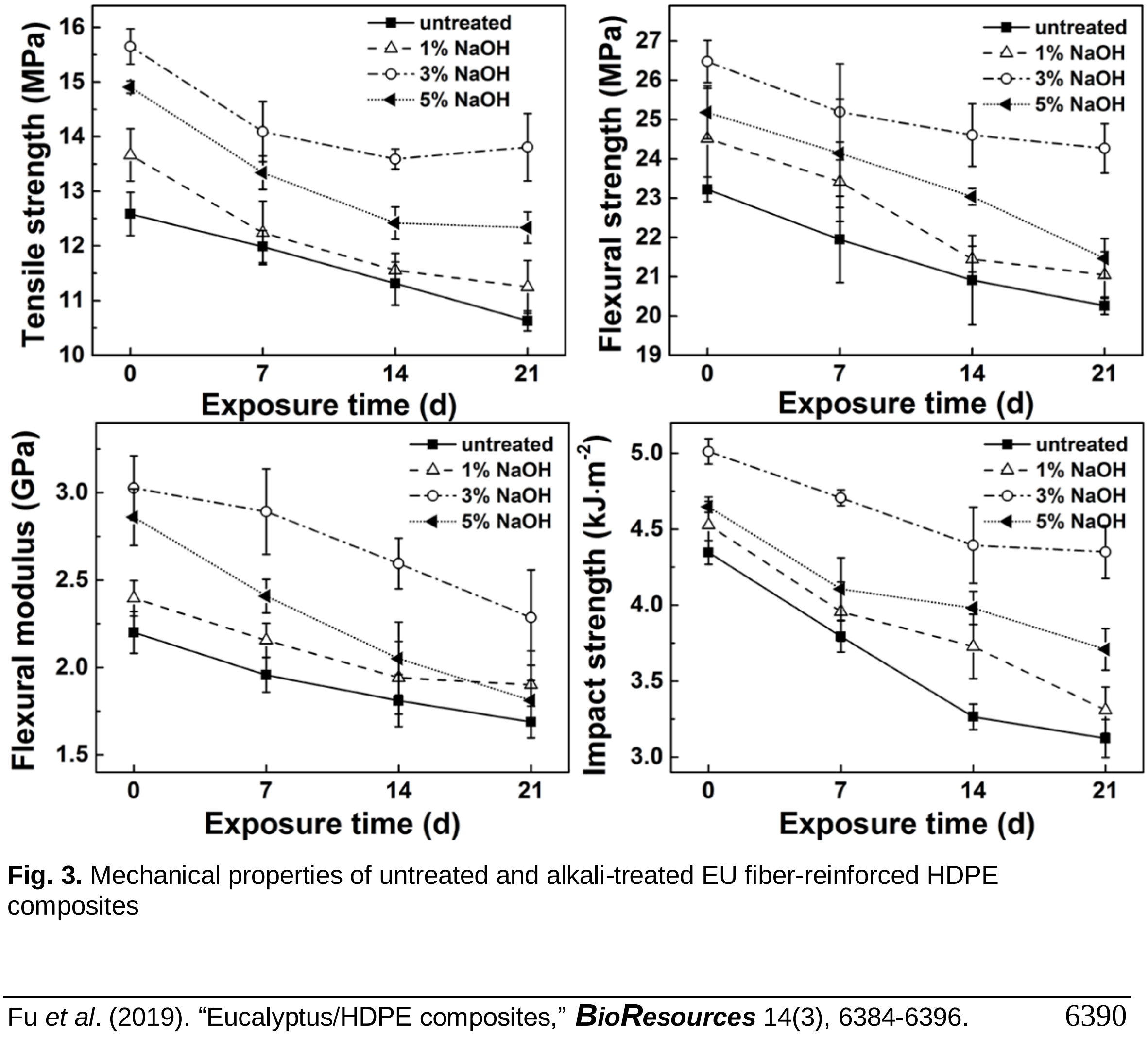

Fig. 3. Mechanical properties of untreated and alkali-treated EU fiber-reinforced HDPE composites

Chemical Structure Analysis of EU/HDPE Composites

The chemical structure of the untreated and alkali-treated composites before and after 21d of simulated sea water exposure was monitored by FTIR spectroscopy (Fig. 3). As expected, all three alkali-treated EU/HDPE composites displayed similar spectra and were clearly different from the spectra of the untreated sample in some ranges before exposure (Fig. 3a). Spectral measurements over a strong, wide band between 3700 cm^{-1} and 3100 cm^{-1} were taken in all samples, which was the characteristic vibration of the -OH groups present in wood fiber (mainly from the cellulose, hemicellulose, polysaccharides, and monosaccharides) (Fu *et al.* 2016). This absorption peak became weaker as NaOH concentration increased, which indicated that the alkali treatment could reduce the polarity and hydrophilicity of the EU fiber (Das and Chakraborty 2006). There was a great difference between the untreated and alkali-treated samples at the wavenumber around 2900 cm^{-1}. A peak at 2919 cm^{-1} for the untreated composite was the C-H stretching vibration of methyl and methylene groups in cellulose and hemicellulose (Negawo *et al.* 2019). The three alkali-treated composites showed two different pattern peaks located at 2920 cm^{-1} and 2849 cm^{-1} that were assigned to C-H stretching of the $-CH_2$ groups, principally of the HDPE polymeric matrix (García-Sánchez *et al.* 2017). This phenomenon manifested itself because the alkali treatment had broken the original linkage between the fiber and polymer; thus some functional groups of the HDPE matrix appeared. In comparison with the alkali-treated composites, the untreated composite was observed to have its own absorption peaks at 1734 cm^{-1}, 1426 cm^{-1}, and 1249 cm^{-1}, which represented the carbonyl (C=O) stretching of the acetyl groups of hemicellulose and pectin (Li *et al.* 2017), the CH_2 stretching of cellulose, and the C=O stretching of hemicellulose, respectively (Senthamaraikannan and Kathiresan 2018). Some peaks were considerably weaker in the alkali-treated samples, such as the peaks at 1595 cm^{-1} and 1031 cm^{-1}, which were attributed to the C=O and C-OH stretching of lignin. Those peaks disappeared or were reduced in the alkali-treated composites, which demonstrated that the alkali treatment caused the removal of the binding materials from the EU fiber bundles and incurred a separation into elementary fibers.

After 21 d of exposure, the untreated and treated samples exhibited similar spectra apart from a few distinctions. The biggest difference was the peak at 1734 cm^{-1} (assigned to the C=O stretching of the acetyl groups of hemicellulose and pectin), which was absent in the three different NaOH concentration treated composites. The untreated composite possessed a stronger peak intensity than the three alkali-treated composites at the wavenumbers of similar absorption peaks, such as the broad band around 3400 cm^{-1} and the peaks at 1595 cm^{-1}, 1426 cm^{-1}, and 1031 cm^{-1}. As with the above analysis, those peaks were attributed to the -OH, C=O, CH_2, and C-OH function groups in the EU fiber. Under the immersion in the simulated sea water, the fibers were stripped from the matrix, leading to more exposure of the cellulose, hemicellulose, and lignin, so that stronger absorption peaks were found in the spectra. The reduction of those peaks in the treated composites contributed to the removal of some cellulose, hemicellulose, and lignin from the EU fiber during the alkali treatment. Similar trends occurred at the wavenumber around 2900 cm^{-1} (the C-H and $-CH_2$ stretching vibrations) and 718 cm^{-1} ($-CH_2$ oscillation vibration) in the functional groups of the HDPE (Hu *et al.* 2013). This also proved that the exposure could cause breakage in the HDPE molecular chain. Those peaks of the alkali-treated samples were weaker after exposure compared to the unexposed samples. This was because the alkali treatment had already removed some soluble parts from the fiber and improved the bonding quality between two phases. The sea water would disrupt the chemical structure of the fiber and matrix, while the alkali-treated composites of good interface bonding would suffer lower molecular chain breakage. The FTIR analysis further supported the conclusion that the alkali treatment could strengthen the interface bonding force between the EU fiber and HDPE from the chemical structural level, even after 21 d of simulated sea water exposure.

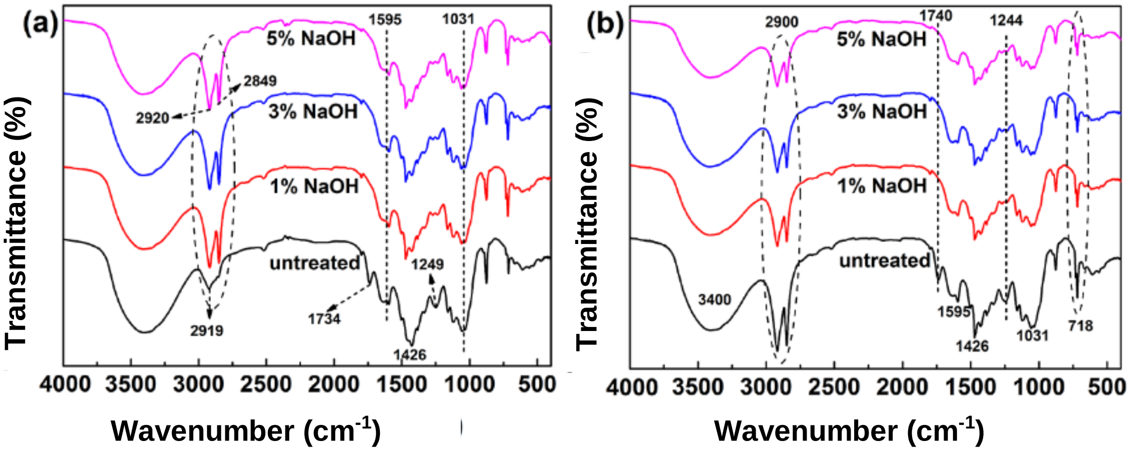

Fig. 4. FTIR spectra of untreated and alkali-treated EU fiber-reinforced HDPE composites

Color Change Analysis of EU/HDPE Composites

The color change properties of the untreated and alkali-treated EU fiber-reinforced HDPE composites after 7 d, 14 d, and 21 d simulated sea water exposure are listed in Table 2. ΔE^* represents the discoloration intensity, and a higher ΔE^* value indicated a great color variance between the exposed and unexposed samples. With increasing exposure time, ΔE^* values of three different concentrations of alkali-treated EU/HDPE composites all increased. The color variance depended on the degree of dissolution of water-soluble pigment in the fiber. The sea water exposure formed fractures and voids between the matrix and fiber, and longer exposure would cause more flaws; thus more fibers suffered from contact with water and leached more water-soluble pigments. From Table 2, the value of ΔE^* was equal to that of ΔL^* (9-12), and the absolute value of Δa^* and Δb^* was smaller (<5), which meant that the composites experienced great color change after exposure, mainly fading. The structural flaw would induce exposure and oxidation of the carbonyl group in fiber, and the conjugation of the oxidation products and benzene rings formed double bond groups, causing discoloration (Chen 2012). While the chromophoric groups (conjugated carbonyl vibration at 1637 cm^{-1} and the double bond bending vibration at 1000 cm^{-1} to 670 cm^{-1}) did not intensify (Fig. 3), the effect of Δa^* and Δb^* on the color change of the exposed samples could be ignored. During the three periods of exposure, each color change property of alkali-treated composites all presented a lower level of degradation in comparison with untreated sample, and the decreasing amplitude order of alkali-treated samples was 3% NaOH > 1% NaOH > 5% NaOH. The alkali treatment endowed the composite with better interfacial bonding, indicating increased fiber encapsulation by the matrix, which created a barrier against the water. This resulted in low swelling and a lower dissolution rate of the water-soluble pigments. Based on the above analysis, the 3% NaOH sample showed better interfacial compatibility and mechanical properties; hence it also had a better improvement of the color change brought by the sea water exposure. In general, the alkali treatment could relieve the discolourization of composites, but it could not totally counteract the degrading effect of sea water on the wood-plastic composites.

Table 2. Color Change Properties of Untreated and Alkali-treated EU Fiber Reinforced HDPE Composites after Simulated Sea Water Exposure

Exposure Time (d)	Untreated			
	ΔL^*	Δa^*	Δb^*	ΔE^*
7	11.34 ± 0.20	-0.17 ± 0.01	1.72 ± 0.04	11.47 ± 0.81
14	12.39 ± 0.56	-0.25 ± 0.01	2.7 ± 0.11	12.69 ± 1.04
21	16.18 ± 0.37	-0.36 ± 0.05	2.99 ± 0.08	16.46 ± 0.95
Exposure Time (d)	1% NaOH			
	ΔL^*	Δa^*	Δb^*	ΔE^*
7	10.03 ± 0.34	1.54 ± 0.04	3.06 ± 0.12	10.60 ± 1.13
14	10.05 ± 0.30	1.90 ± 0.03	3.64 ± 0.22	10.86 ± 0.9
21	11.14 ± 0.45	2.26 ± 0.07	4.17 ± 0.33	12.11 ± 1.24
Exposure Time (d)	3% NaOH			
	ΔL^*	Δa^*	Δb^*	ΔE^*
7	9.13 ± 0.48	0.63 ± 0.06	2.22 ± 0.25	9.15 ± 0.52
14	9.24 ± 0.71	0.67 ± 0.08	2.43 ± 0.46	9.58 ± 1.49
21	9.35 ± 0.89	0.85 ± 0.03	2.54 ± 0.23	9.73 ± 1.25
Exposure Time (d)	5% NaOH			
	ΔL^*	Δa^*	Δb^*	ΔE^*
7	10.74 ± 0.38	1.46 ± 0.06	3.58 ± 0.15	11.41 ± 1.39
14	11.48 ± 0.55	1.53 ± 0.08	3.59 ± 0.28	12.13 ± 1.55
21	12.36 ± 0.25	1.62 ± 0.05	3.65 ± 0.10	12.99 ± 1.25

CONCLUSIONS

1. Eucalyptus fiber/ high density polyethylene (EU/HDPE) composites with improved degradation resistance were prepared by modifying the EU fibers with alkali treatment.
2. The properties of the untreated and alkali-treated composites all exhibited a certain extent of deterioration after three periods of exposure in a simulated sea water condition. The alkali treatment played a vital role in improving the properties of the composites before exposure and decreased the degradation degree of sea water exposed samples. SEM images revealed the interfacial bonding state of the fiber and matrix. It was found that with increasing NaOH concentration, more fiber bundles were dispersed into fine fibers, which resulted in a more effective interfacial interaction between the fibers and matrix. The moisture absorption had a positive relationship with NaOH concentration, which could further strengthen interfacial bonding.

3. The alkali treatment weakened the polarity and hydrophilicity of the EU fiber, and at different concentrations all treatments ameliorated the reduction of the mechanical properties and discoloration of the composites after sea water exposure. The composite prepared with 3% NaOH treated EU fiber possessed the best degradation resistance.

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