Polymer Testing 101 (2021) 107290

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Characterization of weathered MCC / nutshell reinforced composites

Sevda Boran Torun [a,*], Eylem D. Tomak [b], Ayfer Donmez Cavdar [c], Fatih Mengeloglu [d]

[a] Department of Woodworking Industry Engineering, Karadeniz Technical University, 61830, Trabzon, Turkey
[b] Department of Forest Industry Engineering, Faculty of Forestry, Bursa Technical University, 16310, Bursa, Turkey
[c] Department of Forestry Industry Engineering, Karadeniz Technical University , 61080, Trabzon, Turkey
[d] Department of Forestry Industry Engineering, Kahramanmaras Sutcu Imam University, 46100, Kahramanmaras, Turkey

ARTICLE INFO

Keywords:
Weathering
MCC
Nutshell
Composite
Surface characteristics
Mechanical properties

ABSTRACT

Microcrystalline cellulose (MCC) and nutshell fiber reinforced high-density polyethylene (HDPE) composites were exposed to accelerated weathering for total of 672 h. The effects of weathering exposure on the mechanical, surface and morphological properties of the composites were investigated. The results revealed that the weathering exposure caused a slight decrease on tensile and flexural strengths whilst the modulus of elasticity increased up to 62%. The MCC / nutshell reinforced composites had higher color changes and gloss loss than MCC reinforced composites. Addition of MCC and nutshell to HDPE composites increased surface roughness of samples. After the weathering, the polymer band intensities decreased due to the degradation. The SEM observations on the exposed composites are in accordance with the surface roughness of composites after weathering. The investigated properties of MCC/nutshell filled HDPE composites were less affected by weathering exposure than those of composites without nutshell.

1. Introduction

The plastic industry has benefited from inorganic materials such as talc, calcium carbonate, mica, glass, carbon fiber for many years to improve material properties. However, the new restrictions have recently been imposed by many governments due to environmental factors such as global warming, and this encourages the use of natural fibers rather than inorganic materials. These natural fibers have many advantages compared to the inorganic fillers. Their ecological characteristics, biodegradability, low costs, non-corrosive structures, easy fibrillation, high fiber loading capacity, low densities, very wide and different types of fiber variety explain why these fibers attract many industries [1–5]. Recent studies have shown that natural fibers as cotton fiber, wheat straw, paddy, wood pulp, flax, hemp, tea mill waste, walnut shell, sawdust, coconut, bamboo, corn stalk and banana fibers can be used as fillers in polymer matrices [3,5–8].

The natural fiber derived from agricultural wastes has great importance to provide an economic income for farmers and to contribute to waste management [9–11]. Nutshell, which is relatively hard material, can be used as a filler material in plastic matrix composites due to its cellulosic structure. This natural material abundantly presents in Eastern Blacksea region of Turkey but unfortunately it is used generally for heating purposes in houses [9]. The nutshell contains 25–30% cellulose and hemicellulose and 30–40% lignin [8,12]. On the other hand, the microcrystalline cellulose (MCC) obtained from different cellulosic materials has a high specific surface area [13–16]. The MCC which ensures a strong reinforcement in polymer matrix improves some properties of polymer composites [17]. The wood-plastic composites (WPCs) are generally used in outdoor deck floors, window and door frames, fences, landscaping timbers, also used in the automotive industry. The weathering resistance of the composites has been affected by outdoor degrading factors such as moisture, sunlight, heat/cold, chemicals, abrasion by windblown materials, and biological agents [18–20]. Outdoor factors change both appearance and mechanical properties of WPCs. Therefore, the effect of outdoor degrading factors should be minimized to provide sustainable, durable and aesthetic materials to consumers [21,22]. The chromophores in the lignocellulosic materials increase the absorption of ultraviolet light (UV) which causes subsequent photodegradation. Some studies with ultraviolet absorbers, hindered amine light stabilizers, and nanoparticles have ensured promising results [23,24]. There are three main natural wear factors: solar energy, temperature, and humidity. The effect of solar energy consists of two parts. The first is daylight, the energy absorbed by direct sunlight, and the other is diffusion in the atmosphere and reflected light. It is known

* Corresponding author.
E-mail address: sboran@ktu.edu.tr (S. Boran Torun).

https://doi.org/10.1016/j.polymertesting.2021.107290
Received 10 September 2020; Received in revised form 14 January 2021; Accepted 6 July 2021
Available online 7 July 2021
0142-9418/© 2021 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Table 1
The experimental design for composites manufacturing.

Samples	Components[a]			
	PE	PE-g-MA	MCC	Nutshell fiber
HDPE	96	4	–	–
MCC5	91	4	5	–
MCC10	86	4	10	–
MCC15	81	4	15	–
HDPE/N30	66	4	–	30
MCC5/N30	61	4	5	30
MCC10/N30	56	4	10	30
MCC15/N30	51	4	15	30

[a] Components amounts are given in percent; HDPE: high density polyethylene; MCC: microcrystalline cellulose; N: nutshell; and PE-g-MA: polyethylene graft maleic anhydride.

that the sunlight has significant influence on the wood and plastic based materials resulting surface fading, discoloration, surface erosion, and loss of gloss [25]. When the moisture remains on the surface for a long time, it acts as a solvent and leads to a shrinkage of the material [26,27].

The aim of this study was to investigate the weathering resistance of the HDPE composites produced by addition of nutshell fiber and MCC. There has not been sufficient literature on weathering performance of nutshell fiber and MCC reinforced HDPE composites. MCC and MCC/nutshell added polymer composites were exposed to accelerated weathering for 672 h. Color, gloss, and roughness of the composite surfaces measured at regular intervals during weathering period. Surface chemical composition was investigated by ATR-FTIR spectroscopy, and surface morphology was evaluated by scanning electron microscopy (SEM). In addition, the flexural and tensile properties of the weathered composites were determined.

2. Materials and method

2.1. Materials

The high density polyethylene (HDPE) (density: 0.96 g/cm^3) was provided by Petkim Petrochemical Company in İzmir, Turkey. Polyethylene graft maleic anhydride (PE-g-MA) (density: 1.48 g/cm^3) and microcrystalline cellulose (MCC) (average volume diameter ~40 μm) were supplied from Merck. Nutshells were collected from the Eastern Blacksea region of Turkey. The nutshells were milled into small particles by using a lab-scale grinder. The grounded nutshells fibers on the 0.5 mm screen were used.

2.2. Composite manufacturing

The nutshell fibers and MCC were dried. These fibers were blended with MCC and HDPE for 3 min. Then, the blend was fed from the hopper in a single screw extruder (L/D 30, Teknomatik Co., Turkey). The rotor speed was 50 rpm, and the barrel temperature of the extruder was 180 °C. The extruded strand was cooled by a water bath, pelletized, and then granulated by a lab scale grinder. Injection molding for all composite materials were realized in HDX-88 model (Ningbo Haida Plastic Machinery Co., China). Nine different composites with nutshell fiber loadings of 30 wt% and MCC loadings up to 15 wt% were produced. The composite preparation and production process were described in previous study by Boran [8]. The experimental design for composites manufacturing is presented in Table 1.

Atlas-UV accelerated weathering test equipment (Atlas UV test, USA) was used to simulate outdoor degrading factors based on Procedure 1 in ASTM G154 standard [28]. The composites were exposed to a fluorescent UV lamp at UVA 340 nm wavelength for 8 h at 60 °C, and then a condensation for 4 h at 50 °C. The composites were weathered for total of 672 h. The weathering test was carried out with a five replicate composites. The gloss, color, and surface roughness measurements were periodically measured on the exposed surfaces after 24 h, 48 h, 96 h, 120 h, 144 h, 168 h, 336 h, 504 h, and 672 h.

2.3. Surface measurements

The color coordinates (L*, a* and b*) were measured over an 8 mm diameter spot with 10° observer angle by using a Minolta CM-2600d spectrophotometer (New Jersey, USA), and total color change (ΔE*) was calculated according to ASTM D 2244 [30]. Four replicate measurements were recorded for each sample before and after weathering.

The surface roughness of the composites was determined with Mitutoyo Surfest SJ-310 device according to ISO 4287-1997 standards [29]. The roughness was measured with a sensitivity of 0.5 μm. Rz roughness values were measured from four different point on a sample, and their averages were evaluated. The gloss of the composites were measured by a Micro-Tri-Gloss glossmeter (BYK-Gardner, Germany).

ATR-FTIR analysis was performed to evaluate the changes in surface chemical components of the composites after weathering by using Bruker Tensor 37 (Bruker Optics GmbH, Ettlingen, Germany). All measurements were taken directly from the composite surface. The spectra of the samples were collected by averaged 32 spectra at a resolution 4 cm^{-1} in the range from 400 to 4000 cm^{-1}. All spectra were baseline corrected and smoothed by the OPUS software program. Two replicates for each type of composite were measured.

The carbonyl index was calculated by using the following equation [31]:

$$Carbonyl\ index = \frac{I_{1715}}{I_{2915}} \quad (1)$$

where carbonyl index shows the degree of polymer degradation on the sample surface after the weathering exposure.

2.4. Mechanical property testing

Flexural properties (flexural strength, modulus of elasticity in bending) were carried out in accordance to ASTM D 6109 standard [32]. Crosshead speed was set as 1.25 mm/min. Tensile test were performed in accordance with ASTM D 638 standard [33]. Crosshead speed was arranged as 5 mm/min for the test. Five replicate samples were used for mechanical property testing. The retention ratios were figured out using Equations (2) and (3).

Retention ratios of flexural and tensile strength(s):

$$MOR_{ret\ ratio} = \frac{MOR_{after}}{MOR_{before}} \times 100 \quad (2)$$

Retention ratios of flexural modulus:

$$MOE_{ret\ ratio} = \frac{MOE_{after}}{MOE_{before}} \times 100 \quad (3)$$

where the $MOR_{ret\ ratio}$ and $MOE_{ret\ ratio}$ represent MOR and MOE mean values before and after weathering.

2.5. Scanning electron microscope (SEM)

Scanning electron microscopy (SEM) analysis of the composites was performed on a JEOL JSM-5500 scanning electron microscopy (JEOL Ltd., Japan). Before the analysis, the composites were kept in liquid nitrogen for a period of time, and then fractured to obtain a clean fractured surface. In order to eliminate reflections from the sample surface, the fractured surfaces were plated with gold dust at 120 mA for 120 s. SEM images were scanned at 2 kV with 500× magnifications.

Table 2
The changes in mechanical properties of the composites after weathering.

ID	retTMOR	retFMOR	retFMOE
HDPE	68.37	95.10	162.20
MCC5	72.95	95.04	152.50
MCC10	74.64	93.41	143.84
MCC15	74.91	91.29	156.43
HDPE/N30	80.36	98.84	115.01
MCC5/N30	87.46	98.90	120.13
MCC10/N30	87.52	97.65	119.62
MCC15/N30	87.78	98.09	120.69

TMOR: Tensile Strength, FMOR: Flexural Strength, FMOE: Flexural Modulus of Elasticity.

3. Results and discussion

3.1. Mechanical properties of the composites after weathering

Table 2 shows the effect of weathering exposure on the mechanical properties of MCC and nutshell reinforced HDPE composites. Tensile and flexural strengths of the composites decreased with the weathering owing to degradation of thermoplastic polymers. The retention ratios of tensile strength were in the range between 68 and 87%. When polymers were exposed to UV radiation, the photo-oxidative degradation occurs by scission of the polymer chain. This leads to generate free radicals and diminish in the molecular weight, and a decrease in mechanical strength of the polymer [34,35]. The highest decrease was observed in unfilled HDPE composites with a 32% of decrement in tensile strength. It was stated that MCC and nutshell tolerated deterioration effect of weathering factors on the tensile strength of the HDPE composites depending on filler loading. The previous study reported that MCC did not dramatically change the mechanical properties of PLA composites after accelerated weathering [36].

Flexural strength slightly decreased by a maximum of 8.71%. However, the flexural strength had higher retention ratios in comparison with the tensile strength of the MCC and nutshell reinforced HDPE composites after 672 h of weathering. It was observed that the nutshell prevented the loss of mechanical strengths. This result may be due to lignin in nutshell. Chen et al. [37] concluded that the lignin based composites retained greatest mechanical strengths upon the weathering. Lignin contributes to remain other wood components such as cellulose and hemicellulose when exposed to physical aging factors [38].

Flexural modulus unexpectedly increased after the weathering. The highest retention with 162% was obtained from unfilled HDPE

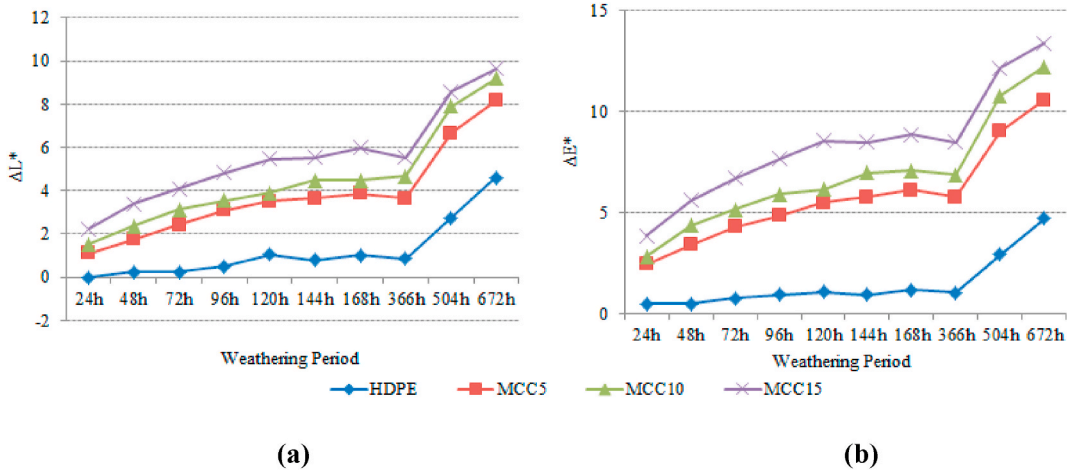

Fig. 1. Color parameters of MCC reinforced composites during weathering period (a: ΔL*; b: ΔE*). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

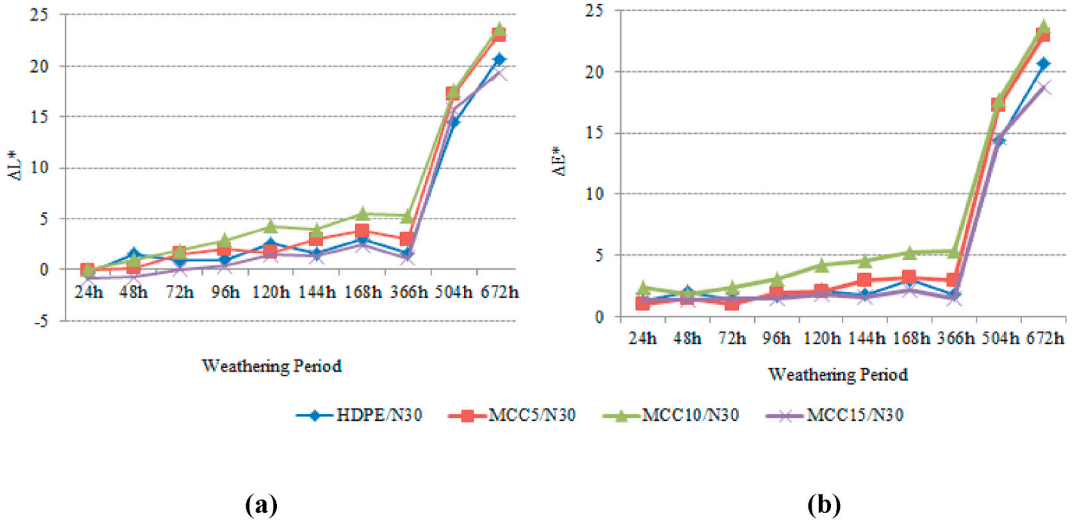

Fig. 2. Color parameters of nutshell/MCC reinforced composites during weathering period (a: ΔL*; b: ΔE*). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

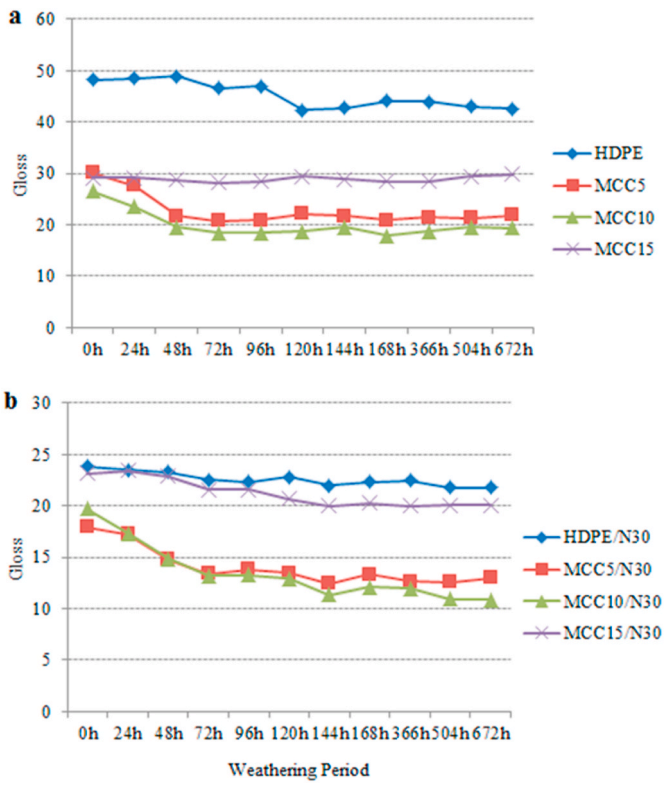

Fig. 3. Surface gloss of (a) MCC reinforced composites and (b) nutshell/MCC reinforced composite along with weathering period.

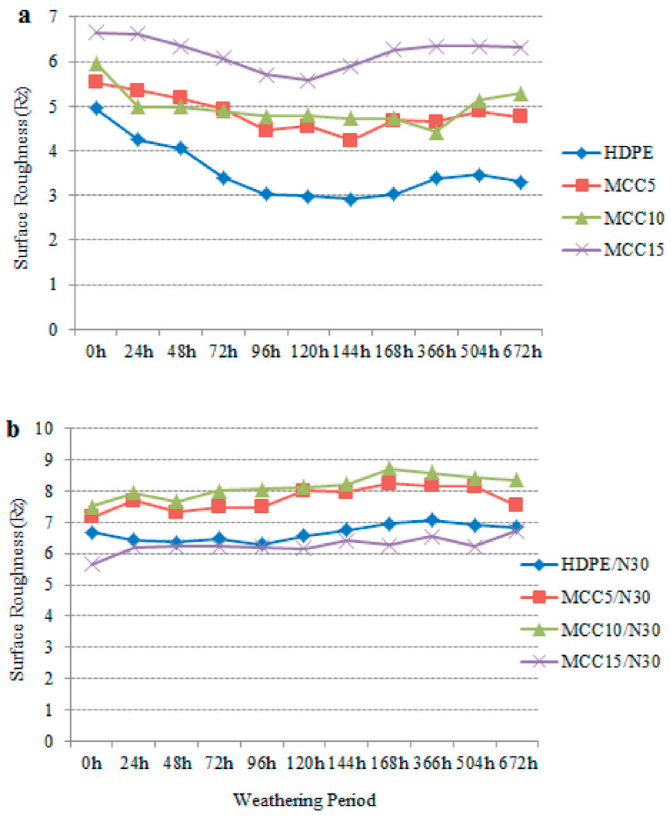

Fig. 4. Surface roughness of (a) MCC reinforced composites and (b) nutshell/MCC reinforced composite along with weathering period.

composites. As the polymer content in the composites decreases, the increment of the ret FMOE decreased to 115%. It is known that a secondary crystallization in HDPE occurs at the early stage of the degradation during the weathering, and this leads the increase of the modulus of elasticity of the HDPE composites [39–42]. Dash et al. [43] recorded a similar increase in modulus values with natural weathering on jute filled polymer composites. They concluded that the reason for this might be the increase in the hardness of the composites by breaking polymer chain upon the weathering.

3.2. Color changes during weathering

Color parameters of MCC reinforced composites during weathering period are given Fig. 1. The ΔE* value indicates the total color change in the samples [44]. The ΔL* and ΔE* values of the HDPE composites increased with addition of MCC. The reason of this is due to UV absorption capacity of MCC. Chen et al. [37] investigated the effects of extracted and delignified wood filler on the properties the weathered HDPE composites. The extractives and lignin in wood were responsible for discoloration of the composites during UV radiation. They also reported the ΔL* values of the delignified wood filled sample did not significantly changed, even the ΔE* values slightly increased after the weathering. The highest ΔL* and ΔE* values were observed to be following order for MCC reinforced composites: MCC15 > MCC10 > MCC5. The first 336 h was not observed a notable change on the ΔL* and ΔE* values of the unfilled HDPE samples afterwards sharply increased ΔL* and ΔE* values were observed.

Fig. 2 shows the effect of accelerated weathering factors on color parameters of the nutshell/MCC reinforced composites. The nutshell/MCC reinforced composites demonstrated different behavior on total color change values compared to the MCC reinforced composites. According to the changes on color coordinates, the MCC10/N30 resulted in more color change on the surfaces due to lignin and extractives in nutshell. It is known that lignin and some extracts are mainly responsible for discoloration of wood or other lignocellulosic materials when exposed to high environment conditions [37,45]. Lignin is susceptible to solar energy which result generation of chromophoric structures by its oxidation [46].

All color coordinates for the MCC reinforced composites and MCC/nutshell reinforced composites showed an increasing tendency during all weathering periods, especially after 366 h. This indicated that the photooxidation of the polymer composites including MCC and nutshell began after 14 days of weathering exposure.

3.3. Surface gloss

The gloss changes of MCC reinforced composites and nutshell/MCC reinforced composites along with weathering period are given in Fig. 3a and Fig. 3b. The nutshell/MCC reinforced composites exhibited lower surface gloss than MCC reinforced composites. The gloss value was increased considerably by adding 15% MCC into the polymer matrix for both groups. The initial gloss of all composites also decreased gradually from the beginning to the end of the weathering period for the nutshell/MCC reinforced composites. The lowest gloss values were obtained from the MCC10 and MCC10/N30 composites. As shown in Fig. 3a, the gloss values of MCC10 and MCC15 diminished after the first 48 h, but there was no significant change in those of MCC reinforced composites along with weathering periods. Fig. 3b showed that presence of MCC (5 and 10 wt%) and nutshell in polymer matrix caused a decrease in the gloss value.

3.4. Surface roughness of composites after weathering

Surface roughness values of composites during the weathering period are presented in Fig. 4. It has been observed that the surface roughness value of the MCC reinforced composites tended to decrease in the first 120 h of weathering period, but then increased. Compared to

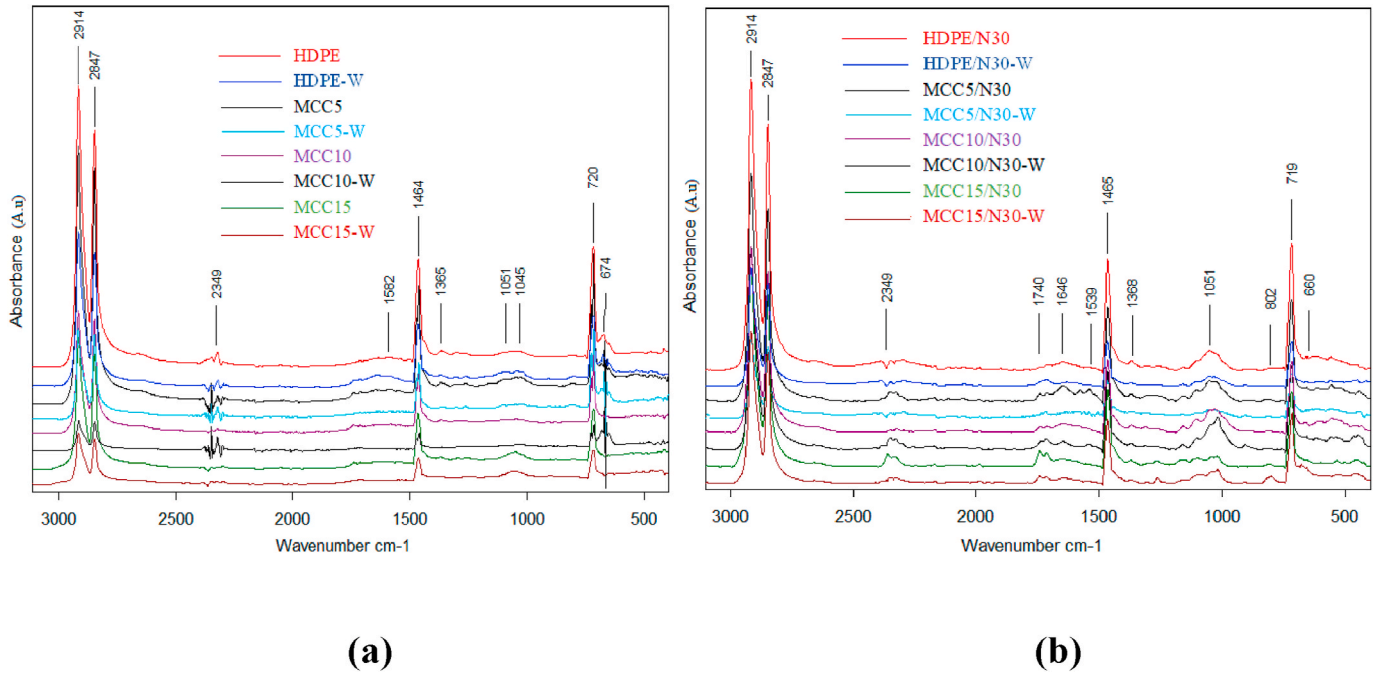

Fig. 5. FTIR results of the reinforced (a) MCC and (b) nutshell/MCC composites before and after weathering.

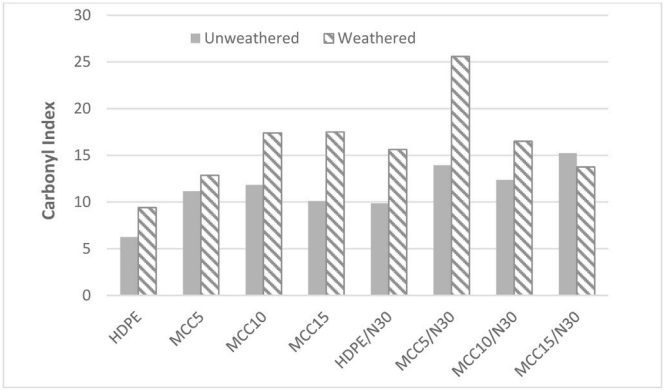

Fig. 6. The influence of weathering on carbonyl index of the composites.

the unfilled HDPE composites, MCC reinforced composites had higher surface roughness value. The weathering factors affect sample surface since decrease in molecular weight of the polymer occurs [47,48]. However, surface roughness of the nutshell/MCC reinforced composites increased slightly during weathering. Addition of MCC and nutshell to HDPE composites increased surface roughness of samples probably due to their UV and moisture absorption capacity. This finding was well correlated with the low rates of strength loss caused by weathering factors in the nutshell/MCC reinforced samples. The increase in surface roughness due to the photooxidation led to loss of mechanical strength for the polymer samples [49].

3.5. ATR-FTIR results after weathering of composites

The FTIR spectra of MCC and MCC/nutshell reinforced HDPE composites before and after weathering illustrates in Fig. 5. The strong peaks of HDPE were observed at 2914 cm^{-1} and 2847 cm^{-1} which were asymmetric and symmetric CH_2 stretching, respectively. Besides, the absorbance peaks at 1464 and 720 cm^{-1} corresponded to bending vibrations in methylene groups of amorphous HDPE. After the weathering, the band intensities decreased due to the degradation. It is known that polyolefin shows poor performance in long-term environmental conditions such as UV radiation [50].

The researches have proven that the changes in the structure of carbonyl groups are directly proportional to the degree of degradation of the polymer [31,51,52]. Fig. 6 shows that the carbonyl peak assigned at 1720 cm^{-1} increased during the weathering except for the MCC15/N30 composite samples. The photo-oxidation of the polymer resulted an increase in carbonyl groups [53,54]. Rajakumar et al. [54] detected higher band intensities of hydroxyl, vinylidene, lactones, ester carboxylic acid peaks as well as the increase in carbonyl index caused by the degradation process using the FTIR technique.

However, it was not observed significant interaction between filler loading and filler type on the carbonyl indices of MCC and MCC/nutshell reinforced composites after the weathering. This may relate to inhomogeneity of the filler in polymer matrix.

The change in spectral region from 1050 to 1030 cm^{-1}, corresponding to C–O extend in nutshell cellulose and deformation of primary alcohol from lignin was less with the UV radiation [31,55]. The peak for the MCC/nutshell reinforced composites (Fig. 5b) detected more apparent in comparison with its MCC reinforced composites (Fig. 5a). Presence of lignin in nutshell contributed the intensity of the band at 1050 cm^{-1} due to overlapping with its cellulose in MCC.

3.6. Surface morphological observation

Figs. 7 and 8 show the SEM images of the MCC reinforced composites and nutshell/MCC reinforced composites, respectively. The SEM micrograph after the weathering exposure indicated some micro cracks, pores and protrusion due to MCC loading. Besides, a rougher fiber surface was seen after weathering exposure. The SEM observations on the exposed composites are in accordance with the surface roughness of composites after weathering. This could be due to the fibers damaged owing to prolonged exposure resulted in excessive defibrillation [56].

4. Conclusions

The weathering resistance of composites is significantly affected by outdoor degrading factors. In the recent years, the use of cellulose-based composites has been increasing due to environmental considerations. In

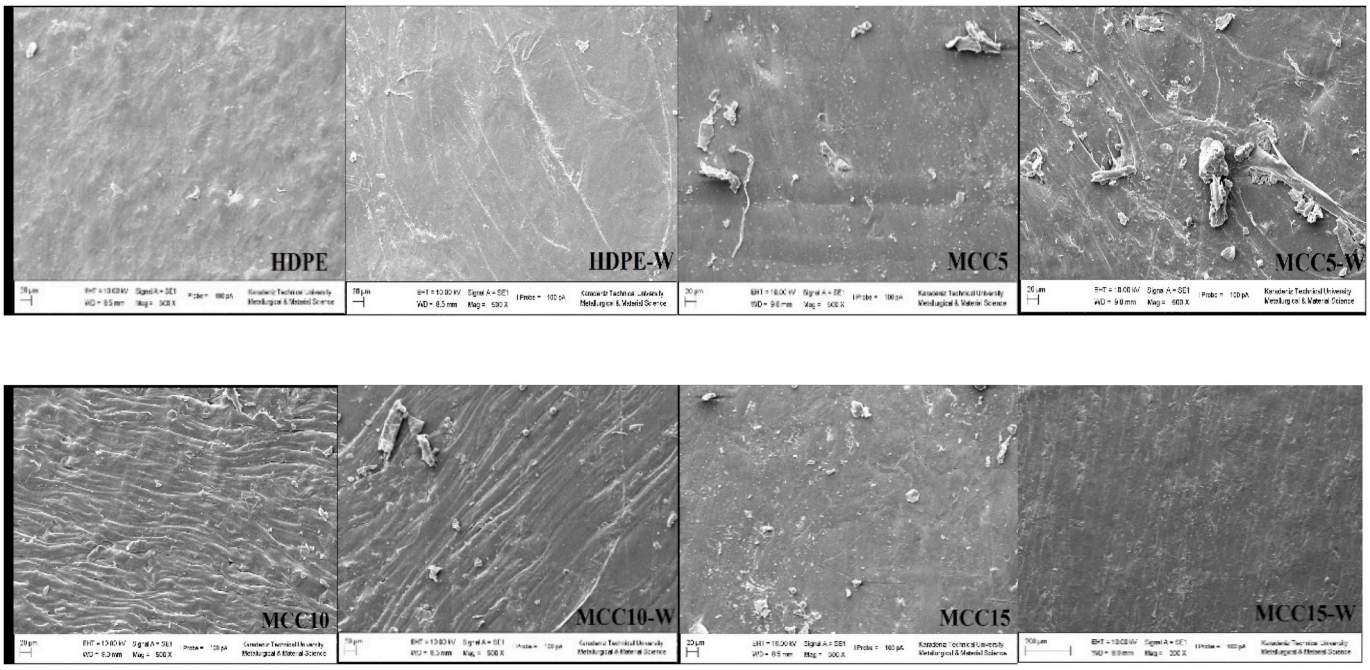

Fig. 7. Micrographs of MCC reinforced composites after weathering.

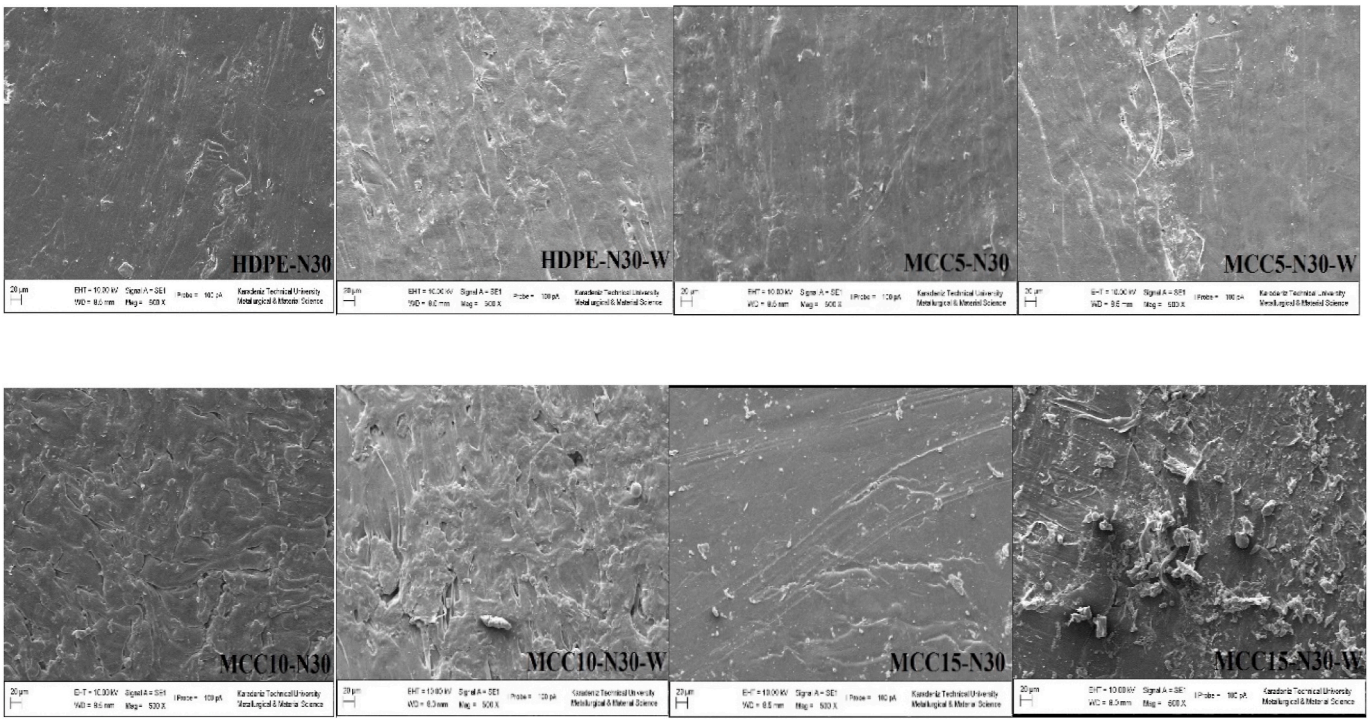

Fig. 8. Micrographs of nutshell/MCC reinforced composites after weathering.

this study, accelerated weathering resistance of MCC/nutshell reinforced composites was investigated in terms of color, gloss, surface roughness, ATR-FTIR, SEM and mechanical characterization. Weathering exposure decreased tensile and flexural strengths while MOE increased by weathering. Color changes by weathering were increased on MCC and nutshell reinforced composites. The highest color change was observed from the MCC10/N30. The surface gloss of the nutshell/MCC reinforced composites was found to be lower compared to the MCC reinforced composites. The MCC addition to HDPE caused higher surface roughness compared to the unfilled HDPE composite. In SEM micrographs, some microcracking, pores and protrusions were detected on the weathered surface of MCC and nutshell reinforced composites.

ATR-FTIR analyzes concluded that the band intensities of the polymer decreased, and those of carbonyl index increased after the weathering exposure.

Author statement

Sevda Boran Torun: Conceptualization, Methodology, Supervision, Writing - Reviewing and Editing. Eylem Dizman Tomak: Visualization,

Measurement, Data Curation, Methodology, Editing. Ayfer Donmez Cavdar: Writing- Original draft preparation, Investigation, Writing - Reviewing and Editing. Fatih Mengeloglu: Supervision, Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by Scientific Research Projects Coordination Unit of Karadeniz Technical University. Project number was BAP03-13504. The authors would like to the contributions of research assistant Şebnem S. Arpaci for the tests of the weathered plastic composites in BTU.

References

[1] S.J. Eichhorn, A. Dufresne, M. Aranguren, N.E. Marcovich, J.R. Capadona, S. J. Rowan, Review: current international research into cellulose nanofibres and nanocomposites, J. Mater. Sci. 45 (2010) 1–33, https://doi.org/10.1007/s10853-009-3874-0.

[2] A. Kiziltas, B. Nazari, D.J. Gardner, D.W. Bousfield, Polyamide 6-cellulose composites: effect of cellulose composition on melt rheology and crystallization behavior, Polym. Eng. Sci. 54 (2013) 739–746, https://doi.org/10.1002/pen.23603.

[3] Y. Peng, R. Liu, J. Cao, Y. Chen, Effects of UV weathering on surface properties of polypropylene composites reinforced with wood flour, lignin, and cellulose, Appl. Surf. Sci. 317 (2014) 385–392, https://doi.org/10.1016/j.apsusc.2014.08.140.

[4] S. Ifuku, H. Yano, Effect of a silane coupling agent on the mechanical properties of a microfibrillated cellulose composite, Int. J. Biol. Macromol. 74 (2015) 428–432, https://doi.org/10.1016/j.ijbiomac.2014.12.029.

[5] N.I. Zulkifli, N. Samat, H. Anuar, N. Zainuddin, Mechanical properties and failure modes of recycled polypropylene/microcrystalline cellulose composites, Mater. Des. 69 (2015) 114–123, https://doi.org/10.1016/J.MATDES.2014.12.053.

[6] A. Donmez Cavdar, H. Kalaycıoglu, F. Mengeloglu, Tea mill waste fibers filled thermoplastic composites: the effects of plastic type and fiber loading, J. Reinforc. Plast. Compos. 30 (2011) 833–844, https://doi.org/10.1177/0731684411408752.

[7] C. Dong, I.J. Davies, Flexural properties of macadamia nutshell particle reinforced polyester composites, Compos. B Eng. 43 (2012) 2751–2756, https://doi.org/10.1016/j.compositesb.2012.04.035.

[8] S. Boran, Mechanical, morphological, and thermal properties of nutshell and microcrystalline cellulose filled high density polyethylene composites, BioResources 11 (2016) 1741–1752, https://doi.org/10.15376/biores.11.1.1741-1752.

[9] Y. Copur, C. Güler, M. Akgül, C. Taşçıoğlu, Some chemical properties of hazelnut husk and its suitability for particleboard production, Build. Environ. 42 (2007) 2568–2572, https://doi.org/10.1016/j.buildenv.2006.07.011.

[10] J. Sahari, S.M. Sapuan, Natural fibre reinforced biodegradable, Rev. Adv. Mater. Sci. 30 (2011) 166–174.

[11] C. Fonseca-Valero, A. Ochoa-Mendoza, J. Arranz-Andres, Mechanical recycling and composition effects on the properties and structure of hardwood cellulose-reinforced high density polyethylene eco-composites, Compos. Part A Appl. Sci. Manuf. 69 (2015) 94–104, https://doi.org/10.1016/j.compositesa.2014.11.009.

[12] A. Idi, S.E. Mohamad, Bioethanol from second generation feedstock (lignocellulose biomass), Intdiscip, J. Contemp. Res. Bus. 3 (2011) 919–935.

[13] A.P. Mathew, K. Oksman, M. Sain, Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC), J. Appl. Polym. Sci. 97 (2005) 2014–2025, https://doi.org/10.1002/app.21779.

[14] S. Spoljaric, A. Genovese, R.A. Shanks, Polypropylene-microcrystalline cellulose composites with enhanced compatability and properties, Compos. Part A Appl. Sci. Manuf. 40 (2009) 791–799, https://doi.org/10.1002/app.21779.

[15] A. Kiziltas, D.J. Gardner, Y. Han, H.-S. Yang, Determining the mechanical properties of microcrystalline cellulose (MCC)-filled PET-PTT blend composites, Wood Fiber Sci. 42 (2010) 165–176.

[16] M.K.M. Haafiz, A. Hassan, Z. Zakaria, I.M. Inuwa, M.S. Islam, M. Jawaid, Properties of polylactic acid composites reinforced with oil palm biomass microcrystalline cellulose, Carbohydr. Chem. 98 (2013) 139–145, https://doi.org/10.1016/j.carbpol.2013.05.069.

[17] S. Boran, A. Kiziltas, E.E. Kiziltas, D.J. Gardner, Characterization of ultrafine cellulose-filled high density polyethylene composites prepared using different methods, BioResources 11 (2016) 8178–8199, https://doi.org/10.15376/biores.11.4.8178-8199.

[18] S. Yildiz, E. Dizman Tomak, U.C. Yildiz, D. Ustaomer, Effect of artificial weathering on the properties of heat treated wood, Polym. Degrad. Stabil. 98 (2013) 1419–1427, https://doi.org/10.1016/j.polymdegradstab.2013.05.004.

[19] H. Kallakas, T. Poltimäe, T.-M. Süld, J. Kers, A. Krumme, The influence of accelerated weathering on the mechanical and physical properties of wood-plastic composites, Proc. Est. Acad. Sci. 64 (2015) 94–104, https://doi.org/10.3176/proc.2015.1S.05.

[20] T.-H. Yang, T.-H. Yang, W.-C. Chao, S.-Y. Leu, Characterization of the property changes of extruded wood-plastic composites during year round subtropical weathering, Construct. Build. Mater. 88 (2015) 159–168, https://doi.org/10.1016/j.conbuildmat.2015.04.019.

[21] E. Dizman Tomak, D. Ustaomer, S. Yildiz, E. Pesman, Changes in surface and mechanical properties of heat treated wood during natural weathering, Measurement 53 (2014) 30–39, https://doi.org/10.1016/j.measurement.2014.03.018.

[22] A. Donmez Cavdar, E. Dizman Tomak, F. Mengeloglu, Long-term leaching effect on decay resistance of wood-plastic composites treated with boron compounds, J. Polym. Environ. 26 (2018) 756–764, https://doi.org/10.1007/s10924-017-0992-7.

[23] B. George, E. Suttie, A. Merlin, X. Deglise, Photodegradation and photostabilisation of wood e the state of the art, Polym. Degrad. Stabil. 88 (2005) 268–274, https://doi.org/10.1016/j.polymdegradstab.2004.10.018.

[24] B. Bahrani, V. Hemmati, A. Zhou, S. Quarles, Effects of natural weathering on the fire properties of intumescent fire-retardant coatings, Fire Mater. 42 (2018) 413–423, https://doi.org/10.1002/fam.2506.

[25] J. Quill, S. Fowler, Test method development for outdoor exposure and accelerated weathering of vinyl siding specimens, in: C.C. White, J. Martin, J.T. Chapin (Eds.), Service Life Prediction of Exterior Plastics, Springer International Publishing, Switzerland, 2015, pp. 135–150.

[26] M. McGreer, Atlas Weathering Testing Guidebook, Atlas Material Testing Technology LLC, Chicago, 2001.

[27] B. Bahrani, Effects of weathering on performance of intumescent coatings for structure fire protection in the wildland-urban interface, in: Conference SAMPE. Long Beach, May, 2015, 2015, pp. 1–14.

[28] Standard Practice for Operating Fluorescent Light Apparatus for Uv Exposure of Nonmetallic Materials, ASTM International, West Conshohocken, PA, 2000. ASTM G154.

[29] Geometrical Product Specifications (GPS) — Surface Texture: Profile Method — Terms, Definitions and Surface Texture Parameters. ISO 4287-1997.

[30] Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates, ASTM International, West Conshohocken, PA, 2016. ASTM D2244.

[31] L.M.S. Matuana, S. Jin, N.M. Stark, Ultaviolet weathering of HDPE/wood –flour composites coextruded with a clear HDPE cap layer, Polym. Degrad. Stabil. 96 (2011) 97–106, https://doi.org/10.1016/j.polymdegradstab.2010.10.003.

[32] Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastic Lumber, ASTM International, West Conshohocken, PA, 2013. ASTM D6109.

[33] Standard Test Method for Tensile Properties of Plastics, ASTM International, West Conshohocken, PA, 2007. ASTM D 638-14.

[34] N.M. Stark, Consideration in weathering of wood-plastic composites, in: The 3rd Wood Fibre Polymer Composites International Symposium. France, March 2007, 2007, pp. 1–10.

[35] E. Yousif, R. Haddad, Photodegradation and Photostabilization of Polymers, Especially Polystyrene: Review, SpringerPlus, 2013.

[36] C. Kaynak, B. Dogu, Effects of accelerated weathering in polylactide biocomposites reinforced with microcrystalline cellulose, Int. Polym. Process. 21 (2016) 410–422, https://doi.org/10.3139/217.3197.

[37] Y. Chen, N.M. Stark, M.A. Tshabalala, J. Gao, Y. Fan, Weathering characteristic of wood plastic composites reinforced with extracted or delignified wood flour, Materials 9 (2016) 610, https://doi.org/10.3390/ma9080610.

[38] V.K. Thakur, M.K. Thakur, Processing and characterization of natural cellulose fibers/thermoset polymer composites, Carbohydr. Polym. 109 (2014) 102–117, https://doi.org/10.1016/j.carbpol.2014.03.039.

[39] N.M. Stark, L.M. Matuana, Characterization of weathered wood-plastic composite surfaces using FTIR spectroscopy, contact angle, and XPS, Polym. Degrad. Stabil. 92 (2007) 1883–1890, https://doi.org/10.1016/j.polymdegradstab.2007.06.017.

[40] J.R. White, Polymer weathering: mechanisms of degradation and failure, in: 9th Congresso Brasileiro de Polímeros. Brazil, December, 2007, 2007, pp. 1–10.

[41] K.C. Hung, Y.L. Chen, J.H. Wu, Natural weathering properties of acetylated bamboo plastic composites, Polym. Degrad. Stabil. 97 (2012) 1680–1685, https://doi.org/10.1016/j.polymdegradstab.2012.06.016.

[42] C. Badji, L. Soccalingame, H. Garay, A. Bergeret, J.-C. Bénézet, Influence of weathering on visual and surface aspect of wood plastic composites:Correlation approach with mechanical properties and microstructure, Polym. Degrad. Stabil. 137 (2017) 162–172, https://doi.org/10.1016/j.polymdegradstab.2017.01.010.

[43] B.N. Dash, A.K. Rana, S.C. Mishra, H.K. Mishra, S.K. Nayak, S.S. Tripathy, Novel low-cost jute-polyester composite. II. SEM observation of the fracture surfaces, Polym. Plast. Technol. Eng. 39 (2000) 333–350, https://doi.org/10.1081/PPT-100100033.

[44] S. Boran Torun, A. Donmez Cavdar, T. Ozdemir, The synergistic effect of titanium dioxide and antimony trioxide on the fire performance and surface properties of the coated spruce and alder wood species, J. Build. Eng. 31 (2020), 101407, https://doi.org/10.1016/j.jobe.2020.101407.

[45] Y. Ouadou, D. Aliouche, M.-F. Thevenon, M. Djillali, Characterization and photodegradation mechanism of three Algerian wood species, J. Wood Sci. 63 (2017) 288–294, https://doi.org/10.1007/s10086-017-1615-6.

[46] C.-A. Teacă, D. Roşu, R. Bodîrlău, L. Roşu, Structural changes in wood under artificial UV light irradiation determined by FTIR spectroscopy and color measurements - a brief review, BioResources 8 (2013) 1478–1507.

[47] M.I. Popa, S. Pernevan, C. Sirghie, I. Spiridon, D. Chambre, D.M. Copolovici, N. Popa, Mechanical properties and weathering behavior of polypropylene-hemp

shives composites, J. Chem. (2013), 343068, https://doi.org/10.1155/2013/343068.
[48] Y. Peng, R. Liu, J. Cao, Characterization of surface chemistry and crystallization behaviour of polypropylene composites reinforced with wood flour, cellulose, and lignin during accelerated weathering, Appl. Surf. Sci. 332 (2015) 253–259, https://doi.org/10.1016/j.apsusc.2015.01.147.
[49] B. Suresh, S. Maruthamuthu, M. Kannan, A. Chandramohan, Mechanical and surface properties of low-density polyethylene film modified by photo-oxidation, Polym. J. 43 (2011) 398–406.
[50] V.K. Thakur, A.S. Siṅgha, Biomass-based Biocomposites, Smithers Rapra Technology, 2013, p. 410.
[51] L.K. Krehula, Z. Katančić, A.P. Siročić, Z. Hrnjak-Murgić, Weathering of high-density polyethylene-wood plastic composites, J. Wood Chem. Technol. 34 (2013) 39–54, https://doi.org/10.1080/02773813.2013.827209.
[52] N.M. Stark, L.M. Matuana, Characterization of weathered wood-plastic composite surfaces using FTIR spectroscopy, contact angle, and XPS, Polym. Degrad. Stabil. 92 (2007) 1883–1890, https://doi.org/10.1016/j.polymdegradstab.2007.06.017.
[53] J.S. Fabiyi, A.G. McDonald, Physical morphology and quantitative characterization of chemical changes of weathered PVC/pine composites, J. Polym. Environ. 18 (2010) 57–64, https://doi.org/10.1007/s10924-009-0152-9.
[54] K. Rajakumar, V. Sarasvathy, A. Thamarai Chelvan, R. Chitra, C.T. Vijayakumar, Natural weathering studies of polypropylene, J. Polym. Environ. 17 (2009) 191–202, https://doi.org/10.1007/s10924-009-0138-7.
[55] J.S. Fabiyi, A.G. McDonald, M.P. Wolcott, P.R. Griffiths, Wood plastic composites weathering: visual appearance and chemical changes, Polym. Degrad. Stabil. 93 (2008) 405–1414, https://doi.org/10.1016/j.polymdegradstab.2008.05.024.
[56] D. Ariawan, M.S. Salim, R.M. Taib, M.Z.A. Thirmizir, Z.A.M. Ishak, Durability of alkali and heat-treated kenaf fiber/unsaturated polyester composite fabricated by resin transfer molding under natural weathering exposure, Adv. Polym. Technol. 37 (2018) 1420–1434, https://doi.org/10.1002/adv.21801.