Check for updates

Received: 10 October 2022 | Revised: 28 November 2022 | Accepted: 12 December 2022

DOI: 10.1111/cote.12666

Coloration Technology

ORIGINAL ARTICLE

The effect of zinc oxide nanoparticles on the weathering performance of wood-plastic composites

Sefa Durmaz[1] | **Ozlem Ozgenc Keles**[2] | **Ugur Aras**[3] | **Yusuf Ziya Erdil**[4] | **Fatih Mengeloglu**[5]

[1]Department of Forestry and Forest Products, Kavaklıdere Vocational School, Muğla Sıtkı Koçman University, Muğla, Turkey

[2]Department of Forest Industry Engineering, Forest Faculty, Karadeniz Technical University, Trabzon, Turkey

[3]Department of Materials and Materials Processing Technology, Arsin Vocational School, Karadeniz Technical University, Trabzon, Turkey

[4]Department of Woodworking Industry Engineering, Technology Faculty, Muğla Sıtkı Koçman University, Muğla, Turkey

[5]Department of Forest Industry Engineering, Forest Faculty, Kahramanmaras Sutcu Imam University, Kahramanmaraş, Turkey

Correspondence
Sefa Durmaz, Department of Forestry and Forest Products, Kavaklıdere Vocational School, Muğla Sıtkı Koçman University, Muğla, Turkey.
Email: sefadurmaz@mu.edu.tr

Funding information
The Scientific and Technological Research Council of Turkey

Abstract

In recent years, wood-plastic composites (WPCs) have become among the most popular engineering materials. Most of their usage areas are outdoors, where they encounter various damaging factors. The weathering conditions cause significant deterioration to WPC surfaces, which negatively influences their service life. In this study, zinc oxide nanoparticles at different concentrations (1%, 3%, 5%, 10%) were added to a high-density polyethylene-based WPC matrix. The effect of zinc oxide nanoparticles on the weathering performance of WPC was evaluated after 840 hours of an artificial weathering test. The highest colour changes (ΔE^*) were monitored with control samples exposed for 840 hours. Adding zinc oxide nanoparticles improved the ultraviolet (UV) resistance and decreased the colour changes. The wood flour content also affected the colour changes on the WPC surface. A combination of 10% zinc oxide nanoparticles and 50% wood flour content provided the lowest colour changes. The barrier effect of nanoparticles protected the WPC surfaces from UV light. Zinc oxide nanoparticles also positively affected the load transfer, which restricted the reduction in mechanical properties after the weathering test. The degradation on the surface of WPCs was also investigated using attenuated total reflectance-Fourier Transform–infrared analysis. The changes in the characteristic bands of polymer and wood indicated that surface degradation was inevitable. Light and scanning electron microscopy images also demonstrated micro-cracks and roughness on the surface of WPCs. It is concluded that UV degradation is unavoidable, but zinc oxide nanoparticles can improve surface resistance against weathering conditions.

1 | INTRODUCTION

In recent years, global warming, drought and forest fires have threatened natural resources. One way to provide sustainability for natural resources, like forests, is to combine different materials, defined as "composites". Composite materials have been used in industries for more than a century. Wood-based composites have also been used in various products, from furniture to construction, and cars to aircraft. However, in outdoor usage, wood is negatively affected by outdoor conditions.[1] Its dimensions change depending on the environment; the appropriate conditions (temperature, humidity, etc.) allow it to be degraded by fungi and insects.[2] Ultraviolet (UV) light causes irreparable colour changes on the surface of the wood.[3] With the effect of rain, it swells and reveals new areas of the surface, which UV light repeatedly affects,[4] eventually resulting in surface erosion.[5]

 © 2022 Society of Dyers and Colourists.

14784408, 0, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/cote.12666 by Karadeniz Technical University, Wiley Online Library on [31/12/2022]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Wood-plastic composites (WPCs) are recognised as a combination of wood and plastic, which restrains most of the shortcomings of outdoor conditions. However, the chromophoric groups in the chemical structure of wood and plastic absorb UV light, causing chain scissions in the structure of plastic as well as colour changes.[6,7] Following that, micro-cracks occur on the surface.[3,8,9] Then the wood fibres swell with the effect of humidity, which causes the cracks to enlargen. Therefore, wood fibres in the sub-section of composites are exposed to much more UV light. In the end, WPCs eventually succumb to UV rays during their service life. Therefore, there is a need for protection on the surface of WPCs. Coating systems were evaluated for this purpose.[10–15] Although the colour changes on the surfaces of WPCs decreased, the significant shortcoming of coating systems is weak adhesion between the surface and coating film, which reduces their protective property.

In recent years, nanotechnology has been developed to improve materials' physical, mechanical and thermal properties. Nanoparticles have a high surface/volume ratio, enabling a high level of interaction.[16,17] Nanomaterials have also been used in composites, mainly plastic-based composites. Increased tensile strength, thermal stability, fire resistance, improved water absorption and biological durability can be gained from WPCs with the help of nanoparticles.[17] Silicon dioxide, titanium dioxide and zinc oxide nanoparticles are the most commonly preferred nanomaterials because of their non-toxic structure and high thermal stability.[18] Clausen et al impregnated wood with zinc oxide nanoparticles to improve the dimensional stability of wood. Water absorption values of wood samples also decreased by up to 32% after the weathering test, which is a crucial factor in obtaining high resistance against weathering conditions.[19] Rasouli et al stated that the tensile strength of WPC samples reinforced with zinc oxide nanoparticles increased instead of decreasing as a result of the crosslinking reactions.[20] Yang et al investigated the weathering performance of WPCs containing different nanoparticles.[21] The nanoparticles did not inhibit the degradation on the surface of WPC samples. However, they did decelerate the degradation rate. Meanwhile, zinc oxide nanoparticles were confirmed as more effective against UV light than silicon dioxide or aluminium oxide. In another study, Devi and Maji reinforced WPCs with modified zinc oxide nanoparticles to improve the weathering performance.[18] After UV light exposure, zinc oxide nanoparticles decreased the weight loss using the effect of the UV barrier of nanoparticles. Rasouli et al also stated that zinc oxide nanoparticles decreased the surface cracks of WPCs.[20]

The main objective of the current study was to improve the weathering performance of WPCs with the reinforcement of zinc oxide nanoparticles, which are mainly preferred for plastic composites. As explained above, zinc oxide nanoparticles can absorb and/or reflect UV light, which is the main reason for them being chosen. However, previous studies only investigated a relatively low amount of zinc oxide nanoparticles because of agglomeration. In the current study, the powder form of high-density polyethylene (HDPE) was used to improve the homogeneous distribution, which enabled examination of a higher content of zinc oxide nanoparticles, by up to 10%. The effect of zinc oxide nanoparticles on the weathering performance of WPCs was investigated using light microscopy and scanning electron microscopy (SEM). The changes in the surface chemistry were revealed by attenuated total reflectance-Fourier Transform–infrared (ATR-FTIR) spectroscopy. Moreover, the effect of weathering on mechanical properties was also determined.

TABLE 1 The wood flour, polymer and nanoparticle content

Group	Wood/polymer ratio (%)	Nanoparticle content (%)
Neat-HDPE	0/100	-
WPC40	40/60	-
WPC50	50/50	-
WPC40-1	40/59	1
WPC40-3	40/57	3
WPC40-5	40/55	5
WPC40-10	40/50	10
WPC50-1	50/49	1
WPC50-3	50/47	3
WPC50-5	50/45	5
WPC50-10	50/40	10

Abbreviations: HDPE, high-density polyethylene; WPC, wood-plastic composite.

2 | EXPERIMENTAL

2.1 | Materials

The filler 40-60 mesh pine wood flour (WF) (*Pinus sylvestris* L.) (Soyhanlar) and the thermoplastic polymer HDPE (Ucar Plastic) were procured from commercial suppliers for use in this study. The powder form of HDPE (~200 mesh) was preferred to improve the homogeneous distribution. The melt flow index and density of HDPE were 5.5 g/10 min (190°C/2.16 kg) and 0.965 g/cm^3, respectively. Maleic anhydride-grafted polyethylene (MAPE) (Licocene PE MA 4351 Fine Grain) was used as a

14784408, 0, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/cote.12666 by Karadeniz Technical University, Wiley Online Library on [31/12/2022]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

coupling agent, whose softening point and density were 123°C and 0.99 g/cm^3, respectively. Zinc oxide nanoparticles with dimensions of 30-50 nm were supplied by Nanografi. The density of the zinc oxide nanoparticles was 5.5 g/cm^3.

2.2 | WPC production

The components (plastic, WF, nanoparticles) were mixed to obtain a homogeneous mixture, based on a scheme provided in Table 1. Then the mixture was extruded with a single screw extruder with a screw speed of 40 rpm. The extruder temperature was set from 180 to 195°C. The extruded samples were cooled in water then pelletised. The pellets were dried at 102 ± 3°C then hot-pressed at 180°C for 15 minutes (CemilUsta SSP 125). The press pressure was set at 24-26 kg/cm^2. The panels had dimensions of 500 mm × 500 mm × 4 mm.

2.3 | Accelerated UV weathering test

A QUV/spray-accelerated weathering tester (Q-Panel Lab Products) was used for the artificial weathering test. The WPC samples were exposed to 313 nm fluorescent UV (UVB) lamps, and the temperature in the chamber was set to 60°C according to ASTM G154-12a.[22] The weathering experiment was carried out in cycles of UV light irradiation for 8 hours, followed by a condensation temperature of 50°C for 4 hours in an accelerated weathering test cycle chamber over 840 hours. Three replicates were prepared for each WPC sample.

2.4 | Colour measurement

The colour measurement was performed by a Minolta CM-600d spectrophotometer (Konica Minolta) equipped with an integrating sphere, according to the ISO 7724 standard.[23] Standard illuminant D65 was preferred. The colour measurements were conducted in an area of 8 mm^2 in the 400-700 nm wavelength range. Six measurements were taken from each sample's surface. A negative value of ΔL^* represents surface darkness, while a positive value indicates a lighter surface.

The Commission International de l'Eclairage colour parameters, L^* (lightness), a^* (red [+] to green [−] along the x-axis) and b^* (yellow [+] to blue [−] along the y-axis), were calculated using Konica Minolta Colour Data Software CM-S100w Spectra Magic NX Lite (ISO 7724-2), from which the colour difference (ΔE^*) was calculated according to Equation 1:

$$\Delta E^* = \left(\Delta L^2 + \Delta a^2 + \Delta b^2\right)^{1/2}. \quad (1)$$

2.5 | ATR-FTIR spectroscopy analysis

The FTIR measurements were carried out with the ATR technique using a Thermo Nicolet iS50 FTIR (Thermo Fisher Scientific Co.) spectrometer equipped with a single-bounce diamond crystal and a deuterated triglycine sulphate detector. The surfaces of the samples were in contact with the ATR crystal so that the surface could absorb the evanescent wave. The resultant attenuated radiation produced an ATR spectrum similar to a conventional absorption spectrum.[24] The FTIR spectra of the samples were acquired in the range of 800-4000 cm^{-1} with a resolution of 4 cm^{-1}. Each spectrum was collected by 64 scans in the absorbance mode. Two measurements were averaged to produce one spectrum.

2.6 | Mechanical properties

The flexural strength (FS) and modulus of elasticity (MOE) were examined in a three-point bending test with a universal testing machine (Marestek) according to the ASTM D790 standard.[25] Eight samples with dimensions of 12.7 × 12.7 × 4 mm were prepared for each group. The tension side was the side of the samples exposed to the light.

The tensile strength (TS) tests were carried out with a universal testing machine (Marestek) according to ASTM D 638-14.[26] Eight replicates were prepared for each sample set for the TS test.

2.7 | Microscopic analysis

WPC sample surfaces were examined using a Zeiss Stemi 305 light microscope and a Zeiss AxiocAM erC 5-s camera.

The SEM investigation was carried out with a Zeiss (Evo LS10) instrument. Samples were oven-dried then gold-coated before SEM imaging (Emitech, SC7620). The samples were investigated by SEM at 250 ×, 500 × and 1000 ×.

2.8 | Statistical analysis

The test data were statistically investigated depending on the analysis of variance (ANOVA). The differences

14784408, 0, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/cote.12666 by Karadeniz Technical University, Wiley Online Library on [31/12/2022]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

TABLE 2 The mechanical properties of WPCs

Groups	Before weathering test			After weathering test	
	Flexural strength (MPa)	Modulus of elasticity (MPa)	Tensile strength (MPa)	Flexural strength (MPa)	Modulus of elasticity (MPa)
Neat-HDPE	39.13f (0.48)	1126a (29)	20.87a (2.13)	30.73cd (0.48)	1037a (69)
WPC40	37.62ef (0.53)	2192b (93)	17.94b (1.10)	31.70de (2.81)	1927b (62)
WPC50	30.44a (1.06)	2745d (88)	14.05e (1.11)	26.11a (2.08)	2292d (134)
WPC40-1	39.10f (1.19)	2597cd (121)	18.38b (0.49)	38.71h (3.56)	2511ef (168)
WPC40-3	38.22ef (1.69)	2550c (145)	17.43bc (1.95)	37.19h (0.95)	2456e (78)
WPC40-5	36.87de (1.32)	2708cd (199)	15.51de (0.55)	36.50gh (2.97)	2606fg (78)
WPC40-10	35.55cd (1.44)	2280b (142)	15.06de (1.90)	34.02ef (1.64)	2085c (80)
WPC50-1	30.59a (0.82)	2920e (148)	15.00de (0.23)	28.54bc (1.86)	2717g (154)
WPC50-3	35.20c (1.87)	2647cd (297)	16.07cd (1.88)	34.64fg (2.16)	2545ef (171)
WPC50-5	33.14b (2.83)	4524f (183)	13.84e (1.37)	32.95def (1.96)	4185i (107)
WPC50-10	31.80ab (0.90)	2985e (195)	14.18e (1.66)	26.37ab (0.88)	2926h (144)

Note: Values in parentheses are standard deviations; letters indicate the differences ($P < 0.05$) between groups depending on the Duncan test.
Abbreviations: HDPE, high-density polyethylene; WPC, wood-plastic composite.

between groups were determined according to the Duncan test ($P < 0.05$).

3 | RESULTS AND DISCUSSION

3.1 | Mechanical properties

The effect of zinc oxide nanoparticles on the mechanical properties of WPCs was examined, and the results are provided in Table 2. The combination of wood with polymer negatively affected the mechanical properties. The inconsistency between the wood and polymer influenced the load transfer, especially from 40% to 50%, which resulted in a decrease.[27,28] Meanwhile, adding zinc oxide nanoparticles to the matrix improved the FS and MOE. However, the nanoparticles were not as effective on the TS. The increase in the nanoparticle content restricted the increase in the mechanical properties because of decreasing polymer content, which is the primary bonding agent in the matrix. Therefore, the decrease in the polymer content negatively affects the load transfer. Moreover, although there was no detected agglomeration in the SEM analysis, this could also be a reason for the limited mechanical properties. Devi and Maji stated that nanoparticles improved the FS by up to 61%, but the highest mechanical properties were obtained from much lower nanoparticle content.[18] Zhang et al also highlighted that agglomeration with the increase in the nanoparticle content results in a decline in mechanical properties.[29] Meanwhile, another study reported that 4% of nano-graphene–based polymer composite displayed the highest elastic modulus, while 8% provided the highest thermal stability.[30]

Mechanical properties were negatively affected after the weathering test. The decrease in FS was between 0.57% and 21.47%, while it was 1.98% to 16.50% for MOE. The highest reduction was obtained from neat-HDPE for FS and WPC50 for MOE. There are scission and crosslinking reactions in the chemical chain of the polymer during photodegradation.[31] The scission reactions are much more intense than crosslinking, which increases the short-chain formation.[32] In this case, stress transfer is inhibited, which induces a decrease in the mechanical properties. However, because of their high surface/volume ratio, UV absorption and reflection, zinc oxide nanoparticles restricted the reduction in mechanical properties, enabling them to transfer stress in the matrix, especially for the lowest nanoparticle content. The highest FS and MOE values were obtained from WPCs containing 1% and 5% zinc oxide nanoparticles, respectively.

3.2 | Colour changes

An aesthetically pleasing appearance is essential for manufacturers and consumers. However, UV light, rain and exhaust gases, etc., cause undesirable changes on the surface of materials outdoors. The colour changes of WPCs reinforced with zinc oxide nanoparticles were evaluated based on different parameters: ΔE^*, ΔL^*, Δa^* and Δb^* after 840 hours of an artificial weathering test (Figure 1).

14784408, 0, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/cote.12666 by Karadeniz Technical University, Wiley Online Library on [31/12/2022]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

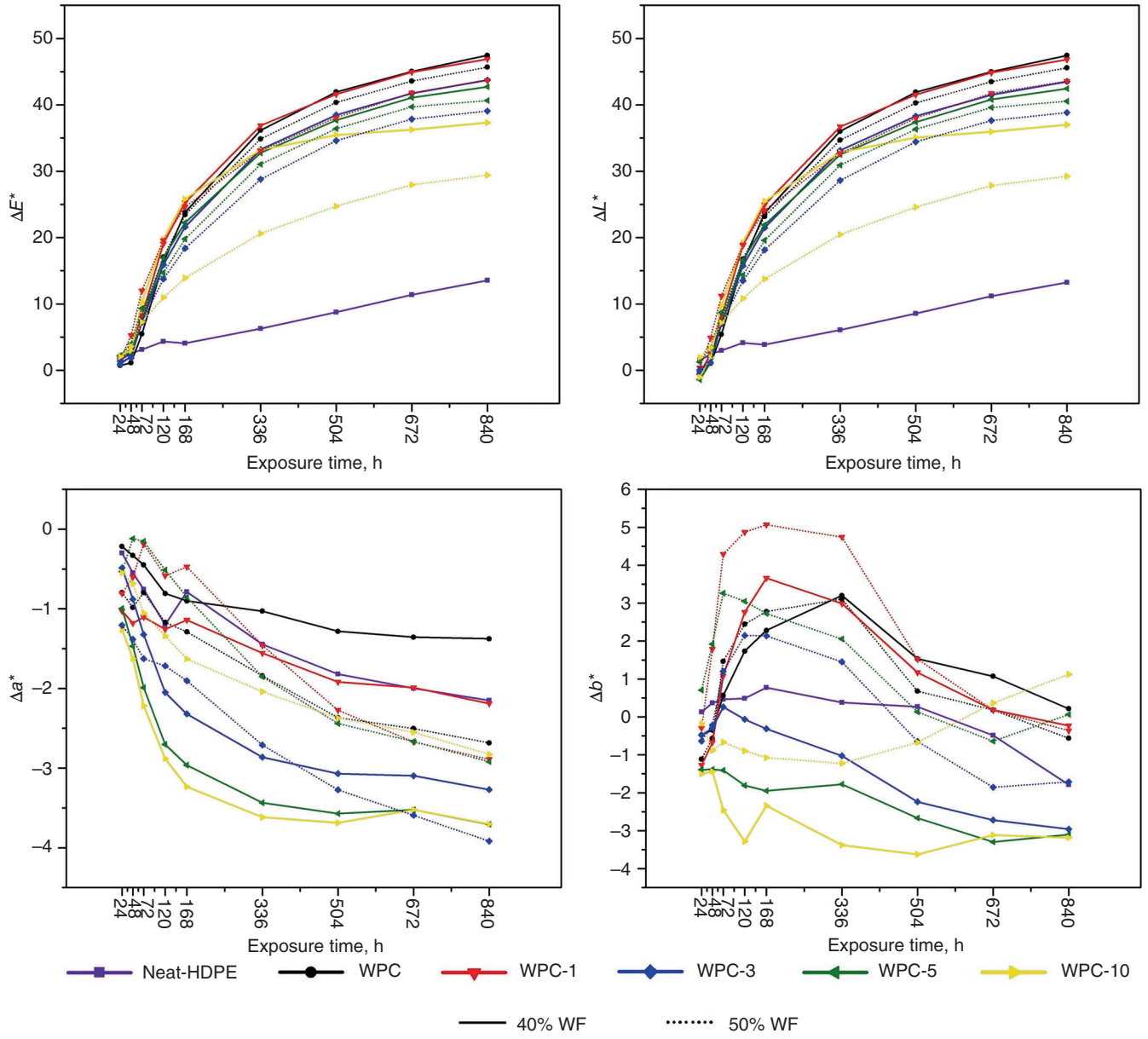

FIGURE 1 Colour changes of WPCs exposed to 840 hours of an accelerated weathering test. WPCs, wood-plastic composites

Colour measurements showed that colour change is inevitable. According to general colour change results (ΔE^*), the most negligible colour change was obtained from neat-HDPE, while the highest colour changes were detected in the WPC40. The combination of wood with HDPE decreased colour stabilisation. Moreover, colour changes could be delayed and/or reduced with the effect of nanoparticles. The addition of zinc oxide nanoparticles improved colour stabilisation. Zinc oxide nanoparticles are recognised as an UV light absorber between 200 and 380 nm.[33] Moreover, they can also be used as a UV shield because of the intense UV absorbance.[19] As the zinc oxide nanoparticle concentration increased, the colour changes decreased. While the lowest zinc oxide nanoparticles (1%) showed a similar trend to control samples, as the content of wood and zinc oxide nanoparticles increased, colour changes reduced.

Similar results were also observed for ΔL^*, which provides information about the surface lightness. As is well known, the surfaces of WPCs tend to whiten during UV exposure. UV light causes damage to the chemical structure of wood and polymer, in which the breaking of chemical bonds results in increasing whiteness.[3] As can be seen from Figure 1, the whitening was very fast during the first 336 hours. After that, its rate decelerated. The addition of WF to the polymer decreased the whiteness. The whiteness of WPCs containing 50% WF was lower than 40% WF, while neat-HDPE was the lowest. Although,

14784408, 0, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/cote.12666 by Karadeniz Technical University, Wiley Online Library on [31/12/2022]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

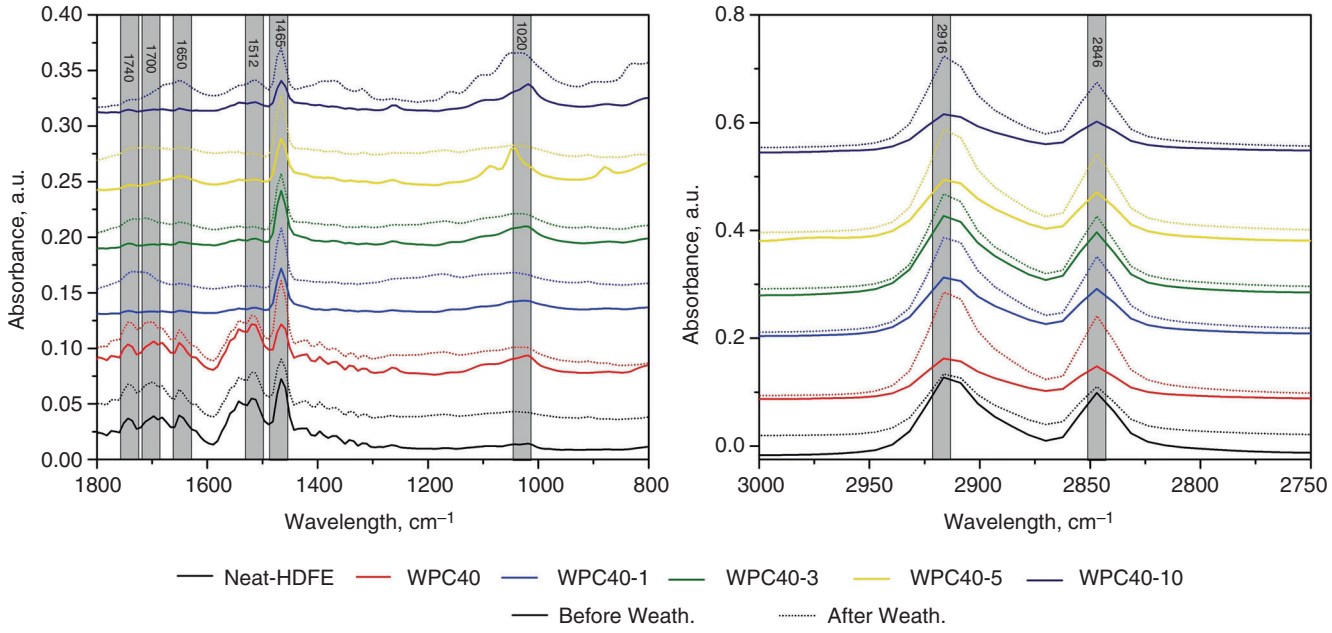

FIGURE 2 ATR-FTIR spectra of WPC samples containing 40% WF. ATR-FTIR, attenuated total reflectance-Fourier Transform–infrared; Weath., weathering; WF, wood flour; WPC, wood-plastic composite

as Kiguchi et al reported, the increased WF content resulted in increasing whiteness, the cracks that occurred during the exposure revealed an inner side of WPCs with darkened surfaces, which reduced the lightness of the surface (ΔL^*).[12,34] On the other hand, the increased zinc oxide nanoparticle content with WF improved the lightness of the surface.

The surfaces of WPCs tended to be green after the 840-hour weathering test. The lowest difference in Δa^* values was obtained from the control samples, while the highest was from WPC50-3. The increase in the wood content increased Δa^* values. The chromophoric groups in the lignin absorb UV light and cause the Δa^* value to increase in the negative direction.[35] The increasing content of zinc oxide nanoparticles increased the occurrence of a greenish surface.

On the other hand, Δb^* values showed that samples tended to have yellowish surfaces during the first 168 hours. After that time, Δb^* values started to decrease. Paraquinone chromophoric groups cause the oxidation of lignin during UV absorption, which results in a yellowish surface. However, paraquinone is reduced to hydroquinone during UV absorption, inhibits a yellowish surface, and causes the surface to be prone to being bluish.[13] The increase in the zinc oxide nanoparticle content decelerated this process. Samples with 10% zinc oxide nanoparticles only accelerated the yellowish colour of the surface after 336 hours of UV exposure. Even although the highest point for Δb^* (peak) was not reached at the end of the test, this provides evidence of the UV shielding ability of zinc oxide nanoparticles.

3.3 | ATR-FTIR spectroscopy analysis

Chemical, as well as physical, changes occurred on the surface of WPC samples exposed to UV light. The effect of zinc oxide nanoparticles on the chemical structure of samples after the weathering test was investigated using ATR-FTIR analysis, as shown in Figures 2 and 3. The bands at 2916 and 2846 cm^{-1}, representing the C–H stretching in the chemical structure of the polymer, were intense, mainly for the control samples.[36,37] The UV absorbance ability of zinc oxide nanoparticles decreased the effect of UV light, which could delay the degradation. However, the nanoparticle content increase was ineffective, while 1% and 3% of zinc oxide nanoparticles provided better protection.

Meanwhile, the intensity of bands in the fingerprint region (1800-800 cm^{-1}) for WPCs containing zinc oxide nanoparticles was weak compared with control samples. Wang et al stated that zinc oxide nanoparticles cover the active groups on the surface of WPCs or interact with active groups, which cuts off the connection, resulting in weak bands' intensity.[38] The bands between 1800 and 1600 cm^{-1} are in the carbonyl region. The band at 1740 cm^{-1} represents the carboxylic acids related to MAPE, the coupling agent used to improve the bonding between wood and polymer. The ester bonds between

14784408, 0, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/cote.12666 by Karadeniz Technical University, Wiley Online Library on [31/12/2022]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

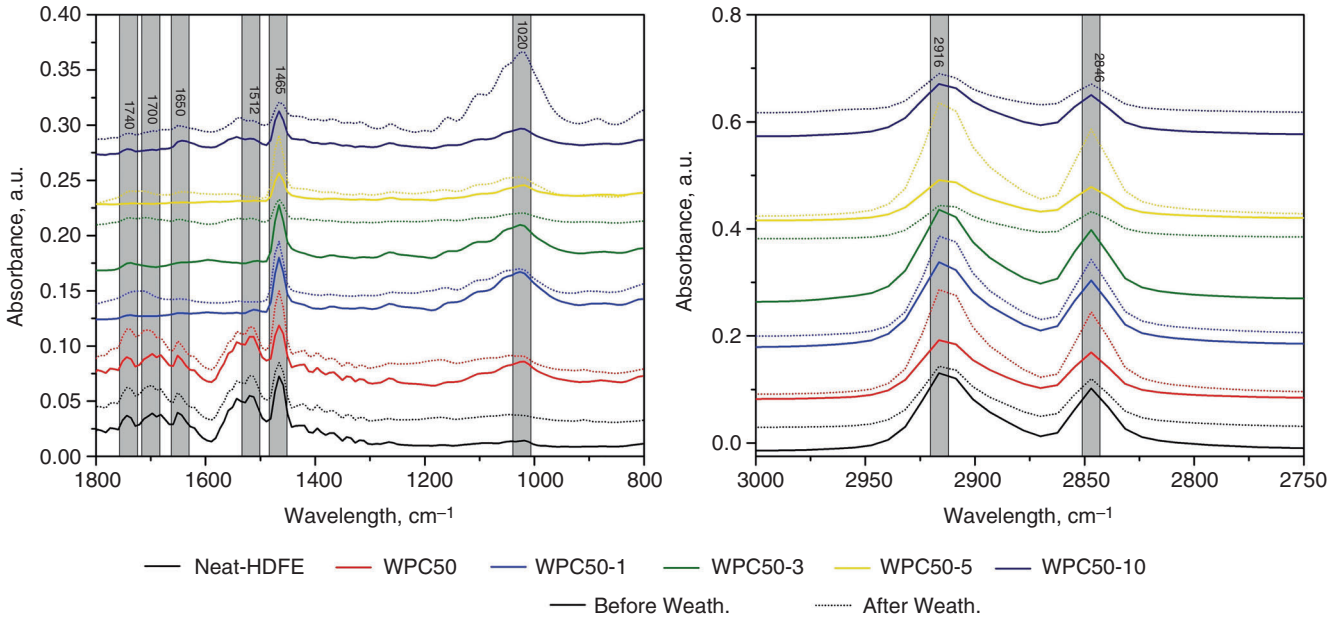

FIGURE 3 ATR-FTIR spectra of WPC samples containing 50% WF. ATR-FTIR, attenuated total reflectance-Fourier Transform–infrared; Weath., weathering; WF, wood flour; WPC, wood-plastic composite

wood and polymer are represented by this band.[39] However, the ester concentration increases with the effect of UV light, which causes scission reactions. Therefore, the intensity of this band increased. However, zinc oxide nanoparticles hindered the rising of the band at 1740 cm^{-1}, which provides evidence of UV protection from zinc oxide nanoparticles. The band at 1700 cm^{-1} is assigned to vinyl and carboxylic acids.[20] There were almost no changes in the intensity of this band. The intensity of the 1650 cm^{-1} band, belonging to vinyl groups, was more intense for control samples, while there were nearly no changes for zinc oxide nanoparticles. Although photooxidation strengthens this band's intensity, zinc oxide nanoparticles hinder or reduce it. The barrier effect of zinc oxide nanoparticles and UV absorption ability delays and/or decreases photodegradation.

The band at 1512 cm^{-1} is a characteristic lignin peak responsible for colour change on the wood. This band's intensity decreased during the weathering process. Badji et al stated that photooxidation increases lignin-related water-soluble by-products, which are removed from the surface.[35] Therefore, the lignin-related peak height decreases. The band at 1465 cm^{-1} is related to the amorphous structure of polyethylene.[40] This band is also representative of CH_3 deformation in the chemical structure of cellulose and hemicellulose.[36,37] While this band was more intense for the control groups, it was not observed for WPCs containing zinc oxide nanoparticles. The peak at 1020 cm^{-1} is assigned to the C–O stretching in cellulose and hemicellulose.[38] After the weathering test, the intensity of this band decreased for the control samples. There were nearly no changes for WPC samples containing zinc oxide nanoparticles. However, the increase in the nanoparticle content increased the peak intensity. The by-products were removed from the surface as a result of photodegradation, which decreased the intensity of this peak. However, carbonyl moieties delayed the photodegradation due to zinc oxide nanoparticles, which resulted in increasing peak height.

3.4 | Light microscopy analysis

The outdoor conditions not only cause colour changes on the surface, but also cracks, surface erosions and roughness. The effect of zinc oxide nanoparticles on the weathering performance of samples was also investigated by light microscopy, as shown in Figures 4 and 5. The light microscopy images clearly show the colour changes on the sample surfaces. Moreover, light microscopy analysis also illustrated that there were not only colour changes on the surface, but also cracks.

UV light triggers scission and crosslinking reactions in the chemical chains of polyethylene.[32] However, chain scission reactions are more dominant during photooxidation, which increases crack formation; moreover, water molecules bond with wood fibres, enlarging cracks. As can be seen from the figures, deep and wide cracks occurred on the surface of the control samples. The increase in the WF content increased crack formation.

14784408, 0, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/cote.12666 by Karadeniz Technical University, Wiley Online Library on [31/12/2022]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

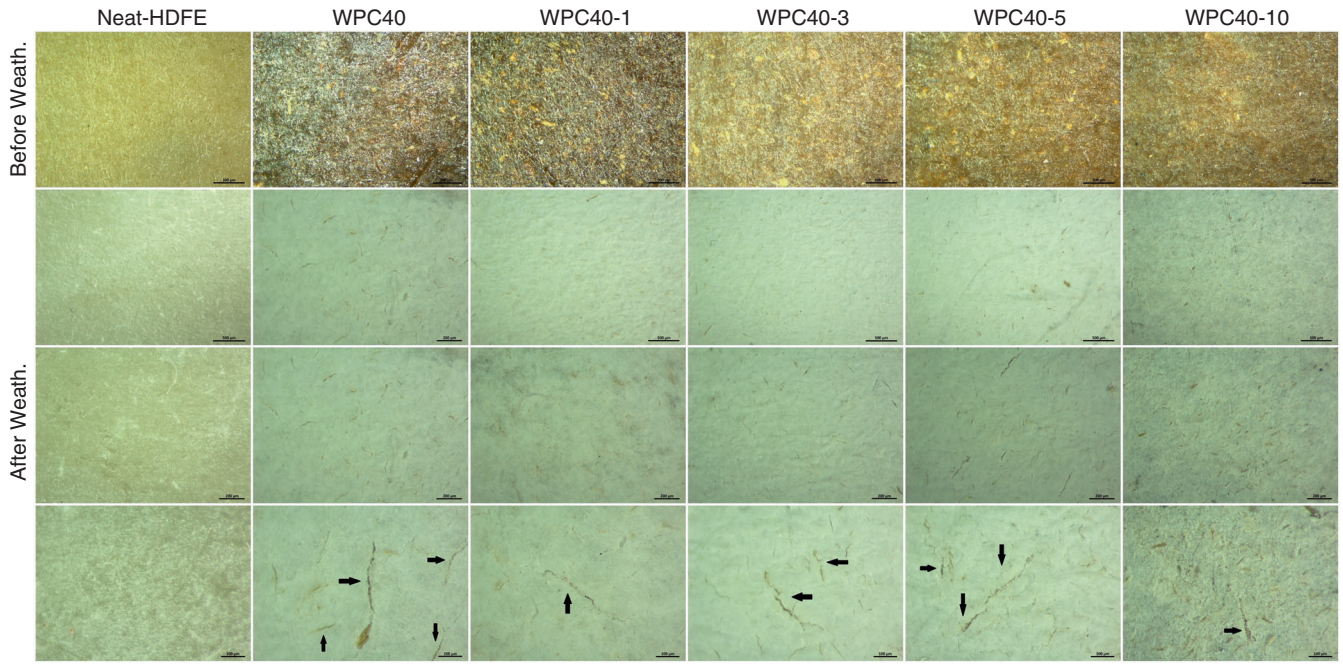

FIGURE 4 Light microscopy images of WPC samples containing 40% WF. Weath., weathering; WF, wood flour; WPC, wood-plastic composite

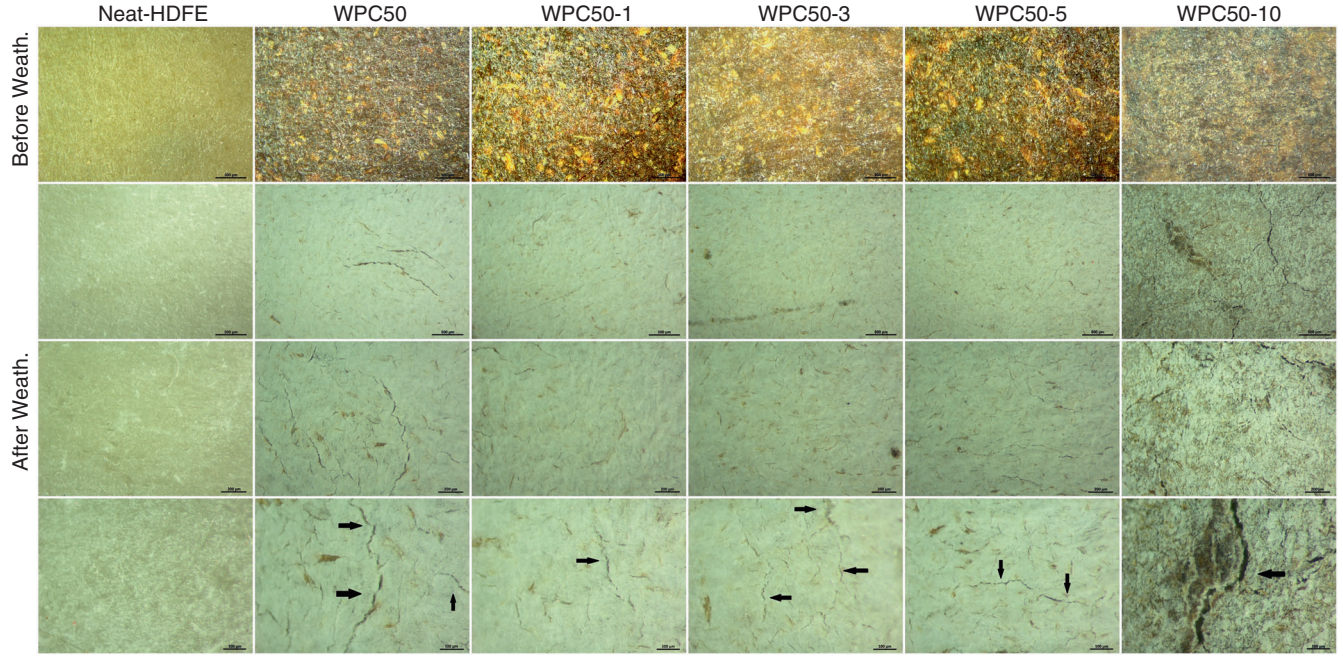

FIGURE 5 Light microscopy images of WPC samples containing 50% WF. Weath., weathering; WF, wood flour; WPC, wood-plastic composite

The cracks were striking on the surface of WPC50. Although zinc oxide nanoparticles decreased crack formation they could not prevent it. The number of cracks and their dimensions were reduced by the effect of the UV shielding ability of the zinc oxide nanoparticles. Rasouli et al also reported that zinc oxide nanoparticles significantly decreased surface crack formation.[20] Moreover, Clausen et al highlighted that the water absorption values of wood samples fell, even after a weathering test.[19] Therefore, the water-repellent properties of zinc oxide nanoparticles also played a vital role in decreasing crack formation.

The increase in the WF and nanoparticle content decreased the polymer content as a binding agent, which

14784408, 0, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/cote.12666 by Karadeniz Technical University, Wiley Online Library on [31/12/2022]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

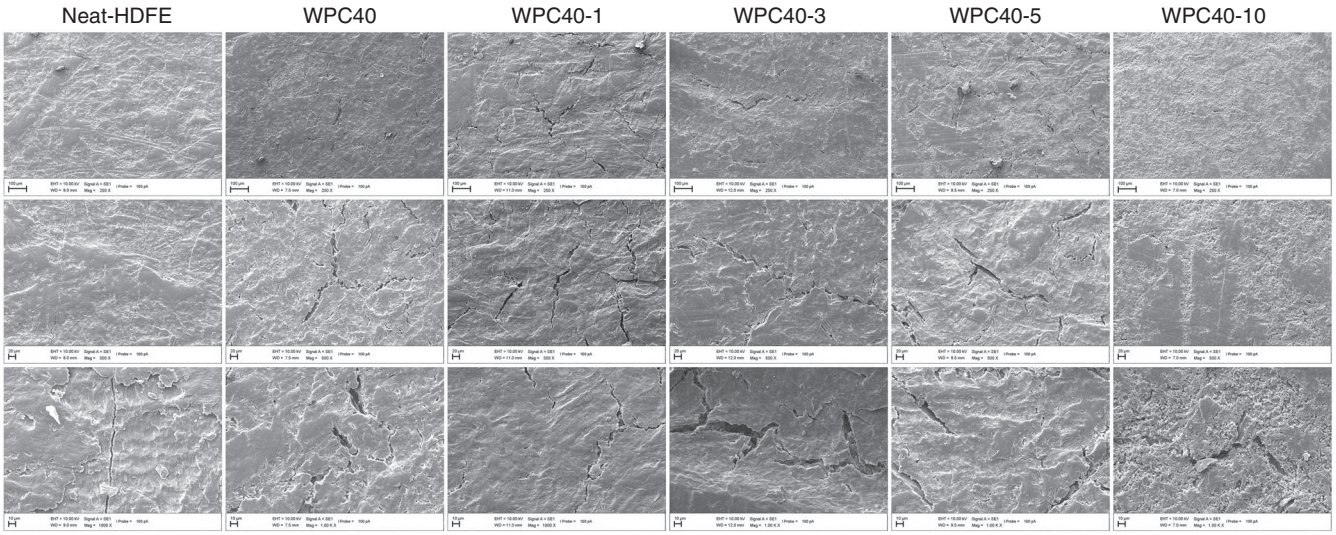

FIGURE 6 SEM images of WPC samples containing 40% WF. SEM, scanning electron microscopy; WF, wood flour; WPC, wood-plastic composite

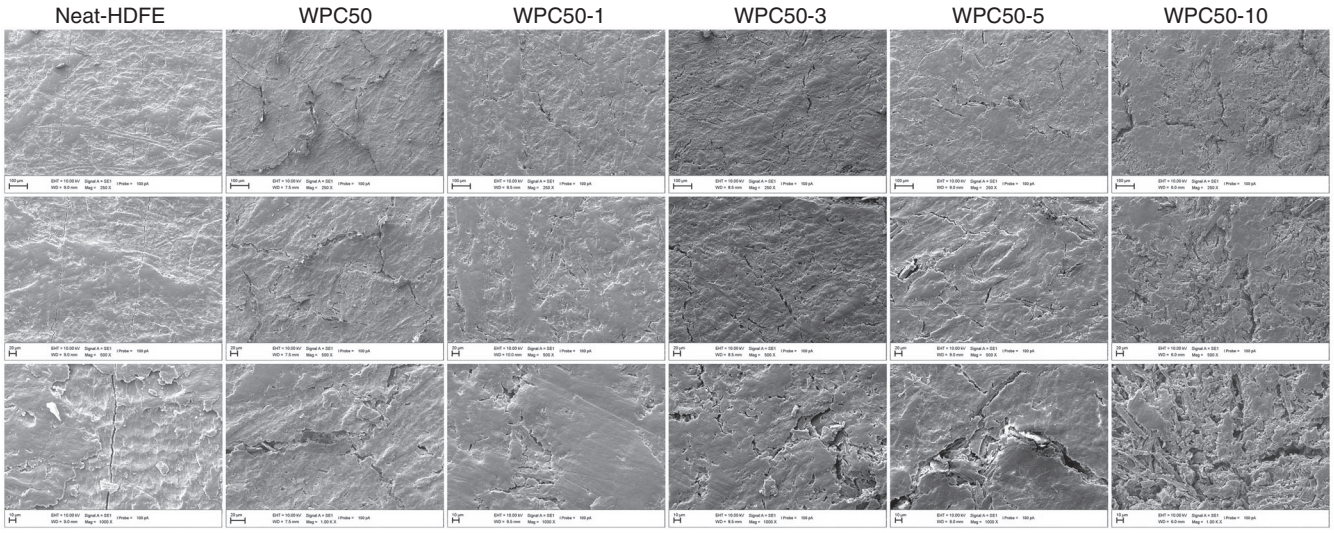

FIGURE 7 SEM images of WPC samples containing 50% WF. SEM, scanning electron microscopy; WF, wood flour; WPC, wood-plastic composite

weakens the binding between the materials. The degradation intensity was more severe with reduced polymer content. Although the deep and wide crack formations were not inhibited entirely for WPC50-10, zinc oxide nanoparticles still provided UV protection for decreasing polymer content.

3.5 | Scanning electron microscopy analysis

The effect of zinc oxide nanoparticles on the weathering performance of samples was also investigated by SEM, as shown in Figures 6 and 7. The negative effects of weathering are inevitable, as can be seen from the SEM images. However, they could be restricted and/or decreased with an agent that has resistance against UV light. SEM analysis thoroughly revealed the effect of photodegradation on the surface. Crack formation occurred with the action of UV light on the short-chain formation of the polymer, which caused micro-crack formation. However, adding WF to the polymer increased the degradation intensity, resulting in deep and big cracks.

As WF content increased, there were not only cracks but also roughness. As seen in WPC50, the surface of the WPC started flaking with the effect of humidity. However, the UV shielding ability of the zinc oxide

14784408, 0, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/cote.12666 by Karadeniz Technical University, Wiley Online Library on [31/12/2022]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

nanoparticles restricted the negative impact of weathering. Meanwhile, as the nanoparticles content increased with WF content, polymer content decreased, acting as bonding between components, which makes WF increasingly vulnerable to humidity. However, there was still no flaking because of the UV shielding ability of the nanoparticles, although there was crack formation on the surfaces of the WPCs. Moreover, the crack formations also explained the reduction in mechanical properties. The scission reactions restricted load transfer, which resulted in the degradation.

4 | CONCLUSIONS

In this study, WPCs were reinforced with zinc oxide nanoparticles to improve the weathering performance. Nanoparticles have a high surface/volume ratio, enabling them to protect the WPC surfaces against UV light, as well as humidity. Moreover, nanoparticles play an essential role in load transfer, which increases mechanical properties. The colour change results indicated that zinc oxide nanoparticles inhibit and/or reduce photodegradation on the surface of WPCs. The increase in the zinc oxide nanoparticle content also reduced the colour changes. On the other hand, adding WF increased colour changes compared with neat-HDPE. However, the lowest colour change was obtained from WPC50-10, which was nearly similar to neat-HDPE. Zinc oxide nanoparticles' barrier effect and UV absorbance ability provided protection against UV light and condensation cycles. ATR-FTIR spectroscopy analysis also indicated that zinc oxide nanoparticles inhibited and/or decreased the changes in the intensity of characteristic peaks of wood and polymer. Because of the zinc oxide nanoparticles, band intensity changes at 2916 and 1512 cm^{-1} were either minor or non-existent.

Light microscopy images also demonstrated that photodegradation is inevitable. Colour changes and surface erosion were clearly seen on WPC surfaces. Moreover, crack formation also occurred on the surfaces. UV light and condensation weakened the structure, as was predominantly observed in the control samples. Mainly, the increase in wood content enhanced the cracks resulting from the scission reactions of the polymer chain and wood swelling. Moreover, micro-crack formation was also monitored by SEM analysis, which explained the decrease in the mechanical properties. Nevertheless, reinforcement with zinc oxide nanoparticles improved the UV resistance and decreased crack formation. However, the increased nanoparticle and WF content decreased the polymer content, creating wide and deep cracks, just like in the control samples. However, low nanoparticle content (up to 5%) significantly protected against UV light and crack formation. Therefore, it was concluded that zinc oxide nanoparticles provide protection against UV light and condensation because of their capability for UV absorption and shielding, both of which improve the weathering performance of WPCs.

ACKNOWLEDGEMENTS

The Scientific and Technological Research Council of Turkey (TUBITAK) (Project No: 121O909). A part of this study was presented at The 30th International Online conference Research for Furniture Industry on 22-23 September 2022.

ORCID

Sefa Durmaz https://orcid.org/0000-0002-3880-0033
Ozlem Ozgenc Keles https://orcid.org/0000-0001-9985-3641
Ugur Aras https://orcid.org/0000-0002-1572-0727
Yusuf Ziya Erdil https://orcid.org/0000-0003-3938-2168

REFERENCES

1. Yalcin M, Pelit H, Akcay C, Cakicier N. Surface properties of tannin-impregnated and varnished beech wood after exposure to accelerated weathering. *Color Technol*. 2017;133:334-340.
2. Schmidt O. In: Czeschlik D, ed. *Wood and Tree Fungi, Biology, Damage, Protection, and Use*. Springer Verlag; 2006.
3. Fabiyi JS, McDonald AG. Effect of wood species on property and weathering performance of wood plastic composites. *Compos Part A-APPL S*. 2010;41:1434-1440.
4. Baysal E, Dizman Tomak E, Ozbey M, Altin E. Surface properties of impregnated and varnished Scots pine wood after accelerated weathering. *Color Technol*. 2014;130:140-146.
5. Durmaz S, Erdil YZ, Avcı E. Accelerated weathering performance of wood-plastic composites reinforced with carbon and glass fibre-woven fabrics. *Color Technol*. 2022;138:71-81.
6. Bajracharya RM, Manalo AC, Karunasena W, Lau KT. An overview of mechanical properties and durability of glass-fibre reinforced recycled mixed plastic waste composites. *Mater Design*. 2014;62:98-112.
7. Feist WC, Hon DNS. In: Rowell RM, ed. *In the Chemistry of Solid Wood*. American Chemical Society; 1984.
8. Martikka O, Kärki T, Puurtinen A. Improving durability of wood-mixed waste plastic composites with compatibilizers. In *IOP Conference Series: Materials Science and Engineering*. IOP Publishing; 2019;490:022001.
9. Stark NM, Matuana LM. Characterization of weathered wood–plastic composite surfaces using FTIR spectroscopy, contact angle, and XPS. *Polym Degrad Stab*. 1883;2007:92.
10. Durmaz S, Özgenc Ö, Avcı E. Weathering performance of waterborne acrylic coating systems on flat-pressed wood–plastic composites. *J Appl Polym Sci*. 2010;137:48518.
11. Fiest WC. Role of pigment concentration in the weathering of semitransparent stains. *Forest Prod J*. 1988;38:41-44.
12. Kiguchi M, Kataoka Y, Matsunaga H, Yamamoto K, Evans PD. Surface deterioration of wood-flour polypropylene composites by weathering trials. *J Wood Sci*. 2007;53:234-238.

14784408, 0, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/cote.12666 by Karadeniz Technical University, Wiley Online Library on [31/12/2022]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

13. Muasher M, Sain M. The efficacy of photostabilizers on the color change of wood filled plastic composites. *Polym Degrad Stab*. 2006;91:1156-1165.
14. Gugumus F. The performance of light stabilizers in accelerated and natural weathering. *Polym Degrad Stab*. 1995;50:101-116.
15. Stark NM, Matuana LM. Ultraviolet weathering of photostabilized wood-flour filled high-density polyethylene composites. *J Appl Polym Sci*. 2003;90:2609.
16. De Filpo G, Palermo AM, Rachiele F, Nicoletta FP. Preventing fungal growth in wood by titanium dioxide nanoparticles. *Int Biodeter Biodegr*. 2013;85:217-222.
17. Chaharmahali M, Tajvidi M, Najafi SK. Effects of nano-graphene on the physico-mechanical properties of bagasse/polypropylene composites. *Polym Bull*. 2014;71:337-349.
18. Devi RR, Maji TK. Effect of Nano-ZnO on thermal, mechanical, UV stability, and other physical properties of wood polymer composites. *Ind Eng Chem Res*. 2012;51:3870-3880.
19. Clausen CA, Green F, Kartal SN. Weatherability and leach resistance of wood impregnated with Nano-zinc oxide. *Nanoscale Res Lett*. 2010;5:1464-1467.
20. Rasouli D, Dintcheva NT, Faezipour M, La Mantia FP, Farahani MRM, Tajvidi M. Effect of nano zinc oxide as UV stabilizer on the weathering performance of wood-polyethylene composite. *Polym Degrad Stabil*. 2016;133:85-91.
21. Yang R, Li Y, Yu J. Photo-stabilization of linear low density polyethylene by inorganic nano-particles. *Polym Degrad Stab*. 2005;88:168-174.
22. ASTM International Standard Practice for Operating Fluorescent Ultraviolet (UV) Lamp Apparatus for Exposure of Nonmetallic Materials, ASTM G154-12a, 2015.
23. ISO (International Organization for Standardization) Paints and varnishes-Colourimetry, ISO 7724, 1984.
24. Khoshhesab ZM. *Reflectance IR Spectroscopy*. 1st ed. Intech Open Access Publisher; 2012.
25. ASTM International Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials. ASTM D790-17, 2017.
26. ASTM International Standard test methods for tensile properties of plastics. ASTM D638-14, 2014.
27. Adhikary KB, Pang S, Staiger MP. Dimensional stability and mechanical behaviour of wood–plastic composites based on recycled and virgin high-density polyethylene (HDPE). *Compos B Eng*. 2008;39:807-815.
28. Ayrilmis N, Jarusombuti S. Flat-pressed wood plastic composite as an alternative to conventional wood-based panels. *J Compos Mater*. 2011;45:103-112.
29. Zhang Y, Fang J, Li J, Guo Y, Wang Q. The effect of carbon nanotubes on the mechanical properties of wood plastic composites by selective laser sintering. *Polymers*. 2017;9:728.
30. Asmatulu R, Khan WS, Reddy RJ, Ceylan M. Synthesis and analysis of injection-molded nanocomposites of recycled high-density polyethylene incorporated with graphene nanoflakes. *Polym Compos*. 2015;36:1565-1573.
31. Matuana LM, Kamdem DP. Accelerated ultraviolet weathering of PVC/wood-flour composites. *Polym Eng Sci*. 2002;42:1657-1666.
32. Grigoriadou I, Paraskevopoulos KM, Chrissafis K, Pavlidou E, Stamkopoulos TG, Bikiaris D. Effect of different nanoparticles on HDPE UV stability. *Polym Degrad Stab*. 2011;96:151-163.
33. He J, Shao W, Zhang L, Deng C, Li C. Crystallization behavior and UV-protection property of PET-ZnO nanocomposites prepared byin situpolymerization. *J Appl Polym Sci*. 2009;114:1303-1311.
34. Yang TH, Yang TH, Chao WC, Leu SY. Characterization of the property changes of extruded wood–plastic composites during year round subtropical weathering. *Construct Build Mater*. 2015;88:159-168.
35. Badji C, Soccalingame L, Garay H, Bergeret A, Bénézet JC. Influence of weathering on visual and surface aspect of wood plastic composites: correlation approach with mechanical properties and microstructure. *Polym Degrad Stab*. 2017;137:162-172.
36. Kaczmarek H, Ołdak D, Malanowski P, Chaberska H. Effect of short wavelength UV-irradiation on ageing of polypropylene/cellulose compositions. *Polym Degrad Stab*. 2005;88:189-198.
37. Turku I, Kärki T. Accelerated weathering of fire-retarded wood–polypropylene composites. *Compos - A: Appl Sci Manuf*. 2016;81:305-312.
38. Wang Y, Wu X, Wang Y, Tian Y, Mu H, Li J. Hydrophobic and UV-resistant properties of environmentally friendly nano-ZnO-coated wood. *Holzforschung*. 2021;75:138-147.
39. Wei L, Cappellazzi J, Manning M, McDonald AG, Foster S, Morrell JJ. Long-term outdoor weathering evaluation of wood plastic composites. *Eur J Wood Wood Prod*. 2022;80:23-34.
40. Nguyen VD, Nguyen TT, Zhang A, Hao J, Wang W. Effect of three tree species on UV weathering of wood flour-HDPE composites. *J Res*. 2020;31:1071-1079.

How to cite this article: Durmaz S, Keles OO, Aras U, Erdil YZ, Mengeloglu F. The effect of zinc oxide nanoparticles on the weathering performance of wood-plastic composites. *Coloration Technology*. 2022;1-11. doi:10.1111/cote.12666

14784408, 0, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/cote.12666 by Karadeniz Technical University, Wiley Online Library on [31/12/2022]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License