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Effect of Natural Weathering on Performance of Wood Flour-Recycled Polypropylene Composites

Utjecaj prirodnog izlaganja vremenskim utjecajima na svojstva kompozita od drvnog brašna i recikliranog polipropilena

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ABSTRACT • *In this study, the effect of natural weathering on the physical and mechanical properties of wood plastic composites (WPC) made from virgin and recycled polypropylene (PP) was studied. To prepare the recycled PP, virgin PP was thermo-mechanically degraded by extrusion under controlled conditions in a single-screw extruder at a router speed of 60 rpm and temperature of 190 °C. PP (virgin and recycled), wood flour, compatibilizer, and UV absorbent were physically blended, and the samples were manufactured by a twin-screw extruder. The samples were exposed to natural weathering for 270 days. The surface characteristics of the samples were investigated before and after weathering. According to the results, the composites from recycled PP exhibited a higher weathering resistance than those from virgin PP. The use of a UV absorber improved the flexural strength and modulus of the composites, but it could not significantly prevent the flexural properties loss and discoloration of the composites after weathering.*

KEYWORDS: *wood plastic composites; recycled polypropylene; natural weathering; discoloration, surface roughness*

SAŽETAK • *U ovom je istraživanju proučavan utjecaj prirodnog izlaganja vremenskim utjecajima na fizička i mehanička svojstva drvno-plastičnih kompozita (WPC) izrađenih od čistoga i recikliranog polipropilena (PP). U postupku pripreme recikliranog polipropilena čisti je polipropilen termomehanički razgrađen ekstruzijom s jednim pužem u konstantnim uvjetima i pri brzini vrtnje od 60 okr./min te pri temperaturi od 190 °C. Pomiješani su čisti i reciklirani polipropilen, drvno brašno, kompatibilizator i UV apsorber, a uzorci su proizvedeni ekstruderom s dva puža. Uzorci su bili 270 dana prirodno izloženi vremenskim utjecajima. Svojstva površine uzoraka ispitana su prije i nakon izlaganja tim utjecajima. Iz rezultata je vidljivo da su kompoziti od recikliranog polipropilena pokazali veću otpornost na vremenske utjecaje nego kompoziti od čistog polipropilena. Upotreba UV apsorbera poboljšala je čvrstoću na savijanje i modul elastičnosti kompozita, ali nije značajno spriječila slabljenje svojstava savijanja i promjenu boje kompozita nakon izlaganja vremenskim utjecajima.*

KLJUČNE RIJEČI: *drvno-plastični kompoziti; reciklirani polipropilen; prirodno izlaganje vremenskim utjecajima; hrapavost površine*

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1 INTRODUCTION
1. UVOD

The use of wood-plastic composites (WPCs) for outdoor applications has found its place in the largest and fastest consumer market for WPCs. Due to the increased use of these products in outdoor construction, attention should be focused on the durability of these products. Prolonged exposure to natural environmental changes, such as ultraviolet (UV) radiation, humidity, temperature, and atmospheric pollution, causes some complex physical and chemical reactions of WPC that lead to changes in their appearance, and physical and mechanical properties. Depending on the type of application, composite formulation, manufacturing process parameters, and environmental and climatic differences, the investigation of the natural weathering behavior of WPCs is necessary.

Since natural weathering testing is time intensive, only a few publications in this field are available (references). Taib *et al.* (2010) and Silva *et al* (2017) reported an initial increase in the flexural strength (MOR) of different WPCs in the first months of weathering, followed by a decrease to values lower than the original strength at the end of the test. The initial enhancement of strength was explained by crystallization with crosslinking after initial chain scissions. Hung *et al.* (2012) and Zhou *et al.* (2016) showed that the MOR of WPCs declined during the natural weathering test. The addition of stabilizers to the formulation significantly decreased the strength loss of WPCs. According to Taib *et al.* (2010), the addition of HALS as an antioxidant was more effective than photo-stabilizers like UV absorbers. In addition, fiber pretreatment by acetylation effectively improved the strength of WPCs against natural weathering (Hung *et al.*, 2012). Badji *et al.* (2017) reported a chain scission phenomenon caused by thermo- and photo-oxidative degradations in the polymer matrix of wood-flour reinforced polypropylene (PP) composites during natural weathering. They indicate that the presence of wood flour stabilizes the polymer against chain scissions. Ratanawilai and Taneerat (2018) studied mechanical property losses from natural weathering of WPCs over 90 days and emphasized that the WPCs based on polystyrene and polypropylene are a better choice than low-density polyethylene (LDPE) for exposure to natural weathering. Gunjal *et al.* (2020) showed that natural weathering increases the lightness and total color change of wood-flour polypropylene composites after one year of exposure. The maximum color change was observed in the initial four months, and the color change of WPCs with larger wood particle size was characterized with better color stability than that with small particle size.

The waste and recycled plastics were used for manufacturing WPCs already in 1990s and the use has significantly increased in developed and developing countries in recent years (Kazemi-Najafi *et al.*, 2006). Since recycled plastics may be obtained from various sources, having been exposed to different storage and reprocessing conditions, they may therefore exhibit different performance depending on their degradation level. Then the post-consumer plastics waste may contain many grades, colors and contaminants, leading to varying outcomes when these plastics are combined with wood flour/fillers. According to the mode of initiation, the following types of degradation can be distinguished: thermal, chemical, mechanical, and biological. Degradation processes are generally quite complex; often more than one type of degradation is operational, e.g. thermo-oxidative degradation, thermo-mechanical degradation, etc.

The degradation of plastics due to repeated processing cycles and environmental exposure complicates recycling, so specific research is required. The effect of recycled plastic on the physical and mechanical properties of WPCs has been extensively investigated by many researchers (Kazemi-Najafi *et al.*, 2006; Adhikary *et al.*, 2008; Kazemi-Najafi *et al.*, 2009) but there are few studies about the durability of WPCs from recycled plastic in outdoor applications. According to Homkhiew *et al.* (2014), Virgin polypropylene showed smaller relative changes of lightness and smaller relative loss of hardness, *MOR*, and *MOE* than recycled polypropylene, both in composites and unfilled plastic during natural weathering tests. Homkhiew *et al.* (2022) revealed that the type of post-consumer plastic influences the mechanical strength loss of WPCs after 6 months of natural weathering. Widiastuti *et al.* (2023) have observed the degradation of mechanical and physical performances, as significant loss of stiffness and increase of whitening area, after 30 days of exposure to natural weathering for ironwood-based recycled polypropylene composites.

Outdoor trials are hardly comparable because ambient climate conditions strongly depend on the location and vary significantly in temperature, humidity, global radiation dosage, and amount of precipitation. On the other hand, the use of recycled plastics in the manufacture of wood-plastic composites is increasing. This underscores the necessity for further research to elucidate the influence of various factors on the degradation of WPCs. The development of strategies to counteract these degradation factors is paramount for improving the durability of WPCs in outdoor settings. Studying the effects of natural weathering on wood-plastic composites (WPCs) made from wood flour and thermo-mechanically degraded polypropylene will provide important insights into their durability and performance in outdoor environments. This research could potentially lead to the development of more resilient WPCs and contribute to the body of knowledge in this field.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Materials
2.1. Materijali

The polypropylene (PP) powder, grade V30S, with a melt flow index of 18 g/10 min, was procured from the Marun Petrochemical Complex (Mahshahr, Iran). Beechwood flour, with a particle size of -60/+40 mesh, was obtained by screening sawdust from a local sawmill. The wood flour was oven-dried at a temperature of (100±5) °C for 24 h. Maleic anhydride-polypropylene (MAPP) (Grade G 6070 3×8), with a melt flow index of 24 g/10min, was sourced from the Kometra Company in Germany. Tinuvin327, a UV absorbent (UVA), was supplied by the Chemical Tools Company (Tehran, Iran).

2.2 Preparation of recycled polypropylene
2.2. Priprema recikliranog polipropilena

To produce the recycled PP, virgin PP was subjected to thermo-mechanical degradation under controlled conditions in a single-screw extruder. This process was conducted at a rotor speed of 60 rpm and a temperature of 190 °C. Subsequently, the degraded PP was ground into fine powder. The melt flow index (MFI) of the recycled PP, measured by the ASTM D 1238-98 standard, was determined to be 23.5 g / 10 min.

2.3 Manufacturing of wood plastic composites
2.3. Izrada drvno-plastičnog kompozita

The wood flour, recycled and virgin PP, and UV absorbent (UVA) were physically mixed in specific weight percentage ratios to produce the composites, as detailed in Table 2. The premixed materials for each formulation were extruded into strips using a counter-rotating twin-screw extruder (model WPC-65132) manufactured by GMW Company (Tehran, Iran). The strips had a cross-section of 1 cm in thickness and 7 cm in width. All strips were conditioned at a temperature of (22±2) °C and relative humidity of (65±5) % for two weeks. Following the conditioning period, they were cut into test specimens for the planned tests.

2.4 Natural weathering test
2.4. Test izlaganja vremenskim utjecajima

This test was performed in accordance with the ASTM D1435-99 Standard. The specimens were positioned on ranks at a 45° angle facing southeast. The impact of natural weathering on WPCs was assessed from January to October (270 days) at a geographic location of 52º 2′ E, 36º 34′ N, with an elevation of 15 meters below sea level. The climatic data for the research period, sourced from the Noshahr synoptic station (Mazandaran, Iran), is presented in Table 2.

Table 1 Wood plastic composite formulations (percent by weight)
Tablica 1. Formulacije drvno-plastičnih kompozita (maseni udio)

Composites code *Oznaka uzorka*	**Wood flour, %** *Drvno brašno, %*	**PP, %**	**UVA*, %**	**MAPP, %**
WVP	65	33	0	2
WRP	65	33	0	2
WRP + UVA	65	33	0.8	2
WRP + UVA	65	33	0.8	2

*by weight of PP / *u odnosu prema masenom udjelu polipropilena*
PP – polypropylene / *polipropilen*, VP – virgin PP / *čisti polipropilen*, RP – recycled PP / *reciklirani polipropilen*, W – Wood flour / *drvno brašno*, UVA – UV absorbent / *UV apsorber*

Table 2 Climatic data of research period
Tablica 2. Klimatski podatci tijekom istraživačkog razdoblja

Month *Mjesec*	**Mean monthly temperature, ºC** *Srednja mjesečna temperatura, °C*			**Mean relative humidity, %** *Srednja relativna vlaga zraka, %*			**Rainfall, mm** *Padaline, mm*		**Sunshine, h** *Sunčani sati, h*
	Min	Max	Mean	Min	Max	Mean	Max	Total	Total
January	3.4	12.6	8	62	93	77	56.3	179	180
February	7.4	14	10.7	68	95	82	20.5	54.4	122.4
March	7.9	14.2	11	70	94	82	31.1	123.8	95.7
April	11.1	16.6	13.9	71	95	83	4.9	22	113.3
May	13.9	21.6	17.7	65	94	79	27.8	66.4	234.8
June	19.1	26.4	22.8	64	93	79	7.6	13.9	239.1
July	22	29.1	25.6	65	92	79	0	0	235
August	22.1	28.2	25.2	69	94	81	15.1	71.5	116.4
September	21.9	28.2	25.1	70	92	81	39.3	69.5	147.9
October	19.6	27.8	23.7	65	93	79	12.5	16.7	72.6

2.5 Microscopic imaging
2.5. Mikroskopsko snimanje

A Dino-Lite digital microscope, with a magnification of 200x, was used to observe the development of cracks, as well as the growth of molds and fungi on the surface of the specimen.

2.6 Contact angle
2.6. Kontaktni kut

The contact angle of water on the surface of the WPC was measured using a goniometer (PGX-Goniometer, Switzerland) at various intervals after weathering. The contact angle for each specimen was determined using a droplet with a volume of 3.5 micro-liters after 300 seconds. Five samples were tested for each formulation.

2.7 Surface roughness
2.7. Hrapavost površine

Two roughness parameters, namely average roughness (*Ra*) and mean peak-to-valley height (*Rz*), were determined using a HUATEC surface roughness tester, model SRT-6200, in a cut-off path line of 2.5 mm. *Ra* represents the average of all individual measurements of surface peaks and valleys, and *Rz* represents the average heights of the five highest-profile peaks and the depths of the five deepest alleys within the evaluation length. Five samples were tested for each formulation.

2.8 Color change
2.8. Promjena boje

The surface color of the five weathered samples was measured every 90 days according to the ASTM 2244-93 standard using a Sheen Spectrophotometer (400 to 700 nm). The machine data are presented in the form of the CIE $L^*a^*b^*$ systems. Color coordinates of each sample were determined before and after exposure to natural weathering. The color change (ΔE^*) was calculated using the following equation:

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{1}$$

Where, ΔL^*, Δa^*, and Δb^* indicate the difference between the initial and final values of L^*, a^*, and b^*, respectively.

2.9 FTIR spectroscopy
2.9. FTIR spektroskopija

The surface chemistry of the WPCs before and after natural weathering was analyzed using FTIR spectroscopy (Nicolet spectroscope). For each WPC, %1 w/w oven dried powder was dispersed in a matrix of KBr and pressed to form pellets. The spectroscopy was conducted in the wavenumber range of 4,000 to 400 cm^{-1}.

2.10 Flexural properties
2.10. Svojstva savijanja

The three-point flexural test was conducted in accordance with the ASTM D 790-90 standard. A span length of 200 mm and a crosshead speed of 6mm/min were set for this test. The flexural modulus (*MOE*) and flexural strength (*MOR*) of WPCs were determined before and after weathering at various intervals using a DARTEC Universal Testing Machine. Five samples were tested for each formulation and each period.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 Morphological analysis
3.1. Morfološka analiza

Natural weathering can alter the appearance of WPCs, leading to discoloration, surface roughening, and checking. The polypropylene-rich surface layer of extruded WPCs acts as a protective barrier against water absorption and colonization of mold fungi and other discoloring microorganisms. However, this surface layer can degrade under the influence of ultraviolet radiation, which increases water absorption and allows these destructive elements to access the wood flour. As a result, these elements can proliferate and spread throughout the WPC, causing changes in surface color and wettability.

All wooden components are prone to UV radiation damage, but lignin is the main absorber, taking in 80-95 % of UV light. Lignin contains chromophoric functional groups such as phenolics, hydroxyl groups, double bonds, and carbonyl groups, and can form free radicals. The photodegradation process starts with UV light attacking the lignin-rich middle lamella, and with prolonged exposure, the secondary walls also degrade (Stark and Gardner, 2008).

UV light transforms lignin into water-soluble compounds that are washed away by rain, leaving a cellulose-rich, fibrous surface. The impact of UV degradation is mostly seen on the surface. However, degradation has been observed deeper than this, suggesting an energy transfer process where the surface molecules absorb UV light and then dissipate excess energy to create new free radicals. These radicals then migrate deeper into the WPCs, causing discoloration (Hon and Minemura, 2001).

Microphotographs of both unexposed and exposed WPCs, with and without UV absorbent, are presented in Figure 1 and 2. As depicted in the images, the surface of all specimens became lighter in color during the initial period of weathering. Over time, the brightness of the specimens decreased, and their surface darkened.

Additionally, cracks developed on the surface of both virgin and recycled polypropylene composites af-

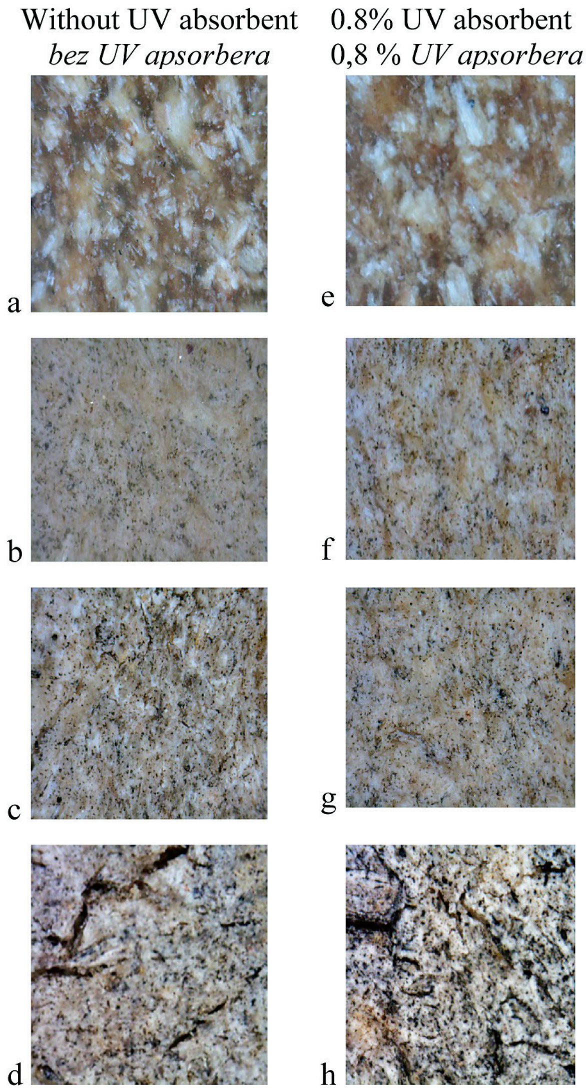

Figure 1 Microscopic images of WPC surface made from virgin polypropylene before natural weathering (a and e), after 90 days (b and f), after 180 days (c-g), and after 270 days (d and h) of natural weathering
Slika 1. Mikrografije površine WPC-a izrađenoga od čistog polipropilena prije prirodnog izlaganja vremenskim utjecajima (a i e), nakon 90 dana (b i f), nakon 180 dana (c-g) i nakon 270 dana izlaganja (d i h)

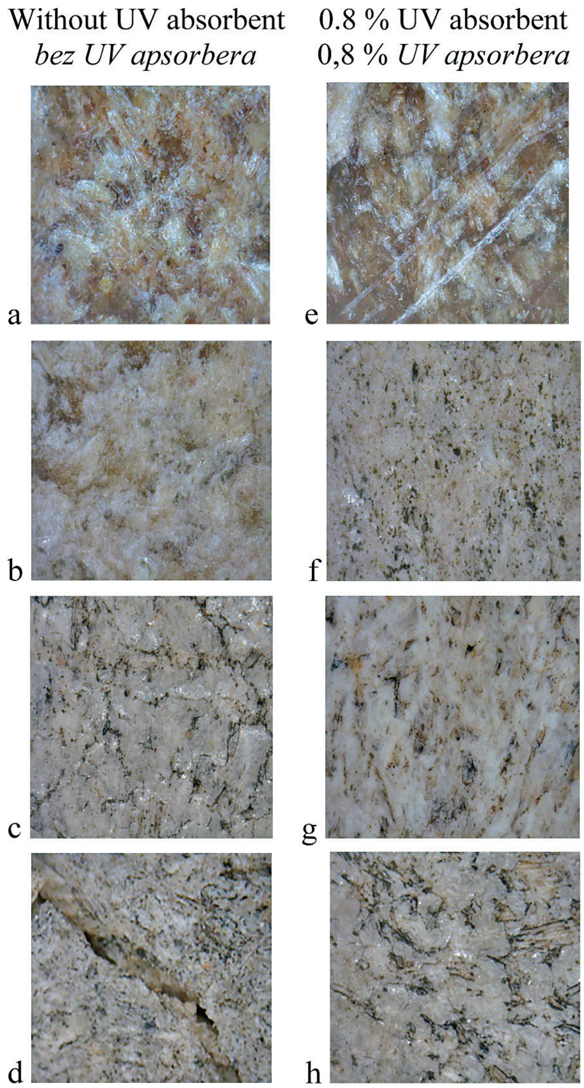

Figure 2 Microscopic images of WPC surface made from recycled polypropylene before natural weathering (a and e), after 90 days (b and f), after 180 days (c-g), and after 270 days (d and h) of natural weathering
Slika 2. Mikrografije površine WPC-a izrađenoga od recikliranog polipropilena prije prirodnog izlaganja vremenskim utjecajima (a i e), nakon 90 dana (b i f), nakon 180 dana (c-g) i nakon 270 dana izlaganja (d i h)

ter 270 days of outdoor exposure. These cracks are associated with polymer chain scission, which results from shrinking and swelling cycles (Peng *et al*., 2014).

The emergence of cracks on the polymer surface paves the way for the entry of microorganisms. In the presence of sufficient moisture, oxygen, and sunlight, these microorganisms intensify their activities, leading to a darkening of the specimen surfaces. The primary color change on the specimen surfaces can be attributed more to the growth and spread of molds, rather than to the color change of the composite itself. This is because molds, due to their extracellular metabolism, produce melatonin pigments, which increase over time and darken the surface (Muasher and Sain, 2006; Chen *et al*., 2016). Fabiyi and McDonald (2010) outlined three main stages of WPC degradation: the initial formation of tiny cuts and cracks on the composite surface; an increase in the size and number of these cracks along with visible signs of microorganism growth on the surface; and finally, the development of small cracks on the weathered surface following the second stage.

Recycling PP increases the melt flow index (MFI), leading to better mixing of wood flour by PP matrix and improved coating of wood flour by recycled PP. As a result, composites made from recycled PP absorb less moisture compared to those made from virgin PP, leading to less surface degradation and providing less opportunity for the growth of micro-organisms. On the other hand, the addition of UV absorbents to PP composites improved the surface degradation of the composites, although not significantly (Fabiyi and McDonald*,* 2010).

3.2 Contact angle
3.2. Kontaktni kut

The contact angle is a measure of the wettability of a surface. The contact angle can provide insights into the relative hydrophilicity or hydrophobicity of the WPCs. Being a hydrophilic material, polypropylene typically has a higher contact angle than wood flour, which is hydrophobic. After natural weathering, the degradation of PP on the surface of the composites is expected to lead to a significant decrease in the contact angle. This indicates an increase in surface wettability and, consequently, higher moisture absorption. This change in wettability can have implications for the performance and durability of the WPCs, particularly in outdoor applications where they are exposed to environmental changes.

Table 3 presents the contact angle of WPCs made from virgin and recycled PP. As shown, all specimens exhibit the maximum contact angle before weathering due to their smooth and hydrophobic surfaces. However, after 90 to 180 days of exposure to weathering, their contact angles decrease. By the end of the weathering period, due to the intense degradation of the WPCs surfaces, it was not possible to measure the contact angle of a water droplet, because it was quickly absorbed on the surface of the weathered WPCs. Similar results have been published by other researchers (Matuana *et al.,* 2001; Kaci *et al*., 2001; Chen *et al*., 2014; Stokke and Gardner, 2001). The addition of UV absorbers to WPCs increases the contact angles of WPCs made from virgin and recycled plastics before and after natural weathering. It means that the UVA could decrease the wettability of the composites. The difference in the contact angles of the WPCs made of recycled PP and virgin PP was not noticeable (before weathering), but more reduction in contact angles of the WPCs made from recycled PP was observed.

The decrease in contact angles of WPC during exposure to weathering can be attributed to the degradation and oxidation of the PP-rich surface layer and then lignin into water-soluble products. When rain falls and washes away the degraded products from the composite surface, the cellulose ratio on the surface increases. Due to its active hydroxyl groups, the presence of cellulose on the surface increases the composite wettability properties (Williams *et al.,* 2001; Stark and Matuana, 2006).

Cyclic water absorption and desorption by cellulose in the cell wall of wood flour causes cyclic shrinkage and swelling of WPCs. The stress resulting from consecutive shrinkage and swelling cycles causes more cracks on the surface of the polymer matrix. Over time, the number and depth of the cracks on the surface increase, and the wettability properties of the specimens significantly increase. Microscopic images confirm that, as a period of weathering passed, tiny cracks appeared on the surface of the specimens, which somewhat reduced the contact angle of the specimen surfaces. With increasing weathering duration, the number and extent of the cracks increased to the point where deep cuts appeared on the surface of the composites in the last period of weathering, the water droplets rapidly absorbed at the surface of the composites, and it was impossible to measure the contact angle.

3.3 Surface roughness
3.3. Hrapavost površine

Figures 3 and 4 illustrate the surface roughness (*Ra* and *Rz* values) of all WPCs after 270 days of natural weathering. The surface roughness values of composites increased with increasing weathering exposure time. Natural weathering causes chain scission in the polymer matrix, which results in surface cracks and embrittlement. The rain helps in removing and washing degraded polymer from the WPC surface and causes much more wood flour to be directly exposed to UV light. Exposure of wood flour to UV light and water induces numerous checks, splits, and cracks on the surface of WPCs which increase surface roughness. The longer the exposure time, the higher the degradation and the higher the surface roughness.

It can be seen from Figures 3 and 4 that the composites made from recycled PP exhibited lower surface roughness than those made from virgin PP. It can be attributed to better mixing and dispersion of wood flour in recycled PP matrix due to its higher melt flow index (MFI). Consequently, composites made from recycled

Table 3 Effect of natural weathering on contact angle variations of composites
Tablica 3. Utjecaj prirodnog izlaganja vremenskim utjecajima na varijacije kontaktnog kuta na kompozitima

Composite code *Oznaka kompozita*	**Weathering time, day** / *Vrijeme izlaganja, dan*							
	0		90		180		270	
	θ_0	θ_U	θ_0	θ_U	θ_0	θ_U	θ_0	θ_U
WVP	77.3	70.0	66.9	43.4	51.4	47.9	-	-
WRP	76.2	71.4	61.3	48.8	62.8	51.4	-	-
WVP + 0.8 % UVA	80.0	76.4	63.8	44.3	58.8	53.1	-	-
WRP + 0.8 % UVA	80.0	75.9	64.7	54.5	66.9	54.6	-	-

θ_0: Contact angle in time zero / *kontaktni kut u vremenu nula*, θ_U: ultimate contact angle / *krajnji kontaktni kut*

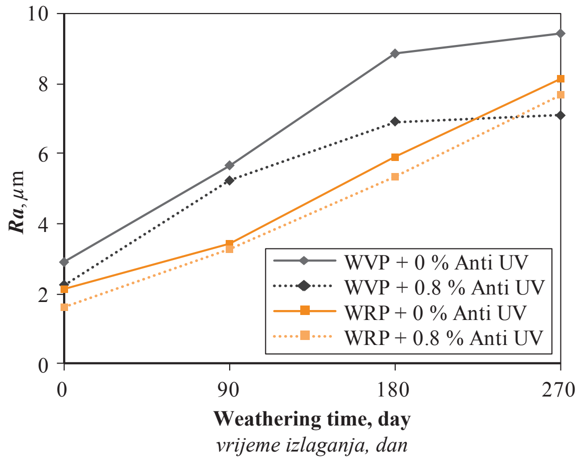

Figure 3 *Ra* variation of WPC surfaces made from virgin and recycled polypropylene
Slika 3. *Ra* varijacije površine WPC-a izrađenoga od čistoga i recikliranog polipropilena

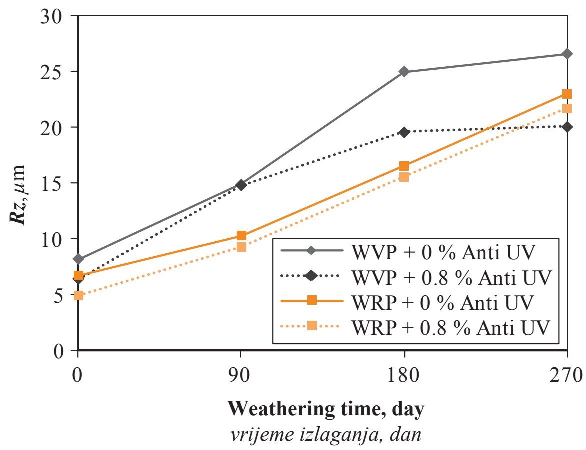

Figure 4 *Rz* variation of WPC surfaces made from virgin and recycled polypropylene
Slika 4. *Rz* varijacije površine WPC-a izrađenoga od čistoga i recikliranog polipropilena

PP absorb less moisture compared to those made of virgin PP, leading to less surface degradation, and providing less opportunity for the growth of microorganisms, and cyclic swelling and shrinkage.

On the other hand, the addition of UV absorbers to WPCS decreased the surface roughness values. A decrease in surface roughness of WPCs containing recycled PP at longer exposure time was noticeable. Improvement of the surface roughness of the WPCs using a photostabilizer has been reported by several researchers (Selden *et al.*, 2004; Fabiyi *et al.*, 2008; Stark and Matuana, 2003; Rabello and White, 1997).

3.4 Color change
3.4. Promjena boje

The changes in the surface color of WPCs (containing virgin and recycled PP), with and without UV stabilizer, were evaluated based on lightness (L^*) and discoloration after 180 days of exposure to natural weathering. The value of L^* varies between 0 and 100 (black and white, respectively). An increase in L^* indicates that the WPC surface is lightening. The variations of the L^* parameter of WPCs after natural weathering are shown in Figure 5. The lightness (L^*) values increased to maximum values after 60 days of natural weathering for all the WPCs, followed by a gradual decrease up to 180 days. The highest and lowest L^* were obtained for WPC containing recycled PP (without UVA) and WPC containing virgin PP (with UVA), respectively. The highest value of ΔL^* was determined after 60 days of weathering for both WPCs (Figure 6).

Discoloration occurred in two stages: initial photo-bleaching within the first 90 days of exposure, followed by darkening up to the last day of weathering. The photobleaching primarily affected the wood component, particularly lignin, which absorbs 80-90 % of the total amount of light absorbed by wood flour (Stark and Gardner, 2008). The absorption of UV radiation by lignin leads to its degradation and breakdown into car-

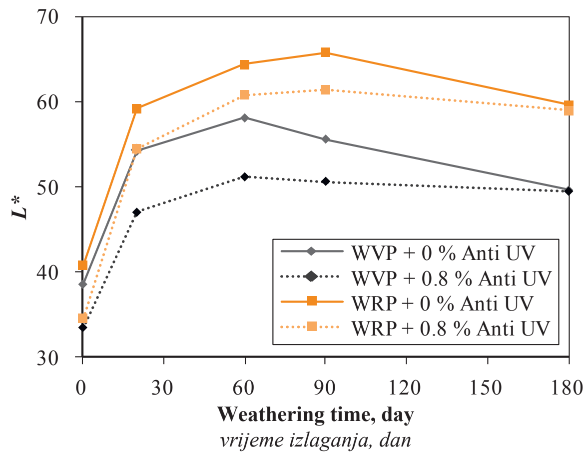

Figure 5 L^* factor variation of WPC made from virgin and recycled polypropylene
Slika 5. Varijacije svjetline WPC-a izrađenoga od čistoga i recikliranog polipropilena

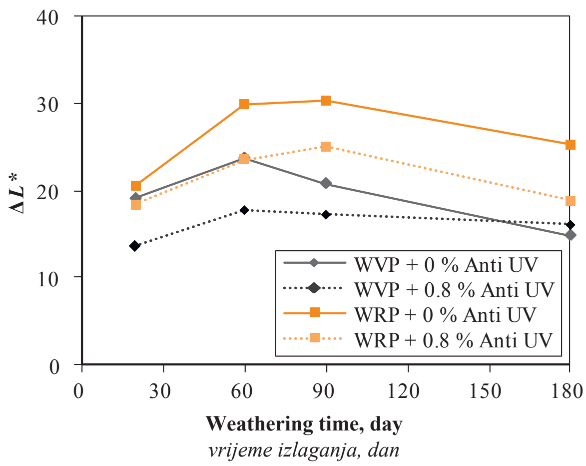

Figure 6 ΔL^* factor variation of WPC made from virgin and recycled polypropylene
Slika 6. Varijacije promjene svjetline WPC-a izrađenoga od čistoga i recikliranog polipropilena

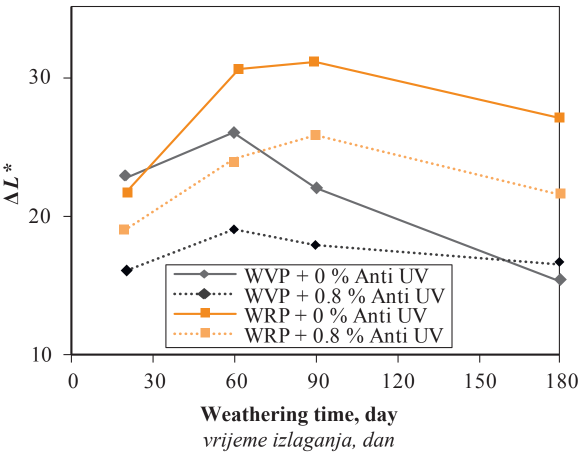

Figure 7 ΔE^* variation of composites made from virgin and recycled polypropylene
Slika 7. Varijacije promjene boje kompozita izrađenoga od čistoga i recikliranog polipropilena

bonyl, carboxyl, and aldehyde chromophores. These are the main factors of light absorption and composite photochemical reactions responsible for the color change (Ayadi *et al*., 2003; Stark, 2006).

Darkening may have been caused by surface oxidation and the presence of mildew on the composite surface. Mildew, a type of fungus, causes surface discoloration due to the production of extracellular metabolism pigments, creating green to red and dark spots (Muasher and Sain, 2005; Rowell *et al.,* 2000).

Composites made from virgin PP showed lower lightness than those made from recycled PP, likely due to the better encapsulation of wood flour in virgin PP, with good dispersion and interfacial bonding between wood flour and polymer.

The result of total color changes or discolorations is shown in Figure 6. The ΔE^* considerably increased in the initial 90 days of exposure to weathering and then slightly decreased up to the last day of weathering. The WPCs containing virgin PP exhibited lower ΔE^* than those containing recycled PP. The addition of 0.8 % UVA reduced the ΔE^* of WPCs but it was more effective for WPCs made from recycled PP.

3.5 FTIR spectroscopy
3.5. FTIR spektroskopija

Fourier Transform Infrared (FTIR) spectroscopy provides a clear insight into material degradation by determining the changes in the surface chemistry of wood plastic composites during weathering. The IR spectra of WPC made from virgin and recycled PP with 8 % UV absorbent, before and after exposure, are depicted in Figure 8 and 9, respectively.

The broad peak around 3400 cm^{-1} band is assigned to hydroxyl groups originating mainly from the cellulose of wood flour (Stark and Matuana, 2004). The peak around 1050 cm^{-1} is associated with both the C-O stretch in cellulose and the C-O deformation in the primary alcohols of lignin. The peaks at 2922 cm^{-1} and around 1450 are due to the C-H stretching and bending of methylene groups, respectively, which appear as strong peaks in PP (Krehula *et al*., 2014). The assigned peak at 1700-1750 cm^{-1} corresponds to carbonyl groups. The absorption at 1630-1650 cm^{-1} belongs to the stretching vibrations of the vinyl groups (C=C) in the polymeric phase (Fabiyi *et al.,* 2008).

After weathering, the intensity of peaks at 3400 cm^{-1} and around 1050 significantly decreased with increasing weathering exposure time indicating a de-

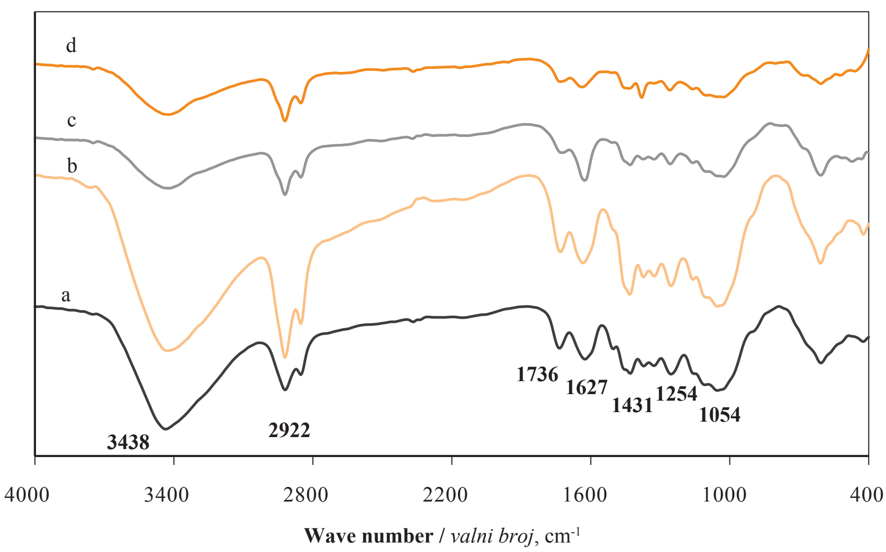

Figure 8 Effect of natural weathering on FTIR spectrum of WPCs made from virgin PP with 0.8 % UVA: before weathering (a), after 90 days of weathering (b), after 180 days of weathering (c), and after 270 days of weathering (d)
Slika 8. Utjecaj prirodnog izlaganja vremenskim utjecajima na FTIR spektar WPC-ova izrađenih od čistog polipropilena s 0,8 % UVA: prije izlaganja (a), nakon 90 dana izlaganja (b), nakon 180 dana izlaganja (c), nakon 270 dana izlaganja (d)

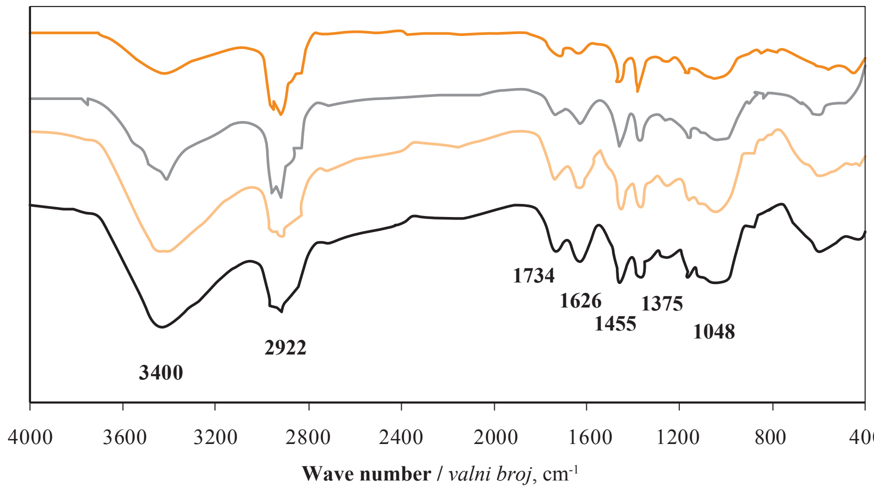

Figure 9 Effect of natural weathering on FTIR spectrum of WPCs made from recycled PP with 0.8 % UVA: before weathering (a), after 90 days of weathering (b), after 180 days of weathering (c), and after 270 days of weathering (d)
Slika 9. Utjecaj prirodnog izlaganja vremenskim utjecajima na FTIR spektar WPC-ova izrađenih od recikliranog polipropilena s 0,8 % UVA: prije izlaganja (a), nakon 90 dana izlaganja (b), nakon 180 dana izlaganja (c), nakon 270 dana izlaganja (d)

crease in hydroxyl groups at the surface of WPCS (Wang *et al*., 2010).

It is well known that the carbonyl groups are formed after PP degradation under UV light, which can be monitored by change in intensity of peak at 1700-1750 cm^{-1} (Fabiyi *et al*., 2008). However, degradation of PP in the first step, manifested as the chain scission, must be detected through the monitoring of peaks absorbance intensity at 2922 cm^{-1} assigned to CH stretching in –CH2- groups (Krehula *et al*., 2014). In this research, no noticeable changes were observed in the intensity peak of 2922, and on the other hand, the intensity peaks at 1700-1750 cm^{-1} were slightly decreased especially in prolonged exposure. This phenomenon can probably be attributed to the washing of the damaged surface of the samples by rainwater and the appearance of a new surface, free of degraded PP.

3.6 Flexural properties
3.6. Svojstva savijanja

Figures 10 and 11 display the flexural strength (*MOR*) and flexural modulus (*MOE*) of WPCs, respectively. It can be seen that the *MOR* of most WPCs slightly increased in the initial 90 days of exposure to weathering and decreased after 270 days. The initial increase in *MOR* can be attributed to crystallization with crosslinking after initial chain scissions. Similar results have been reported by Taib *et al.* (2010) and Silva *et al.* (2017). At higher exposure times, severe chain scission occurs, whereby the crystalline regions are also affected, leading to a decrease in crystallinity and MOR. Additionally, exposure to moisture degrades the mechanical properties of composites due to the cyclic shrinkage and swelling of the wood particles. The stress caused by cyclic shrinkage and swelling of wood particles creates micro-cracks in the matrix, causing a decrease in flexural strength and reducing the efficiency of stress transfer from fiber to the matrix, which results in a decrease in strength (Rangaraj and Smith, 2000; Wei *et al*., 2013; Saputra and Simonsen, 2004).

The composites containing recycled PP exhibited higher *MOR* than those containing virgin PP both before and after weathering. The statistical analysis showed that the differences were significant. The higher *MOR* for recycled plastics-based WPCs has been reported by several researchers (Kazemi-Najafi *et al.*, 2006; Adhikary *et al.*, 2008; Kazemi-Najafi *et al.*, 2009). The higher MOR of recycled PP composites can be attributed to the lower melt viscosity of the recycled PP. Lower melt viscosity yielded a better dispersion of the wood flour and enhanced the mechanical properties. The addition of UVA increased the *MOR* of the

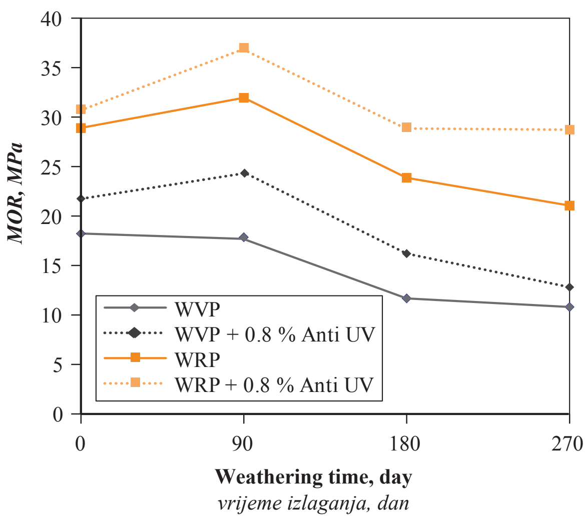

Figure 10 Flexural strength of WPCs made from virgin and recycled polypropylene
Slika 10. Čvrstoća na savijanje WPC-ova izrađenih od čistoga i recikliranog polipropilena

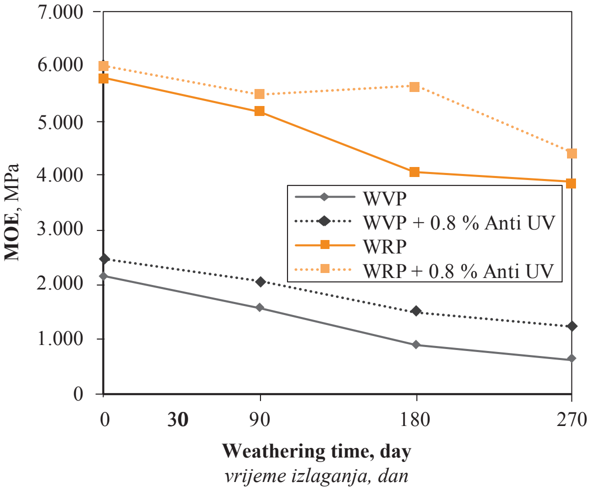

Figure 11 Flexural modulus of WPCs made from virgin and recycled polypropylene
Slika 11. Modul na savijanje WPC-ova izrađenih od čistoga i recikliranog polipropilena

WPC made from both virgin and recycled PP. A similar result has been reported by Ovali and Sancak for natural fiber LDPE composite (Ovali aad Sancak, 2022). They showed that the addition of UV additives improved the flexural strength of the composites between 46 % and 68 %. The UVA could not prevent the loss of flexural strength with increasing weathering exposure time.

Figure 11 shows that the *MOE* of WPCs decreases with increasing exposure time. Exposure to UV lights affected the modulus of the WPC negatively because of matrix polymer crystallinity loss, surface oxidation, and interfacial degradation. Additionally, water absorption during exposure can negatively affect *MOE* of the composites.

The composites made from recycled PP exhibited significantly higher flexural modulus than those made from virgin PP. This phenomenon can be attributed to the better dispersion of wood flour in recycled PP matrix due to an increase in the MFI of PP after thermos-mechanical degradation. Similar to *MOR*, the addition of UVA increased the *MOE* of the WPC made from both virgin and recycled PP. The addition of UVA could not prevent the decrease of the modulus after natural weathering.

4 CONCLUSIONS
4. ZAKLJUČAK

This research examined the impact of natural weathering on the physical and mechanical properties of wood flour polypropylene composites, both virgin and recycled. Both types of composites underwent changes in physical properties and a loss of mechanical properties due to weathering. The use of a UV absorber improved the properties of the composites made from virgin and recycled polypropylene in the short term, but it was not effective in the long term. Natural weathering severely damaged the surface of both types of composites made from virgin and recycled polypropylene. Composites made from virgin polypropylene need more UV absorbers compared to composites made from recycled polypropylene. To achieve higher resistance characteristics in the long term for both types of composites, higher amounts of UV absorbers or simultaneous use of antioxidants and pretreatment of wood flour and polymer are probably needed. This research provides valuable insights into the behavior of these composites under weathering conditions and can guide future efforts to improve their performance. In addition, the results of this research provide the possibility of choosing the appropriate polymer matrix based on the desired physical and mechanical properties of WPCs and for developing various applications of these products.

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