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Effect of TiO₂ Nanoparticle Loading on the Physical, Mechanical, Thermal, and Weathering Behavior of HDPE-Based Wood–Plastic Composites

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This study concerned the possibility of enhancing the outdoor performance and thermal properties of wood–plastic composites (WPCs) by incorporating nanoparticles (NPs). Titanium dioxide (TiO₂) NPs were selected, being one of the most commonly used types, and were added to the matrix in concentrations up to 10%. Their addition improved the mechanical properties of WPCs due to the strong interaction between TiO₂ and the composite components. Furthermore, the good reflectivity properties of TiO₂ improved the surface color stability of WPCs. Even under intensive UV light exposure, the surface color changes in WPCs containing TiO₂ were moderate compared with the control samples. Microscopic analysis indicated that TiO₂ NPs significantly reduced crack formation. Although surface erosion was not completely inhibited, it was reduced. The condensation cycle of weathering weakened the bonds between the wood and polymer, leading to mechanical losses. Scanning electron microscopy (SEM) images revealed micro-cracks, which explained the decreased values obtained for the mechanical properties of reinforced WPCs. However, the decrease was limited to 0.46% for composites containing 5% TiO₂. The TiO₂ NPs also acted as a thermal barrier, retarding thermal degradation, which occurred more moderately than in the controls. Additionally, the fire performance of reinforced WPCs was enhanced by TiO₂ NPs, which improved char formation and increased the limit oxygen index (LOI) values to 25.9% O₂.

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Introduction

Wood–plastic composites (WPCs) are engineering materials that offer the advantages of biological durability, abrasion and corrosion resistance, and high dimensional stability provided by plastic materials, as well as the resistance to bending and cracking

and natural appearance provided by wood [Zang et al., 2021; Qi et al., 2023]. Moreover, WPCs can be produced and processed more quickly than pure polymers. Therefore, their popularity in the wood-based materials industry is increasing [Ashori, 2023]. Although they first emerged as a deck material, they are now often preferred in many applications, such

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as construction, car parts, furniture, and structures [Schwarzkopf and Burnard, 2016].

Although WPCs have a wide range of applications for which they offer excellent properties, their components also have shortcomings. It is well known that wood is sensitive to humidity and microorganisms, despite being a renewable and biodegradable material [Schmidt, 2006]. Moreover, its porous structure retains water, providing an environment for the accumulation of pollutants and the reproduction of microorganisms [Ramos et al., 2025]. Above 200 °C, there is also a combustion risk. Outdoor conditions cause surface coloration and erosion [Feist and Hon, 1984]. Combining wood flour with polymer overcomes nearly all of these deficiencies. However, the absorption of UV light by chromophoric groups in the wood and polymer cannot be eliminated entirely. Therefore, an undesirable sequence of events begins with initial surface color changes followed by crack formation, leading to a shortening of WPCs' service life [Fabiya and McDonald, 2010]. Meanwhile, various solutions have been proposed to improve the UV resistance of WPCs, including coatings, finishing with UV absorbers, and hindered amine light stabilizers (HALS) [Stark and Matuana, 2003; Durmaz et al., 2020]. However, the poor adhesion between the materials and the surface limits the improvement of UV resistance.

Nanomaterials have brought a new dimension to composite materials. Their small size, with a high surface-to-volume ratio, is a promising option for enhanced interaction between the components, which provides an improvement in the properties of composites [Deka and Maji, 2011; Chaharmahali et al., 2014]. Therefore, there has been growing interest in using nanoparticles as UV absorbers and stabilizers for various materials over the past few decades. In polymer science, numerous studies have investigated the effect of different types of nanoparticles on the UV resistance of polymers. For instance, TiO₂ nanoparticles have been found to effectively absorb UV radiation and reduce the rate of photodegradation in polymers [Butylina et al., 2015; Fei et al., 2016; Turku and Kärki, 2016; Xuan et al., 2017]. Similarly, zinc oxide (ZnO) nanoparticles have been demonstrated to possess excellent UV-absorbing properties, which can enhance the UV resistance of polymer films and coatings [He et al., 2009; Rasouli et al., 2016]. Other types of nanoparticles, such as carbon black and iron oxide (Fe₂O₃), have also been explored for their potential to improve the UV resistance of polymers [Wang et al., 2017; Jiang et al., 2020]. However, the high cost of nanoparticles still makes their evaluation difficult.

Due to its nontoxic properties, TiO₂ is one of the most preferred nanomaterials, alongside ZnO and silicon dioxide (SiO₂). It is also recognized as a brightening agent with high reflectivity (2.76), which facilitates the

reflection of UV light and reduces photodegradation. Therefore, TiO₂ nanoparticles are a preferred additive for this purpose due to their ability to absorb UV radiation and prevent photo-oxidation, which can lead to degradation and reduced performance of WPCs over time. TiO₂ nanoparticles deposit in the structure and reduce the surface energy, increasing hydrophobicity [Zanatta et al., 2017]. Moreover, Fei et al. [2016] reported that reinforcement with ~5% TiO₂ nanoparticles limited the deterioration in the mechanical properties of WPCs even after a weathering test. Xuan et al. [2017] achieved high thermal stability in wheat straw fiber/polypropylene-based composites by reinforcing with 3% TiO₂. Furthermore, TiO₂ nanoparticles are considered safe and environmentally friendly, essential properties for sustainable materials. Overall, the combination of effectiveness, affordability, and safety makes TiO₂ nanoparticles a preferred choice for improving the weathering properties of materials.

This study concerned the possibility of enhancing the outdoor and thermal performance of WPCs using TiO₂ NPs. The UV absorbance and reflectance ability of TiO₂ NPs are well-known, which is the main reason for their common use as reinforcement agents. However, in many studies, the effect of TiO₂ NPs has been investigated only at lower concentrations (up to ~5%). Therefore, further investigations are needed on the effects of higher contents of nanoparticles, given their tendency to agglomerate. In this study, this shortcoming was overcome by using fine-grain polymer in production. Furthermore, the practicality of TiO₂ nanoparticles, being both cost-effective and readily available, makes them a sound choice for the large-scale production of WPCs. This confidence in their practicality led to a comprehensive investigation into the effects of higher loading of nanoparticles on weathering performance, thermal stability, fire performance, and mechanical properties. The surface of WPCs was also characterized by means of light and scanning electron microscopy analysis.

Materials and methods

1. Materials

Pine wood flour (WF) (*Pinus sylvestris* L.) (Soyhanlar, Istanbul, Türkiye) with dimensions of 40–60 mesh, as a lignocellulosic material, and high-density polyethylene (HDPE) (Ucar plastic, İzmir, Türkiye) as a thermoplastic polymer were procured from commercial suppliers. HDPE was preferred as a fine grain for a homogeneous mixture. Its melt flow index (MFI) was 5.5 g/10 min (190 °C/2.16 kg), and its density was 0.965 g/cm³. Maleic anhydride grafted polyethylene (MAPE) (Lico-cene PE MA 4351 Fine Grain) was used to improve the

bonding, with a softening point of 123 °C and a density of 0.99 g/cm³. TiO₂ NPs (Nanografi, Ankara, Türkiye) with dimensions of 28 nm and a density of 4.5 g/cm³ were selected as a reinforcement agent.

2. Production of WPC

The contents of WF, HDPE, and NPs were determined according to Table 1. WF was oven-dried at 80 °C until a constant weight was reached. Subsequently, WF, HDPE, and NPs were mixed with a mechanical mixer (1200 rev/min). The mixture was then combined with a single screw extruder. The screw speed and the temperature for the extruder were set at 40 rpm and between 180 to 195 °C. The molten mixture was cooled in water and then pelletized. The pellets were oven-dried at 102±3 °C and laid on an aluminum plate with dimensions 500 mm x 500 mm x 4 mm. The draft was hot-pressed at 180 °C for 15 min under a pressure of 24–26 kg/cm² (CemilUsta SSP 125, Istanbul, Türkiye). The panels were removed from the press after cooling and conditioned according to the ASTM D618-21 standard [ASTM D618-21, 2021].

3. Accelerated UV weathering test

The artificial weathering test was performed in a QUV/ spray-accelerated weathering tester (Q-Panel Lab. Products), in accordance with ASTM G154-12a [ASTM G154-12a, 2017]. The temperature in the test chamber was set to 60 °C, and 313 nm fluorescent UV lamps (UVB) were used for the weathering test. The WPC samples were exposed to 8 hours of UV irradiation and a 4-hour condensation (50 °C) cycle during an 840-hour period. Three replicates from each group were subjected to weathering tests.

4. Color measurement

The surface discoloration was determined using a Minolta CM-600d spectrophotometer (Konica Minolta) equipped with an integrating sphere, based on the CIE L*a*b color system. The standard illuminant D65 was preferred. The color measurements were taken in an area of 8 mm² in the 400–700 nm wavelength range. Six measurements were taken from each sample surface and averaged. Color measurements were taken at 24, 48, 72, 120, 168, 336, 504, 672, and 840 hours of the artificial weathering test.

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 X-Rite SP60 software, from which the color difference (ΔE^*) was calculated according to equation (1):

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

5. Microscopic analysis

The WPC surface was examined with a light microscope (LM) (Zeiss Stemi 305) equipped with a camera (Zeiss Axiocam ERc 5s). Further examination was performed using SEM (Zeiss Evo LS10, Germany). The sample surface was gold-coated before inspection (Emitech, SC7620, France).

6. Mechanical properties

A three-point bending test was conducted to determine the modulus of rupture (MOR) and modulus of elasticity (MOE) in a universal test machine (Marestek, Istanbul, Türkiye) according to ASTM D790-21 [ASTM

Table 1. The ratios of components (%)

ID	Wood	MAPE	Polymer	Nanoparticle
Neat-HDPE	-	2	98	-
W40	40	2	58	-
W50	50	2	48	-
T40-1	40	2	57	1
T40-3	40	2	55	3
T40-5	40	2	53	5
T40-10	40	2	48	10
T50-1	50	2	47	1
T50-3	50	2	45	3
T50-5	50	2	43	5
T50-10	50	2	38	10

D790-21, 2021]. Eight samples with dimensions of 127 mm × 12.7 mm × 4 mm were tested for each group. For weathered WPCs, the tension side was the part of the samples exposed to light.

7. Thermal and fire properties

The thermal stability of samples at temperatures between 30 °C and 600 °C was investigated using a Perkin–Elmer STA 6000 thermogravimetric analyzer (USA). The heating rate was set to 10 °C/min, and heating took place under a nitrogen atmosphere. Two samples were tested for each group. The LOI test was used to determine the fire performance according to ASTM D2863-19 [ASTM D2863-19, 2019]. Five samples with dimensions of 127 mm × 12.7 mm × 4 mm were tested for each group.

8. Statistical analysis

The data were examined statistically using analysis of variance (ANOVA). Differences between groups were determined according to the Tukey test ($P < 0.05$).

Results and discussion

1. Morphological investigation

1.1. Surface coloration

The discoloration on the surface of WPCs exposed to weathering conditions was investigated, as illustrated in Fig. 1. The effect of TiO₂ NPs on the surface

discoloration of WPCs was evaluated using E^* , L^* , a^* , and b^* values. The total color changes were also statistically evaluated, as shown in Table 2. The chromophoric groups in the wood and polymer absorb UV light, leading to surface discoloration. Consequently, discoloration is inevitable for WPCs when exposed to outdoor conditions.

The values of overall color change (E) indicated that while the discoloration was linked to exposure time, the neat HDPE was least affected during the exposure. After 840 h of exposure there was minimal color fading. However, lignin, one of the main components of wood, absorbs UV light under 400 nm and causes surface discoloration [Sadeghifar and Ragauskas, 2020]. Consequently, the most significant changes in appearance over the 840 hours were observed in W40 and W50. Meanwhile, UV light first degrades the surface of wood particles, resulting in color fading. Subsequently, the degraded parts are removed from the surface, exposing the intact inner parts and limiting color changes. Consequently, increased wood flour content can limit discoloration [Yang, 2015]. This phenomenon is more pronounced in WPCs with a higher WF content.

On the other hand, TiO₂ NPs significantly restricted discoloration. As previously mentioned, TiO₂ NPs are recognized for their ability to reflect and/or absorb UV light. Additionally, TiO₂ NPs covered the surface, acting as a UV shield and limiting the penetration of UV light. Discoloration sharply increased during the first 168 h; subsequently, TiO₂ NPs stabilized the color, while color changes gradually increased for the control samples. Although the nanoparticle loading was not sufficiently

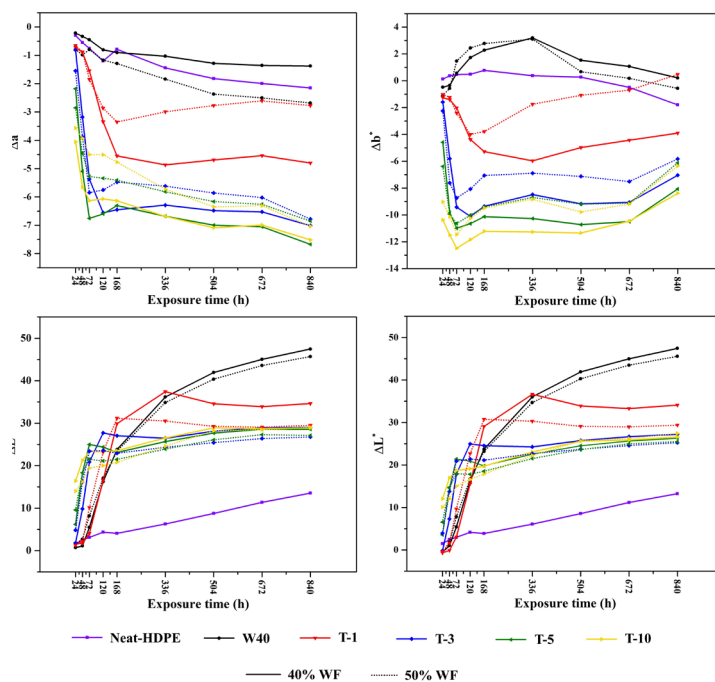


Fig. 1. Color changes of WPCs

Table 2. Total color change Analysis of Variance (ANOVA)

Source	Sum of Squares	Degrees of freedom	Mean Square	F. Value	P≤0.05
Exposure time (ET)	11575.000	8	1446.000	5787.000	0.000*
Nano ratio (NR)	316.000	4	79.000	316.000	0.000*
Wood ratio (WR)	5912.000	2	2956.000	11825.088	0.000*
ET * NR	8691.000	32	271.000	1086.000	0.000*
ET * WR	3542.000	16	221.000	885.000	0.000*
NR * WR	34.000	4	8.000	34.000	0.000*
ET * NR * WR	452.000	32	14.000	56.000	0.000*
Error	49.000	198	0.000		
Total	172478.000	297			
Corrected Total	39955.000	296			

* The difference is significant compared to 0.05.

effective against UV light, it was evident that increasing the nanoparticle percentage enhanced color stabilization. It is notable that increasing the nanoparticle percentage provided color stabilization within a short period of 48 h. In particular, T50-10 underwent the least color change during this time. Compared with the polymer, the primary reason for the surface color change is the chromophoric groups in wood. Although T50-10 contained the highest amount of wood flour, the least color change was observed in the first 48 h due to its having the highest NP loading. The TiO₂ NPs acted as a UV barrier. The higher rate of NPs increased the barrier's thickness, making UV light penetration difficult. Therefore, better color stabilization was provided as the TiO₂ NP ratio increased, especially during the first 168 h. Similarly, in previous studies it was observed that the efficiency of ZnO NPs against UV light improved with an increase in NP percentage [Durmaz et al., 2023].

The surface of WPCs is prone to whitening when exposed to UV radiation. As illustrated in Fig. 1, the increase in whitening is directly related to exposure time. However, whitening increased gradually for neat HDPE and control samples after 168 h of exposure, while it was minimal for TiO₂-reinforced WPCs. Similarly, WF content positively reduces whiteness due to the phenomenon mentioned above. The 3% TiO₂ NP percentage provided color stabilization and delayed the discoloration for both whiteness and overall color changes.

The Δa values indicated that surface color changes tended to be towards greenish tones. TiO₂ NPs increased the intensity of the greenish surface. The higher the NP percentage, the more the surface of WPCs was dominated by a greenish hue. This greenish discoloration occurred more rapidly, especially within the first 72 hours of exposure. On the other hand, TiO₂-reinforced WPCs

tended to develop a yellowish tint during the first 72 h, although this effect was less pronounced in the control samples. The oxidation of lignin initiates the production of paraquinone, which contributes to the surface's yellowing [Muasher and Sain, 2006]. As the exposure time increases, the paraquinone is reduced to hydroquinone, causing the surface color to shift toward a bluish tint. Paraquinone production began after 336 h of exposure, but was hindered for TiO₂-reinforced WPCs after 72 h, indicating that NPs retard the oxidation of lignin. The results suggest that TiO₂ NPs preserve the surface of WPCs against UV light, which is crucial for maintaining their aesthetic appearance.

1.2. Light microscopy (LM)

LM was used to analyze the surface morphology of WPCs after weathering exposure, as presented in Fig. 2 and 3. The surface of the WPCs was whitened due to UV exposure. Moreover, crack formation is inevitable due to the polymer's scission reactions as the exposure time increases, which leads to increased interaction of the wood fibers with outdoor factors. Consequently, the wood fibers swell, resulting in greater degradation. The phenomenon is depicted in Figs. 2a and 3a. The harsh outdoor conditions degraded the surface of W40 and W50. The fiber/polymer debonding was more significant as the WF content increased. On the other hand, the impact of the outdoor conditions was more moderate for neat HDPE (Figs. 2d and 3d). However, UV light abraded the surface of neat HDPE, disrupting the surface morphology and resulting in surface erosion and roughness.

TiO₂ is recognized for having a higher reflectivity for UV light. Therefore, for reinforced WPCs, the effect of outdoor conditions was reduced by TiO₂. No crack formation on the surface of the reinforced WPC was

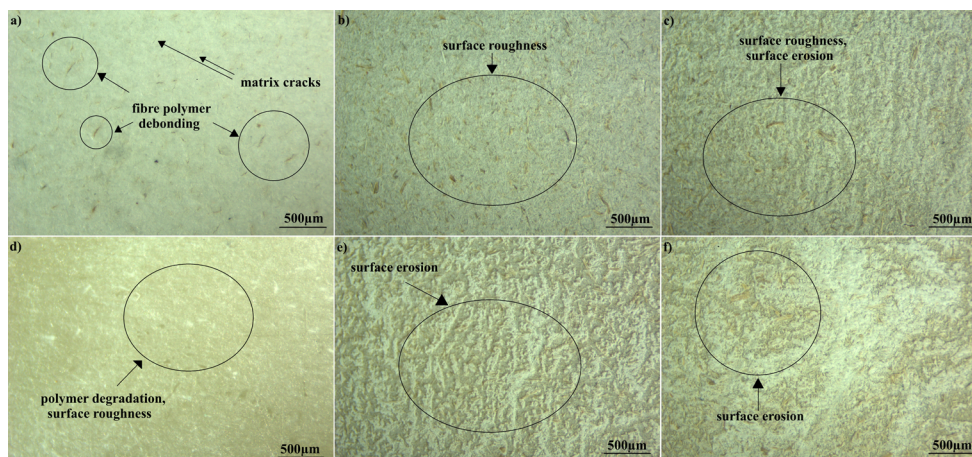


Fig. 2. LM images of weathered WPCs: a) W40, b) T40-1, c) T40-3, d) neat HDPE, e) T40-5, f) T40-10

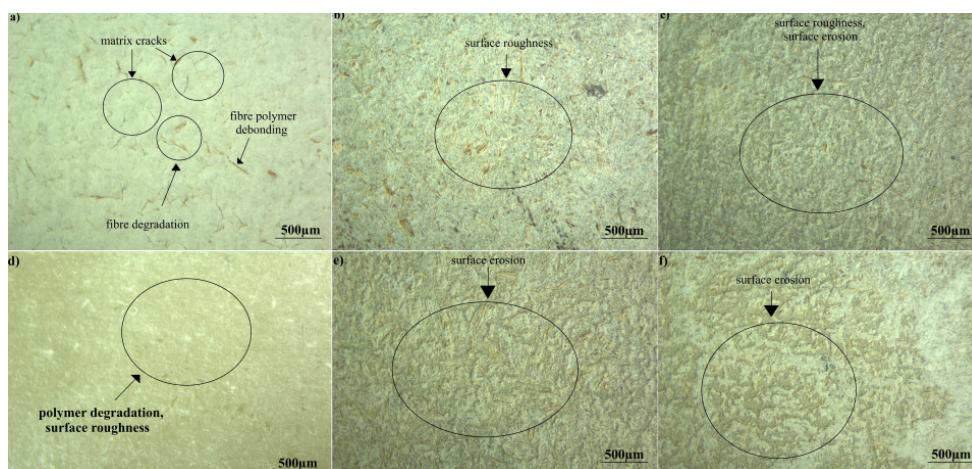


Fig. 3. LM images of weathered WPCs: a) W50, b) T50-1, c) T50-3, d) neat HDPE, e) T50-5, f) T50-10

detected by LM. However, surface erosion was dominant for the lower percentage content of TiO₂, and decreased with an increase in that content. The scission reactions in the polymer's structure increased with UV light degradation, resulting in the polymer chain's being shortened and eventually removed from the surface. Therefore, there are valleys and peaks on the surface (surface roughness), as seen in Figures 2 and 3. Although TiO₂ NPs limited the effect of outdoor conditions, it was observed that the surface of WPCs was irreparably degraded.

1.3. Scanning electron microscopy (SEM)

The surface morphology of WPCs after weathering exposure, as analyzed by SEM, is illustrated in Figs. 4 and 5. It is well known that the variation in the chemical structures of wood and polymers results in the decomposition of WPCs when exposed to a humid environment, for example. As seen in Figs. 4a and 5a, the swelling of wood fiber broke down the encapsulated polymer and emerged, leading to a significant mechanical loss after weathering exposure. However, although no lignocellulosic materials were present, crack formation

is inevitable for neat HDPE, as seen in Figs. 4 and 5. As stated above, the chromophoric groups are responsible for absorbing UV light, which triggers the scission reaction of the chemical structure.

On the other hand, the severity of weathering conditions was reduced by TiO₂ NPs, which can absorb and/or reflect UV light. TiO₂ has a high reflectivity index. As seen in Figs. 4 and 5, roughness was distinctly observed in NP-reinforced WPCs due to the coverage of the wood fibers by the NPs. Moreover, the dispersion of NPs in the polymer created a layer that inhibits or limits the ability of UV light to be reflected and/or absorbed. Therefore, restricted scission reactions also reduce microcracks in the polymer, which acts as a barrier against humidity and UV light. The thickness of the barrier increased with increasing NP content, making UV light penetration difficult. Therefore, the increase in the percentage of TiO₂ NPs also limited crack formation in WPCs compared with W40 and W50. Despite higher NP concentration, significant agglomeration was not observed on the surface of WPCs. It is assumed that the fine-grain polymer form plays a crucial role in the effective dispersion of NPs.

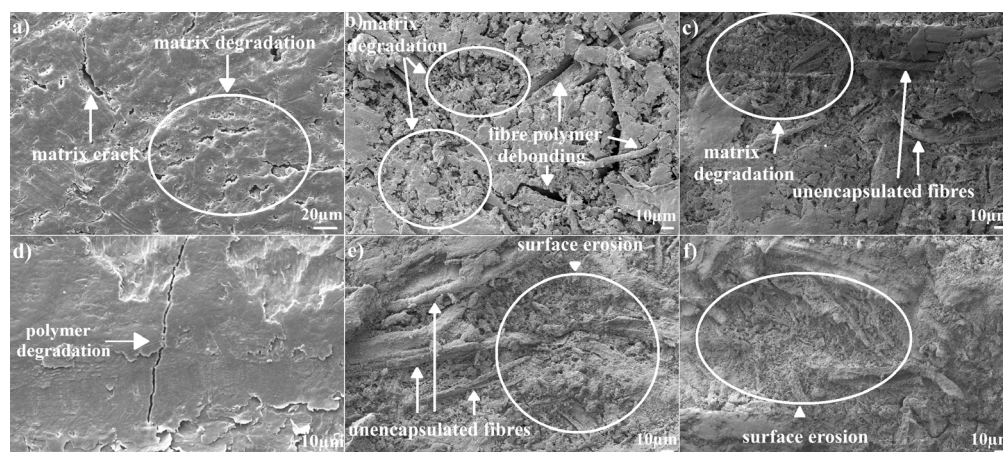


Fig. 4. SEM images of weathered WPCs: a) W40, b) T40-1, c) T40-3, d) neat HDPE, e) T40-5, f) T40-10

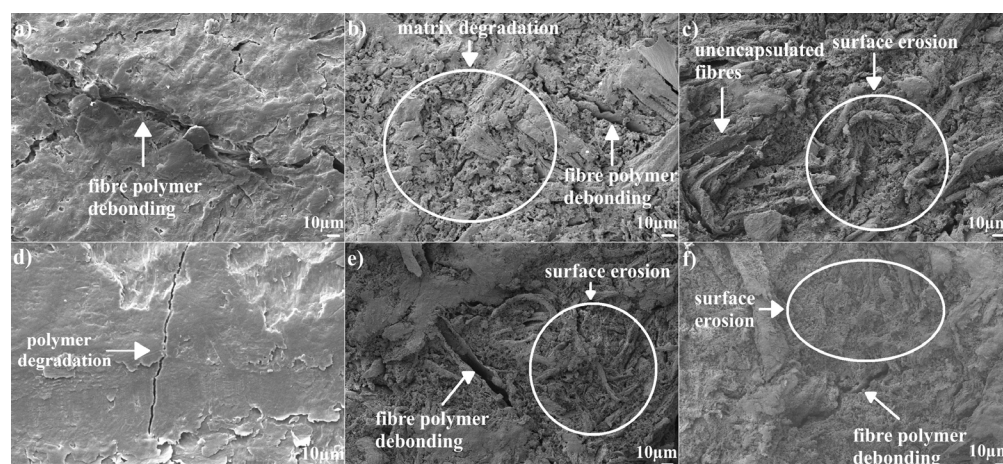


Fig. 5. SEM images of weathered WPCs: a) W50, b) T50-1, c) T50-3, d) neat HDPE, e) T50-5, f) T50-10

2. Mechanical properties

The effect of TiO₂ NPs on the mechanical properties of WPCs was also investigated, as presented in Fig. 6. The chemical differences between wood fiber and polymer are seen with an increase in WF, resulting in a considerable loss in mechanical properties. The loss in MOR exceeded 20%, with a corresponding rise in WF compared with neat HDPE. The stress transfer may be interrupted because wood and polymer are not well integrated, inevitably resulting in poor mechanical properties. However, the loss was mitigated by the addition of nanoparticles, which enhanced load transfer. NPs act as reinforcement agents, which occur within the polymer chain, limiting its mobility [Deka and Maji, 2011; Najafabadi et al., 2014]. This incorporation enhances the mechanical properties of the material. However, the tendency for agglomeration increases with a higher percentage of NPs. (SEM images depict the surface of WPCs, but their inner part was not investigated.) Therefore, MOR decreased with increasing NP percentage, which might result from agglomeration. Meanwhile, there was a decrease in the polymer content

with increasing NP loading, which might also have affected MOR. On the other hand, the MOE of WPCs was improved with increasing WF, in contrast to MOR. It is recognized that lignocellulosic materials exhibit higher elastic behavior than polymers [Chaharmahali et al., 2008]. Similarly, NP addition also enhanced the MOE of WPCs. Deka and Maji [2011] highlighted that the MOE of WPCs was improved by up to 400% with NP reinforcement. However, as the NP percentage increased, the improvement was limited due to the possibility of agglomeration.

After weathering exposure, the loss of mechanical properties increased due to the harsh weathering conditions. UV light initiates scission reactions that result in crack formation, allowing water molecules to more easily penetrate the wood fiber. Subsequently, the swollen wood fiber accelerates the degradation. As noted below, crack formation is inevitable, despite the UV absorption and/or reflection ability of TiO₂ NPs. However, the degradation was more moderate than in the control samples. As a result, the loss in mechanical properties was significantly limited by TiO₂ NPs. There was only a 0.46% reduction in MOR for T40-5,

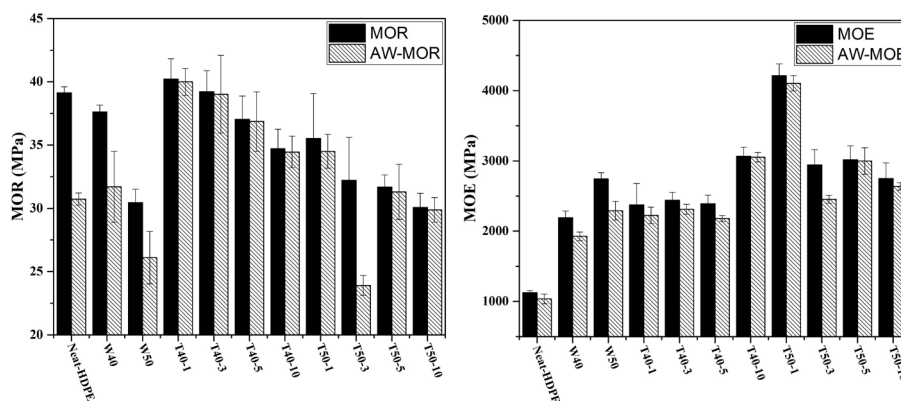


Fig. 6. Mechanical properties of WPCs (AW = after weathering test)

which is negligible considering the severe weathering conditions. As observed, the homogeneously dispersed nanoparticles (NPs) in the matrix serve as both reinforcing and binding agents, while performing other additional tasks such as UV absorption and/or reflection. This multifaceted functionality prolongs the service life of WPCs when used outdoors.

3. Thermal stability and fire performance

3.1. TGA analysis

The effect of TiO₂ NP loading on the thermal behavior of WPCs was investigated using TGA analysis, which involved gradual temperature increases and the determination of corresponding weight losses, as shown in Table 3. Fig. 7 shows the thermal degradation of WPCs. As stated above, wood fibers are affected by humidity, despite being encapsulated in polymer. Therefore, the release of water absorbed by fibers accelerated above 50°C in the first stage. This release increased with an increase in wood content. The thermograms of neat HDPE differ from those of the WPCs at that point.

It is well known that polymers have higher thermal stability than wood [Ramesh et al., 2022]. As a result, the wood fibers thermally degraded in the second stage. Wood is a natural bio-composite consisting of hemicellulose, cellulose, and lignin, whose degradation temperature varies [Rowell, 2022]. Firstly, hemicellulose degrades above 180°C, followed by cellulose and lignin degradation. Therefore, an increase in the wood content reduces the thermal stability of WPCs. However, the DTG thermograms indicated that degradation occurred over a broad region for WPCs containing 50% WF. On the other hand, it is narrow for higher polymer content, especially for neat HDPE. The carbonization of the wood fiber surface decelerates the degradation [Guo et al., 2019]. At the same time, the polymer thermally degrades rapidly, as clearly seen in Fig. 9. Moreover, the residue of WPCs was slightly higher due to the presence of inorganic materials, such as ash. This increased residue is crucial for flame resistance, as evaluated in the subsequent analysis.

The thermal stability of polymers is also reduced with increasing temperature due to oxidation reactions triggered by free radicals. Chain scission reactions occur, inevitably resulting in weight loss. Most of the

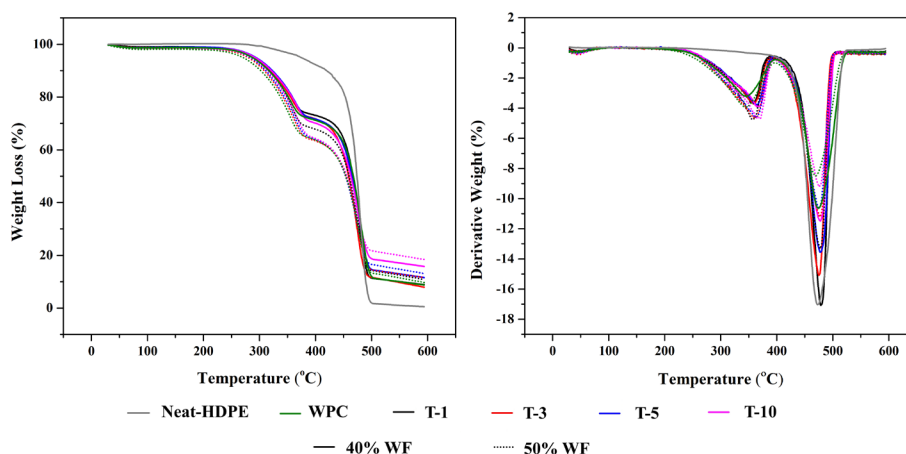


Fig. 7. TGA and DTG thermograms of WPCs

Table 3. TGA values of WPCs

ID	Stage	T _{onset}	T _{endset}	T _{deg.}	Weight Loss	Wight onset	Weight endset
Neat-HDPE*	-	328.30	525.50	474.10	95.72	97.09	1.70
W40*	1 st	180.35	399.50	346.65	28.44	97.70	72.28
	2 nd	397.50	530.80	475.00	61.70	72.28	11.57
W50*	1 st	176.20	395.70	345.50	35.20	97.10	64.93
	2 nd	397.70	524.30	50.20	52.45	62.93	13.49
T40-1	1 st	212.53	395.44	355.06	25.51	98.83	73.32
	2 nd	395.44	509.39	478.91	62.22	73.32	11.10
T40-3	1 st	210.78	391.61	358.57	26.39	98.63	72.24
	2 nd	391.61	503.96	475.07	60.73	72.24	11.50
T40-5	1 st	215.57	393.68	364.47	26.85	98.84	71.98
	2 nd	393.68	506.2	478.27	57.64	71.98	14.35
T40-10	1 st	219.72	397.19	366.71	28.21	98.49	70.29
	2 nd	397.19	509.07	477.31	51.97	70.29	18.31
T50-1	1 st	194.66	392.72	356.97	30.37	98.65	68.28
	2 nd	392.72	505.88	477.15	54.26	68.28	14.02
T50-3	1 st	197.05	394.32	361.92	34.45	98.21	63.76
	2 nd	394.32	505.72	476.99	49.48	63.76	14.29
T50-5	1 st	208.54	395.75	363.04	34.06	98.37	64.31
	2 nd	395.75	504.44	475.39	47.92	64.31	16.39
T50-10	1 st	206.79	395.75	367.98	33.61	98.20	64.58
	2 nd	395.75	506.83	476.03	43.13	64.584	21.45

polymer structures convert into gases: carbon monoxide (CO), carbon dioxide (CO₂), and water (H₂O) [He et al., 2012]. In contrast to wood, neat HDPE has no residue because it is converted into volatile compounds at temperatures above 550°C [Dorigato et al., 2016].

The DTG thermogram for neat HDPE features a relatively narrow region with rapid degradation. Moreover, the carbonization of wood fiber decelerates the degradation velocity in a relatively large region, although it has lower thermal stability. However, adding TiO₂ NPs to the matrix did not significantly affect degradation speed, while improving the degradation temperature. It was even observed to increase the degradation speed slightly compared with WPCs. TiO₂ has high thermal conductivity [Wang et al., 2023], which may accelerate the scission reaction of the polymer, leading to rapid degradation. It is believed that NPs embed in the gaps and cover the fiber's surface, which insulates the wood fibers from heat. Therefore, NPs influenced the thermal behavior of WPCs, improving

the degradation temperature, and acting as thermal shielding. The increase in the percentage of NPs also improved the degradation temperature, but negatively affected degradation velocity due to thermal conductivity. The interaction of NPs with polymers might restrict the mobility of the polymer chain, resulting in higher degradation temperatures [Jawad and Ahmed, 2023]. Meanwhile, the loading of NPs also contributes to the residue yield, which in turn facilitates isolation. Therefore, char formation inhibits heat and O₂ penetration to the inner part, and this retards degradation.

3.2. LOI test

The LOI test is one of the easiest test methods to assess the fire performance of materials. Thus, the requirement for oxygen for the flaming combustion of WPCs was determined to evaluate the effect of nanoparticles on the fire resistance of WPCs. As seen in Fig. 8, the oxygen demand increased from 18.5% to 25.9%

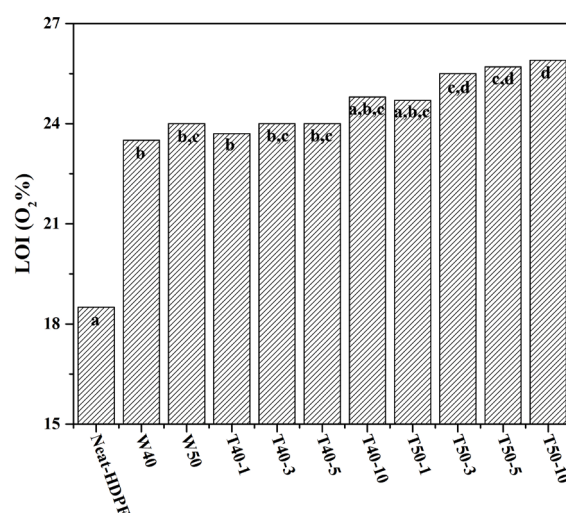


Fig. 8. LOI values of WPCs. Letters indicate the differences ($P < 0.05$) between groups according to the Tukey test

with the reinforcement of polymers with TiO₂ NPs. As the temperature rises, oxidative reactions cause the formation of alkyl or alkyl peroxide free radicals, resulting in the degradation of the polymer chain [He et al., 2012; Pan et al., 2017]. Moreover, these radicals transform into gases and water as the thermal degradation proceeds. There is almost no residue for polymer, which is also crucial for char forming, as shown in the TGA thermogram. Consequently, the fire resistance of the neat HDPE is relatively low. However, adding wood fibers to the polymer improved the fire resistance of WPCs. The carbonization of the wood surface limits O₂ penetration into the inner part of the structure. Moreover, wood fiber reduces the heat release rate of WPCs, which retards the combustion. The inorganic structure of wood enhances char formation during carbonization. Therefore, the dripping of the polymer improved with the addition of wood fibers. However, NP addition had virtually no significant effect on the fire resistance of WPCs. Nanoparticles' heat-shielding ability is well recognized, and leads to improved LOI values. As discussed above, the high thermal conductivity of TiO₂ accelerated the scission reactions, which increased the degradation. Thus, it can be stated that the fire performance of WPCs was limited due to the thermal conductivity of TiO₂ NPs. However, the LOI values increase with higher NP content, which may also be attributed to increased char formation resulting from the reduced polymer content. The LOI test indicated that the fire performance of TiO₂ nanoparticles is not as effective as their UV resistance.

Conclusions

This study investigated the effect of higher TiO₂ NP contents on the weathering durability, thermal stability, and fire performance of WPCs. The tendency for agglomeration was addressed by using fine-grain plastic at higher concentrations. TiO₂ NPs significantly limited the UV light degradation. Discoloration was reduced, despite the UV absorbance ability of the chromophoric groups of wood and polymer. Rapid discoloration was restricted for the first 168 h. The microscopic analysis also demonstrated that NPs significantly mitigate the negative impacts of outdoor exposure. LM images showed no crack formation for TiO₂ NPs, and only micro-cracks were detected by SEM. It has been demonstrated that extensive weathering conditions inevitably lead to surface erosion. Meanwhile, the NPs already play a crucial role in continuous stress transfer. The hydrophobic nature of TiO₂ NPs and their high UV reflectance provided superior protection even after the weathering test. This explains why the decrease in mechanical properties was limited, which is significant for maintaining structural integrity. However, the high thermal conductivity of TiO₂ NPs limited the improvement of thermal stability. The heat-shielding ability of NPs has practical implications, as it reduces the degradation rate in case of increased concentrations. Char formation also increased with the content of NPs, leading to enhanced LOI values. This research also showed that fine-grain plastic significantly reduces the agglomeration of NPs. This finding is crucial for improving the mechanical, thermal, and fire performance and weathering durability of WPCs in real-world applications.

Conflict of interest

The author(s) declare(s) that there is no conflict of interest concerning the publication of this article.

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