Outdoor Performance of Wood-plastic Composites Enhanced with Nano Graphene-Epoxy Coating

Mehmet Acar,[a,*] Uğur Aras,[b] and Sefa Durmaz,[a]

This study evaluated the outdoor performance of wood-plastic composites (WPCs) coated with epoxy-based coatings containing graphene nanoplatelets (GNPs) after 336 h of artificial weathering. Results indicated that color change is inevitable. The GNPs covered the surface of the WPCs and restrained the UV degradation. The lowest color changes were observed in the 0.5% GNPs coating. Contrastingly, crack formations were noted on the coating surface without GNPs. Scanning electron microscopy analysis clearly revealed the splitting of the coating due to UV exposure. As the GNPs ratios increased, the crack formation decreased. Similarly, the macroscopic investigation showed that the surface roughness of the coatings decreased with increasing GNPs. Color stabilization also improved with the increased GNPs. Meanwhile, color changes occurred more rapidly in WPCs coated with pure epoxy. Epoxy-based coatings containing GNPs effectively stabilized the surface color. Additionally, GNPs restricted mechanical losses, with a reduction of only 3.68% for the epoxy coating containing 1% GNPs, compared to a 19% loss in pure epoxy-coated WPCs. In conclusion, coatings containing GNPs considerably enhanced the weathering performance of WPCs.

DOI: 10.15376/biores.20.2.3075-3084

Keywords: Graphene nanoplatelets; Wood-plastic composites; Color change; Scanning electron microscopy

Contact information: a: Department of Wood Products Industrial Engineering, Technology Faculty, Mugla Sitki Kocman University, 48000, Mugla, Turkey; b: Department of Materials and Materials Processing Technology, Arsin Vocational School, Karadeniz Technical University, 61080, Trabzon, Turkey;
** Corresponding author: macar@mu.edu.tr*

INTRODUCTION

The aesthetic appearance of wood-plastic composites (WPCs) appeals to consumers in many areas of usage such as furniture, fences, siding, and decks. However, no matter how attractive they are, sometimes the conditions of exposure negatively affect the appearance of materials. Color fade is the main drawback for materials whose visual appearance is at the forefront. Discoloration reduces attraction, worth, as well as the service life of materials. Both customers and manufacturers do not desire this due to economic reasons.

The WPCs have been one of the most preferred materials in recent years. Interest in WPCs has gradually increased due to environmental concerns. The estimated market size of WPCs was 4.57 billion US dollars ($) in 2023, and it is expected to increase from 5.09 billion $ in 2023 to 10.83 billion $ by 2032 (Jaiswal 2024). The WPCs have a huge market share in the forest products industry. They are particularly utilized outdoors because they are renowned for their endurance against outdoor conditions. Lignocellulosic materials, as the main component of WPCs, are sensitive to UV light, humidity, and biological threats. As the other main component, polymer covers and isolates the lignocellulosic materials against biotic and abiotic factors. However, discoloration of the surface is inevitable during the service life.

The chromophoric groups in the chemical structure of wood and polymer absorb UV light. Lignin, one of the main cell wall components of lignocellulosic material, is mainly responsible for UV absorption (Badji *et al.* 2017). Not only do lignocellulosic materials absorb UV light, but chromophoric groups in the polymer also have this ability, leading to inevitable surface discoloration because of UV absorption. Moreover, crack formation occurs as the polymer's molecular chain shortens (Martikka *et al.* 2019). Consequently, the service life of these materials is often shorter than expected. For instance, the Environmental Product Declaration identifies a reference service life for WPCs (30 years for decking and 40 years for claddings) in Germany in 2015 (Sommerhuber *et al.* 2017). However, the uncertainty of weather conditions can make this estimate challenging. Turku *et al.* (2018) also noted that the interaction of various factors initiates thermal- and photo-oxidation, which significantly deteriorates mechanical and physical properties

Light stabilizers, coating systems, *etc.*, are applied to the surface of WPCs to improve UV resistance. However, the differences in the chemical structure can reduce the wettability of such polymers. Consequently, weak bonding between the surface and coating results in removal of coating from the WPC surface. Despite this shortcoming, coatings help restrain surface discoloration. Bekhta *et al.* (2016) coated the surface of WPCs with veneer, impregnated paper, film, and a polymer layer to improve their properties. Due to decreasing water contact, the water resistance of WPCs improved, which is vital for their long service life. Liu *et al.* (2018) added light stabilizers to WPCs and obtained color stabilization. Durmaz *et al.* (2020) also investigated the effect of two different UV absorbers on surface discoloration, which significantly helped, and mechanical properties were improved as well.

Nanomaterials (NMs) have been preferred in recent years due to their unique properties. Their high surface area compared to volume makes them desired for most materials (Shaji and Zachariah 2017). Recent studies have shown that NMs improved composites' physical, mechanical, thermal, and fire performance. Moreover, inorganic nanostructured fillers in addition to the polymeric matrix, improved not only weather resistance but also increased barrier performance of the coatings (Yari *et al.* 2021). The NMs cover up the surface of the material and interrupt the UV light penetration (Durmaz *et al.* 2023). The high refractivity and morphological structure of NMs are responsible for blocking UV light. There have been several studies about coating systems containing NMs (Nguyen *et al.* 2016; Mohamed *et al.* 2019; Tuong *et al.* 2019).

This study investigated the outdoor performance of epoxy resin containing GNPs-coated WPCs. There have been limited studies on the behavior of GNPs in the photodegradation process. Likewise, for other NMs, their high surface area with UV absorption and scavenging ability is why GNPs are preferred for this study (Amrollahi *et al.* 2019; Maadani *et al.* 2020). The WPCs were produced using the flat-pressed method, which provides cheap, large-size, and high-rate production (Benthien and Thoemen 2012). The outdoor performance of WPCs was determined using an artificial weathering test with 336 h exposure. Macroscopic evaluation was also carried out. The structure of coatings was investigated after a weathering test by scanning electron microscopy (SEM). The mechanical properties of WPCs were also determined after the weathering test.

EXPERIMENTAL

Materials

Pine wood flour (*Pinus sylvestris* L.) with a mesh size of 40 to 60, combined with high-density polyethylene (HDPE), was utilized to produce WPC samples. The HDPE's melt flow index (MFI) and density were 5.5 g/10 min (190 °C/2.16 kg) and 0.965 g/cm^3, respectively. As a coupling agent, maleic anhydride grafted polyethylene (MAPE) (Licocene PE MA 4351 Fine Grain) was added to the matrix to improve the bonding. The softening point and density of MAPE were 123 °C and 0.99 g/cm^3, respectively. Epoxy resin (76A) (Epoart) and polyamine-based hardener (Epoart-b) were provided by Polisan (Kocaeli, Türkiye). The GNPs were provided from Nanografi (Ankara, Türkiye). The specific surface area of GNPs was 170 m^2/g. The thickness and diameter were 5 nm and 30 µm.

WPC Production

The wood flour (WF) was dried in the oven until the constant weight was 102 ± 3 °C. The WF and polymer were mixed first with a mechanical blender at 1200 rev/min and then with a drum blender (30 to 40 rev/min) for 5 min. The mixture was laid on the aluminum plate with dimensions of 500 mm x 500 mm x 4 mm. Wax paper was used to prevent the mold from sticking to the plate. The draft was hot-pressed under the 100-bar pressure at 170 °C for 15 min. After pressing, the draft was left to cool under the press. Panels were cut to size to 130 mm x 70 mm x 4 mm. All panels were conditioned according to ASTM D618-21 (2021).

Coating Application

The GNPs were mixed with epoxy resin using an ultrasonic bath for 30 min. After cooling, the hardener was added to the mixture (1.6:1 w/w) and mixed with a mechanical mixer for 10 min at 850 rpm (Fig. 1). The coating was applied in two layers to the WPCs' surface. Each layer was about 10 gr per sample's surface area. The coated WPCs were cured in an oven at 100 °C for 1 h.

Fig. 1. The preparation of coatings: a) ultrasonic bath, b) mechanical mixer

Outdoor Performance Test

The outdoor performance of WPCs was determined using a QUV accelerated weathering tester (Q-Panel Lab Products, Cleveland, USA)) with 336 h exposure time according to ASTM G154-12a (2015). The UV light from 313 nm fluorescent UVB lamps and condensation at 50 °C were selected for outdoor testing. The UV irradiation was applied for 4 h, followed by a 4-h condensation cycle. Three replicas were prepared for each group, each with dimensions of 130 mm x 70 mm x 4 mm.

Color Measurement

The changes on the surface of WPCs were determined by a Minolta CM-600d spectrophotometer (Konica Minolta) equipped with an integrating sphere, according to the ISO 7724 (1984) standard. The color measurements were performed in an area of 8 mm^2 in the 400 to 700 nm wavelength range.

The Commission International de l'Eclairage color 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 1984), from which the color difference (ΔE^*) was calculated according to Eq. 1:

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

Microscope Analysis

The coatings were removed from the surface of the WPCs after the weathering test. The coating films were analyzed by SEM (Zeiss Evo LS10).

Mechanical Tests

The flexural strength (FS) and modulus of elasticity (MOE) of WPCs were measured using a universal testing machine (Marestek, İstanbul) in a three-point bending test according to ASTM D790-17 (2017). The eight samples were tested for each group, and the results were averaged. The dimensions of the samples were 127 mm x 12.7 mm x 4 mm.

RESULTS AND DISCUSSION

Color Changes

The outdoor performance of coatings containing GNPs regarding color changes in WPCs was assessed using four parameters: ΔE^*, ΔL^*, Δa^*, and Δb^*. The color changes after 336 h of outdoor testing are shown in Fig. 2. Longer exposure time resulted in more noticeable color changes; however, coatings with GNPs slowed and reduced these changes. The epoxy-coated control samples exhibited the greatest color change, as indicated by ΔE^*, while the coating with 0.5% GNPs showed the least color change. Epoxy-coated WPCs experienced more rapid color change, whereas WPCs with 1% and 2% GNPs exhibited moderated color changes. Pereira *et al.* (2020) also reported that 1% of GNPs reduced the UVA and UVB penetration due to their ability to absorb wavelengths shorter than 281 nm.

The UV absorption of wood and polymer causes the degradation of chemical structure, which results in surface bleaching. The surface bleaching of WPCs increased with increasing exposure time. Like ΔE^*, ΔL^* values for epoxy-coated WPC rapidly increased during the outdoor test, while the GNPs helped it to be more moderate. The covering of the surface by GNPs limited the bleaching up to 168 h. However, after that time, the bleaching was inevitable even with GNPs-containing coating. Yet, it could be stated that there was nearly no color change for 0.5% and 1% GNPs-containing coating, as shown in Fig. 2. Meanwhile, as the GNPs ratio increased, the color stability decreased. It could be attributed to the agglomeration of GNPs.

The Δa^* values reflect the greenish or reddish tint of the surface. As depicted in Fig. 2, the WPC surfaces tended to develop a greenish hue, with epoxy-coated WPCs showing a more rapid shift toward green. The most pronounced greenish surface was observed on the surface of pure epoxy-coated WPCs.

The Δb^* values indicate the bluish or yellowish tint on the surface. Initially, the WPC surfaces appeared more yellowish. Still, there was a shift towards a bluish tint up to 96 h, after which the color sharply turned yellowish, particularly for epoxy-coated WPCs. The yellowing is attributed to the oxidation of lignin, which forms paraquinone chromophoric groups (Muasher and Sain 2006). The GNPs effectively slowed down the yellowing, with the color stability maintained for up to 336 h. This suggests that the presence of GNPs on the WPC surface helps limit UV light penetration, thereby improving color stability.

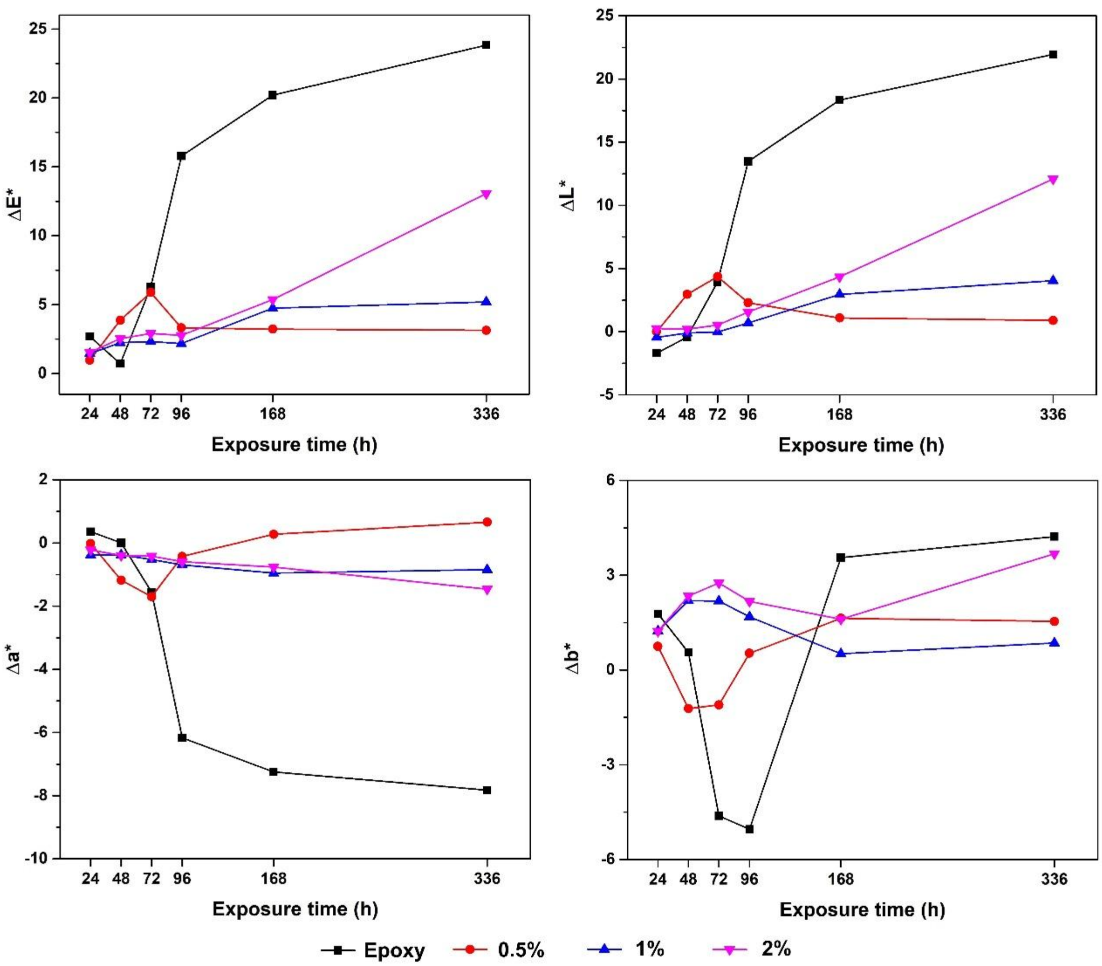

Fig. 2. The color changes of WPCs

Mechanical Properties

Outdoor conditions affect not only visual appearance but also mechanical properties. The mechanical properties of WPCs after the weathering test were investigated, and results are presented in Table 1. There were decreases in flexural strength and modulus of elasticity of WPCs compared to control samples not exposed to weathering after the weathering test. Rain, snow, and humidity pose considerable challenges to hydrophilic materials; thus, exposure to these elements can adversely affect their dimensional stability. Polymer encapsulates the wood fiber and provides dimensional stability. However, photodegradation by UV light damages the polymer's chemical structure, resulting in a shortening of the chemical chain followed by crack formation. Subsequently, wood fibers are revealed to be swollen, reducing mechanical properties of WPCs. Coatings delay and/or hinder the photodegradation. As mentioned above, GNPs offer substantial protection against UV degradation, which can affect mechanical properties. This UV protection helps maintain the polymer's chemical structure and stability. As a result, the reduction in mechanical properties was less significant in samples coated with GNP-containing coatings. The chemical structure and stability of the polymer were better preserved in these coatings, leading to a more limited decrease in mechanical properties. This is evident from the results, where pure epoxy-coated samples experienced an 18.9% loss in FS, while the samples with 1% GNPs only showed a 3.68% reduction in this study. The UV light reflection and/or absorption ability of GNPs restricted the mechanical loss, which is vital for prolonged service life. The GNPs' barrier effect is also effective in inhibiting UV light. Rejeb *et al.* (2021) stated that epoxy-based coating restricted WPCs' water absorption and thickness swelling. As noted by Lin *et al.* (2002), water absorption often occurs through water penetration into micro gaps and cracks. Therefore, a coating with remarkable water-repellent properties can effectively restrict water absorption, which in turn has a notable impact on the material's mechanical properties.

Table 1. Mechanical Properties of WPCs After Weathering Test

Groups	FS (MPa)	MOE (MPa)
Control*	27.5 (1.75)	1872 (145)
Epoxy	22.3 (1.44)	2009 (240)
0.5%	22.9 (1.26)	2155 (236)
1%	26.5 (2.55)	1908 (208)
2%	25.2 (2.33)	1884 (102)

* The control group was uncoated and not exposed to artificial weathering tests; Values in the parentheses are standard deviations

SEM Analysis

The coatings were investigated by SEM analysis after 336 h of weathering test, as shown in Fig. 3. Extensive weathering conditions noticeably damaged the coating without GNPs (Fig. 3a). The UV light broke chemical bonds in the epoxy coating, leading to crack formation. Cavities and hills resulted from UV degradation. The crack formation facilitated the water vapor penetration during the condensation cycle, which resulted in the removal of coating from the surface. Tuong *et al.* (2019) stated that nanoparticles cause rough surface at epoxy coating that can result in superhydrophobicity, which is significant for WPCs outdoors. Moreover, GNPs dispersed in the coating cover the surface and limit UV light penetration through their barrier effect, thereby improving the service life of the coating.

As can be seen in Fig. 3, the rise in the NMs ratio limited the crack formation. Compared to coating without GNPs, some pores developed in the coating of the lowest GNPs ratio. Although the crack formation was initiated, there was no splitting of the coating. Moreover, as the NM ratio increased, the crack formation was largely inhibited, thus demonstrating the effectiveness of GNPs.

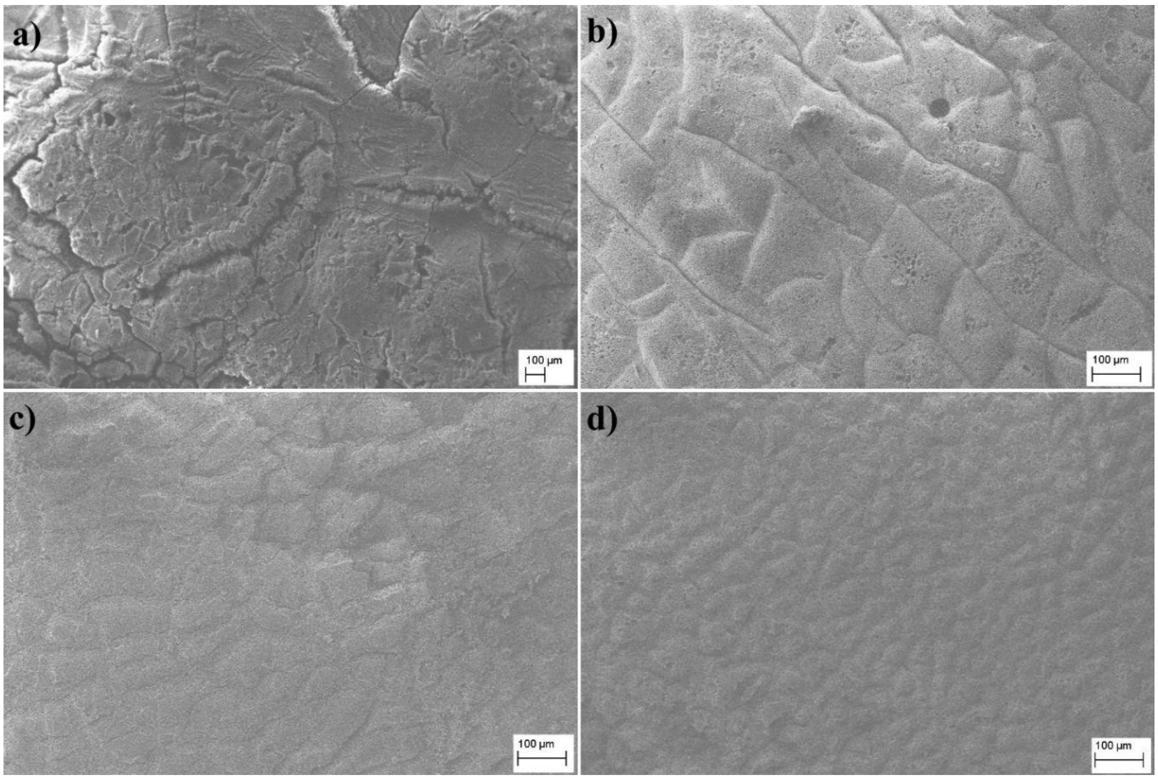

Fig. 3. The SEM images of coatings after weathering test: a) coating without GNPs, b) 0.5% GNPs, c) 1% GNPs, and d) 2% GNPs

Macroscopic Evaluation

The macroscopic evaluation of WPCs was performed after 336 h of artificial weathering. The effects of extensive weathering conditions are visible in Fig. 4. It is evident that color changes on the surface were inevitable, with noticeable bleaching occurring due to UV degradation, which is a major issue for WPCs. In addition to color change, surface erosion was also observed. UV light induces the breaking of chemical bonds, leading to the shortening of chemical chains and resulting in surface erosion, increased surface roughness, and crack formation.

Surface erosion was more severe with pure epoxy coating, while the GNPs effectively limited the surface degradation. As observed in a previous study, nanoparticles reduced surface crack formation due to their UV shielding ability, but did not completely inhibit it (Durmaz *et al.* 2023). As the ratio of GNPs increased, surface erosion decreased, and surface smoothness was better maintained. Additionally, the higher GNPs ratios contributed to improved color stabilization. Pereira *et al.* (2020) highlighted that GNPs decreased the UV lights transmittance, which improved the UV protection.

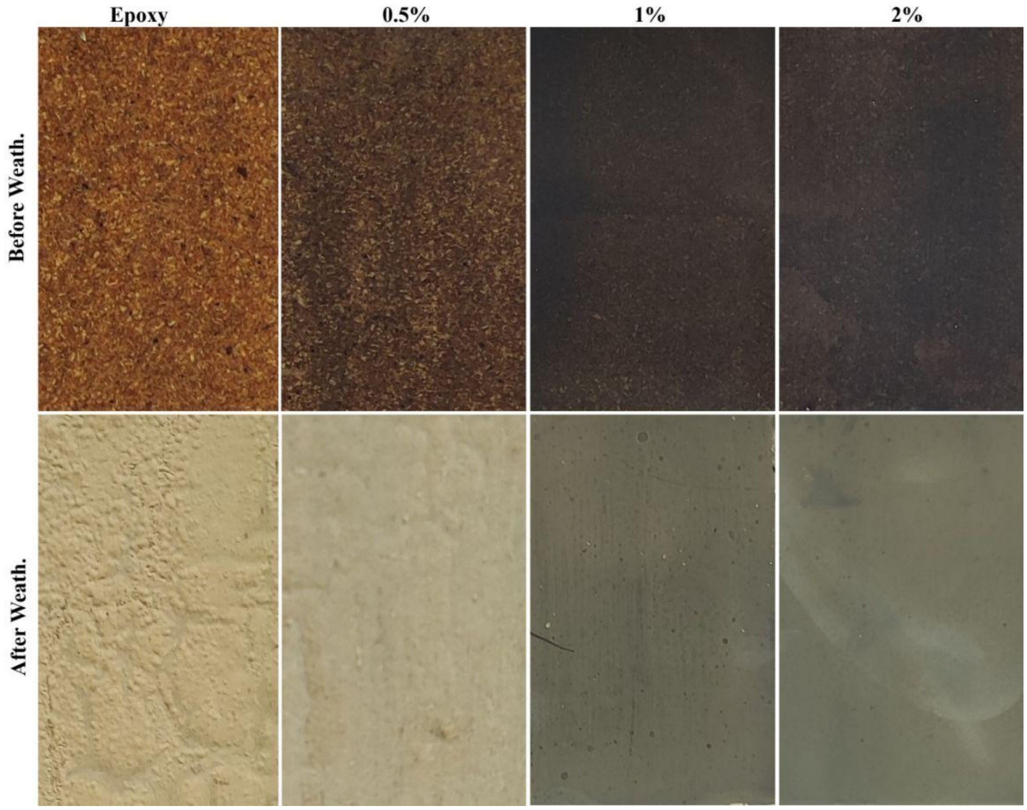

Fig. 4. The visual appearance of WPCs

CONCLUSIONS

Color fading remains a critical obstacle for wood-plastic composites (WPCs) exposed to outdoor conditions. Various methods, such as light stabilizers, coatings, and paints, have been employed to address this issue, but it persists.

1. This study investigated the effect of epoxy-based coatings containing graphene nanoparticles (GNPs) on enhancing the outdoor performance of WPCs. The coatings containing GNPs limited the effect of weathering.
2. The surface erosion was considerably decreased by GNPs. The scanning electron micrograph (SEM) images confirmed that GNPs covered the WPC surfaces, decreasing the UV degradation and slowing down the degradation process. This delay in the chemical bond breaking and reduction in crack formation contributed to improved color stability, with 0.5% GNPs providing the highest level of color stabilization. Moreover, GNPs limited the mechanical loss by up to 3%.
3. Visual assessments of WPCs demonstrated the enhanced color stabilization achieved with GNPs. The extended service life of WPCs is crucial for economic and environmental reasons, given their increasing market share. The obtained results suggest that epoxy-based coatings containing GNPs could be evaluated as a promising solution for improving the outdoor performance of WPCs.

REFERENCES CITED

Amrollahi, S., Ramezanzadeh, B., Yari, H., Ramezanzadeh, M., and Mahdavian, M. (2019). "*In-situ* growth of ceria nanoparticles on graphene oxide nanoplatelets to be used as a multifunctional (UV shield/radical scavenger/anticorrosive) hybrid compound for exterior coatings," *Prog. Org. Coat.* 136, article ID 105241. DOI: 10.1016/j.porgcoat.2019.105241

ASTM D618-21 (2021). "Standard test methods for Standard practice for conditioning plastics," ASTM International, West Conshohocken, PA, USA.

ASTM D790-17 (2017). "Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials," ASTM International, West Conshohocken, PA, USA.

ASTM G154-12a (2015). "Standard practice for operating fluorescent ultraviolet (UV) lamp apparatus for exposure of nonmetallic materials," ASTM International, West Conshohocken, PA, USA.

Badji, C., Soccalingame, L., Garay, H., Bergeret, A., and Bénézet, J. C. (2017). "Influence of weathering on visual and surface aspect of wood plastic composites: Correlation approach with mechanical properties and microstructure," *Polym. Degrad. Stab.* 137, 162-172. DOI: 10.1016/j.polymdegradstab.2017.01.010

Bekhta, P., Lyutyy, P., and Ortynska, G. (2016). "Effects of different kinds of coating materials on properties of flat pressed WPC panels," *Drvna Industrija* 67(2), 113-118. DOI: 10.5552/drind.2016.1444

Benthien, J. T., and Thoemen, H. (2012). "Effects of raw materials and process parameters on the physical and mechanical properties of flat-pressed WPC panels," *Compos. Part A- Appl. S.* 43(4), 570-576. DOI: 10.1016/j.compositesa.2011.12.028

Durmaz, S., Özgenç, Ö., Avci, E., and Hakki Boyaci, İ. (2020). "Weathering performance of waterborne acrylic coating systems on flat-pressed wood–plastic composites," *J. Appl. Polym. Sci.* 137(14), article ID 48518. DOI: 10.1002/app.48518

Durmaz, S., Keles, O. O., Aras, U., Erdil, Y. Z., and Mengeloglu, F. (2023). "The effect of zinc oxide nanoparticles on the weathering performance of wood-plastic composites," *Color. Technol.* 139(4), 430-440. DOI: 10.1111/cote.12666

ISO 7724 (1984). "Paints and varnishes – Colourimetry," International Organization for Standardization, Geneva, Switzerland.

Jaiswal, C. (2024). "Wood plastic composites market research report information by type (polyethylene, polyvinyl chloride, others), by end-use industry (building & construction, automotive, consumer goods, others), and by region (North America, Europe, Asia-Pacific, And Rest Of The World) –Market Forecast Till 2032," Market Research Future, (https://www.marketresearchfuture.com/reports/wood-plastic-composites-market-8311?utm_term=&utm_campaign=&utm_source=adwords&utm_medium=ppc&hsa_acc=2893753364&hsa_cam=20269362920&hsa_grp=148912616334&hsa_ad=661977011274&hsa_src=g&hsa_tgt=dsa-2089395937864&hsa_kw=&hsa_mt=&hsa_net=adwords&hsa_ver=3&gad_source=1.%2005.08.2024), Accessed 05 Aug 2024.

Lin, Q., Zhou, X., and Dai, G. (2002). "Effect of hydrothermal environment on moisture absorption and mechanical properties of wood flour–filled polypropylene composites," *J. Appl. Polym. Sci.* 85(14), 2824-2832. DOI: 10.1002/app.10844

Liu, C., Mei, C., Xu, B., Chen, W., Yong, C., Wang, K., and Wu, Q. (2018). "Light stabilizers added to the shell of co-extruded wood/high-density polyethylene composites to improve mechanical and anti-UV ageing properties," *R. Soc. Open Sci.* 5(5), article ID 180074. DOI: 10.1098/rsos.180074

Maadani, M., Jafari, H., Saeb, M. R., Ramezanzadeh, B., Najafi, F., and Puglia, D. (2020). "Studying the corrosion protection behavior of an epoxy composite coating reinforced with functionalized graphene oxide by second and fourth generations of poly (amidoamine) dendrimers (GO-PAMAM-2, 4)," *Prog. Color Color. Coat.* 13(4), 261-273. DOI: 10.30509/pccc.2020.81655

Martikka, O., Kärki, T., and Puurtinen, A. (2019). "Improving durability of wood-mixed waste plastic composites with compatibilizers," *Mater. Sci. Eng.* 490(2), article ID 022001. DOI: 10.1088/1757-899X/490/2/022001

Mohamed, M. R., Naguib, H. M., El-Ghazawy, R. A., Shaker, N. O., Amer, A. A., Soliman, A. M., and Kandil, U. F. (2019). "Surface activation of wood plastic composites (WPC) for enhanced adhesion with epoxy coating," *Mater. Perform. Charact.* 8(1), 22-40. DOI: 10.1520/MPC20180034

Muasher, M., and Sain, M. (2006). "The efficacy of photostabilizers on the color change of wood filled plastic composites," *Polym. Degrad. Stabil*. 91(5), 1156-1165. DOI: 10.1016/j.polymdegradstab.2005.06.024

Nguyen, T. A., Nguyen, T. V., Thai, H., and Shi, X. (2016). "Effect of nanoparticles on the thermal and mechanical properties of epoxy coatings," *J. Nanosci. Nanotechnol.* 16(9), 9874-9881. DOI: 10.1166/jnn.2016.12162

Pereira, P., Ferreira, D. P., Araújo, J. C., Ferreira, A., and Fangueiro, R. (2020). "The potential of graphene nanoplatelets in the development of smart and multifunctional ecocomposites," *Polymers* 12(10), article 2189. DOI: 10.3390/polym12102189

Rejeb, M., Koubaa, A., Elleuch, F., Godard, F., Migneault, S., Khlif, M., and Mrad, H. (2021). "Effects of coating on the dimensional stability of wood-polymer composites," *Coatings* 11(6), article 711. DOI: 10.3390/coatings11060711

Sommerhuber, P. F., Wenker, J. L., Rüter, S., and Krause, A. (2017). "Life cycle assessment of wood-plastic composites: Analysing alternative materials and identifying an environmental sound end-of-life option," *Resour. Conserv. Recy.* 117, 235-248. DOI: 10.1016/j.resconrec.2016.10.012

Tuong, V. M., Huyen, N. V., Kien, N. T., and Dien, N. V. (2019). "Durable epoxy@ ZnO coating for improvement of hydrophobicity and color stability of wood," *Polymers* 11(9), article 1388. DOI: 10.3390/polym11091388

Turku, I., Kärki, T., and Puurtinen, A. (2018). "Durability of wood plastic composites manufactured from recycled plastic," *Heliyon* 4(3), article e00559. DOI: 10.1016/j.heliyon.2018.e00559

Yari, H., Mahdavian, M., Ramezanzadeh, B., and Mahmudzadeh, M. (2021). "Enhanced outdoor durability of polyurethane nanocomposite coatings with green reduced graphene oxide nanoplatelets," *Prog. Org. Coat.* 154, article ID 106212. DOI: 10.1016/j.porgcoat.2021.106212

Article submitted: December 6, 2024; Peer review completed: February 22, 2025; Revised version received and accepted: February 26, 2025; Published: March 5, 2025.
DOI: 10.15376/biores.20.2.3075-3084