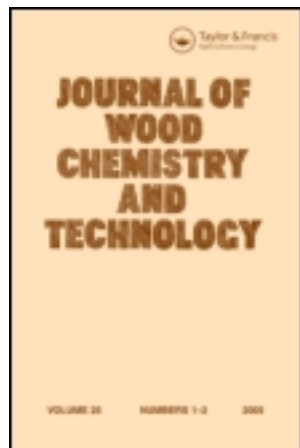


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Weathering of High-Density Polyethylene-Wood Plastic Composites

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Abstract: Due to the widespread use of wood-plastic composites (WPCs), high-density polyethylene-wood flour composites (HDPE/WF) were studied in order to determine their stability in different application conditions. UV degradation and periodic absorption/desorption of moisture cause damaging changes to material during WPCs' exterior application, so it is necessary to ensure WPCs' durability against atmospheric influences. Samples were characterized by FTIR spectroscopy and scanning electron microscopy (SEM) in order to study the degradation after simulated weathering. The degree of water absorption was also determined. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used for the determination of composites' thermal properties. Results show that the stability of the HDPE/WF composites to UV treatment highly depends on stabilizer content and its dispersion in the polymer matrix. Incompatibility of HDPE and wood particles is a major problem that should be solved to achieve good durability and satisfying properties in use.

Keywords Polyethylene, wood-plastic composite, degradation, weathering, UV stabilizer

Introduction

The production of wood plastic composites (WPCs) in the thermoplastic industry has gained much acceptance in recent years and is expected to keep growing. This type of composite material has become an important family of engineering materials due to the increasing need for sustainable and biodegradable renewable materials, which are known as “green composites.” WPCs have sustainable character due to the presence of wood as a natural component, which enables environmental protection and minimization of waste formation. Such materials offer significant advantages which justify their use. The most common thermoplastic used in the manufacturing of WPCs is polyethylene, while polypropylene, poly(vinyl-chloride), and polystyrene are also often being used.^[1–3] The advantage of wood component (wood flour) is its availability in large quantities, its lightness and cheapness, so it can be considered an economically profitable material.^[1–4] The main application area of wood plastic composites is in the building and automotive industries, but they are also applied for packaging, for the preparation of various household articles, furniture, office appliances, and other items.^[1,2,5]

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The main drawbacks of such composites are their susceptibility to degradation during exposure to environmental conditions due to the deterioration caused by many weather factors, including heat/cold, sunlight, moisture, oxygen, and a large number of atmospheric contaminants. However, the radiation of the sun is a critical factor in outdoor applications, since it generally initiates the reactions that are subsequently promoted by other weather factors. The ultraviolet (UV) radiation absorbed by colorless and colored polymeric materials, as well as visible radiation absorbed by colored polymers, has sufficient energy to break many types of chemical bonds. Such bond breakage is an essential step in the photodegradation process.^[6] UV degradation of polymer materials results in irreversible changes in the chemical structure that affect polymer properties and reduce the useful life of the material. Outdoor natural weathering requires a long period of time, so accelerated laboratory tests have been developed. UV exposure causes changes due to photodegradation of the composite surface, leads to discoloration, and makes materials aesthetically unappealing. Furthermore, prolonged UV exposure undoubtedly leads to loss in mechanical integrity.^[7] However, it seems that this can be improved by using appropriate additives (thermo- and photostabilizers), which are used in very low concentrations but can significantly lengthen the lifetime of most organic polymeric materials.^[6] The aim of the present paper is to study the chemical aspects of the HDPE/wood composites' photostabilization and to determine the stabilizer efficiency in degradation prevention. The photochemical behavior of HDPE/wood composites with different amounts of the UV stabilizer Tinuvin 783 was studied under artificially accelerated conditions of weathering.

Tinuvin is a stabilizer from the HALS group (hindered amine light stabilizers), which are a unique class of stabilizers where the parent compound has to be oxidized to the corresponding stable nitroxyl radical before becoming effective. The nitroxyl radical inhibits photooxidation by scavenging alkyl radicals in competition with oxygen. Then alkoxy-hindered amine derivatives are formed and further oxidation is inhibited.^[6] If the reaction rate k_2 (which represents reaction of stabilizer with oxygen) is higher than reaction rate k_1 (polymer oxidation), degradation of the polymer will be prevented and fewer carbonyl groups in polyethylene will be formed.

The chemical changes of HDPE/wood composites resulting from UV treatment were investigated by FTIR spectroscopy. SEM, TGA, and DSC methods were also used to characterize the structure changed during aging. All used experimental techniques gave us insight into UV stabilizer activity and the durability of the studied HDPE/wood composites.

Experimental

Materials

High-density polyethylene (HDPE KT 10000 UE, MFR: 8.0 g/10 min at 190°C/2.16 kg, density 964 kg/m³) was obtained from Dow Chemical Company. Pine wood flour (WF) was obtained from a local wood processing plant, with particle size from 50 to 100 μ m. UV stabilizer Tinuvin 783 from the group of HALS stabilizers was used (CIBA, thermal stability to 280°C). Plasticizer diisodecyl phthalate (DIDP) was obtained from Fluka Analytical. Zinc stearate, produced by Sigma Aldrich, was used (technical grade, stearate salt 65%).

Sample Preparation

Pine wood flour was dried for four hours at 100°C; final moisture content was then below 0.1%. HDPE was mixed with diisodecyl phthalate (DIDP) in 30 mass% suspension

Table 1
Formulation of HDPE/WF samples

Sample	Wood flour %	HDPE %	Zn stearate phr	UV stabilizer Phr
Without stabilizer	30	70	8	—
0.25 phr UV stab.	30	70	8	0.25
0.50 phr UV stab.	30	70	8	0.50
1.00 phr UV stab.	30	70	8	1.00
1.50 phr UV stab.	30	70	8	1.50

for 30 minutes at 75°C, with DIDP concentration 40 mg/L. Prior to extrusion, all components were premixed in a Turbula T2F shaker for 10 min. The high-density polyethylene/wood flour composites (HDPE/WF) were prepared by melt blending using a Rondol Top Bench 21 co-rotating twin screw extruder. Temperature profile in the extruder was set to 150/160/170/175/175/180°C (from hopper to die) and the screws' rotation speed was set to 100 rpm. The extrudate was granulated and flexural specimens (80 × 10 × 4) mm were pressed by hydraulic Dake press. Pressing conditions were as follows: temperature 185°C, pressure 3.5 MPa, and time 8 min. Composition of the WPC samples is listed in Table 1.

Artificial Weathering

HDPE/WF composites were thermally treated in a Memmert oven for 24 h at 80°C. After that, composites were exposed to ultraviolet (UV) light for 10, 20, and 30 days in a SUNTEST CPS apparatus (Heraeus Industrietechnik GmbH, $\lambda = 290$ nm). Lamp type: Xenon lamp NXE 1500 B. The temperature in the UV chamber was approximately 40°C.

Characterization

FTIR Spectroscopy. To observe changes in a material caused by thermal and UV treatment, HDPE/WF composites were characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR FTIR), Spectrum One FTIR spectrometer, Perkin Elmer, in the range from 4000 to 650 cm^{-1} . Each sample was pressed with the flat pressure tip at the maximum pressure. From each sample, five parallel spectral measurements were carried out, performed on different measurement points at WPC surface. FTIR spectra were normalized using automatic baseline correction from software Spectrum One, Perkin Elmer.

Scanning Electron Microscopy. Scanning electron microscopy (SEM) was utilized to examine the specimens' surfaces after weathering using a FEI FE SEM QUANTA FEG 250 at 10 kV.

Determination of Water-Absorption Degree. To study the water sensitivity of HDPE/WF samples, the weight of each specimen was measured and they were then immersed in water for 24, 48, and 120 h at a temperature of 40°C. After this period of time, all samples were weighed to calculate the moisture content. The values of the water absorption degree (α)

were calculated using the following equation^[8]:

$$\alpha(\%) = 100 (m_2 - m_1)/m_1 \quad (1)$$

α = water absorption degree, %; m_2 = mass after swelling, g; m_1 = mass before swelling, g.

Water absorption degree was measured for three replicate samples.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) studies were performed on a Mettler Toledo DSC 2910 (TA Instruments). Samples of 10 ± 0.1 mg were sealed in aluminum pans, heated from 25°C to 170°C (first heating scan), then cooled to 25°C (cooling scan) and, finally, heated from 25°C to 170°C (second heating scan) at the same heating/cooling rate of 10°C/min. Nitrogen flow rate was 40 ml/min. Measurement of each sample was performed three times. All experiments were carried out under nitrogen atmosphere.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) of studied samples was carried out using a TA Instruments Q500 analyzer. The samples were heated from room temperature to 550°C at a heating rate of 5°C/min. For each sample, three measurements were done. Nitrogen was used as a carrier gas with a constant flow rate of 100 ml/min during analysis.

Results

Infrared Analysis

FTIR spectroscopy can be successfully used for the determination of the HDPE/WF composites' surface chemistry changes during weathering, which represents clear insight into material degradation. The IR spectra of the HDPE/wood composite before irradiation can be seen in Figure 1. It unites the absorption bands of the PE matrix and the characteristic absorption bands of the cellulose and lignin. Characteristic peaks for polyethylene are at 2850 and 2912 cm^{-1} assigned to CH stretching in $-\text{CH}_2-$ groups; at 1470 cm^{-1} there is a C-H bending band of CH_2 groups, and at 722 cm^{-1} CH_2 rocking mode of the sequence of CH_2 groups in paraffin structure.^[9] Cellulose is characterized by the peak at 1023 cm^{-1} associated with both the C-O stretch in cellulose and the C-O deformation in the primary alcohols of lignin.^[10,11]

The modifications of the IR spectra of HDPE/WF composites after 30 days of UV treatment with and without Tinuvin stabilizer are also shown in Figure 1. The spectrum shows significant decrease of the intensity of characteristic peaks due to the degradation process. More detailed insight into degradation can be seen in Figure 2, where differences in spectra due to composite degradation can be observed. Furthermore, Figure 3 shows the mechanism of polyethylene degradation. It is known that photooxidation reactions occur preferentially close to the surface of the specimen and initiate and comprehensively affect material degradation.^[12] It can be seen that polyethylene degradation mostly results with the formation of carbonyl groups (Figures 2a and 3). However, degradation of polyethylene in the first step manifests as the chain scission and can be detected through the monitoring of peaks absorbance intensity at 2912 cm^{-1} and 2850 cm^{-1} assigned to CH stretching in $-\text{CH}_2-$ groups. It is obvious that the intensity of these groups decreases after UV treatment (Fig. 2b). Further polyethylene degradation results with the formation of carbonyl end

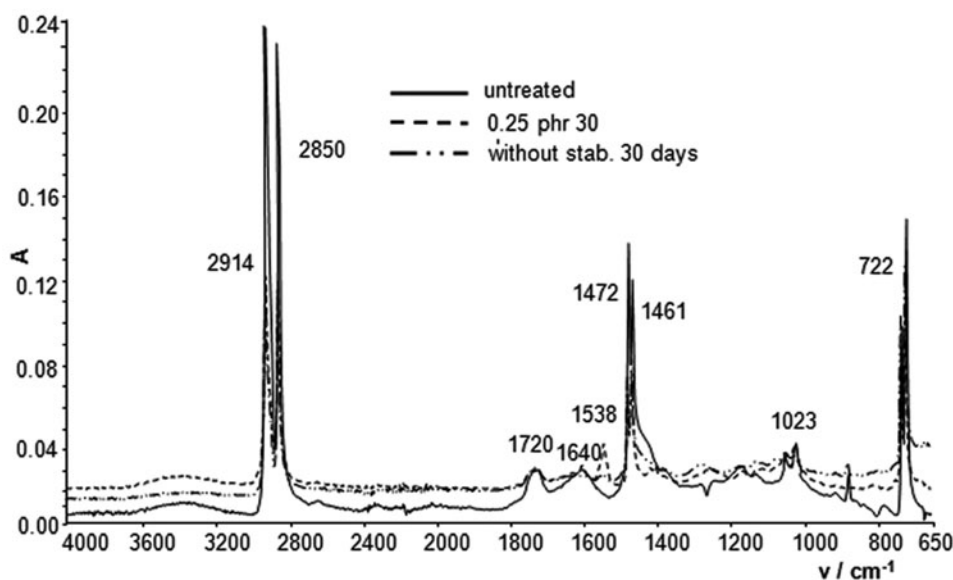


Figure 1. FTIR spectra of HDPE/WF composites before and after weathering.

groups. The assigned peak at 1720 cm^{-1} corresponds to carbonyl groups, which are the main result of the thermo- and photooxidation of polyethylene (Fig. 3). From Fig. 2, it can also be seen that the sample with 0.25 phr of stabilizer Tinuvin shows lower carbonyl groups absorbance; i.e., the lower degradation degree than the sample prepared without the stabilizer. The effect of UV stabilizer Tinuvin (hindered amine stabilizer, HALS) is also included in Fig. 3.

In studied WPC samples, degradation of cellulose in wood is also present and was detected by monitoring the absorbance intensity of C-O groups at 1023 cm^{-1} , Fig. 2c). The mechanism shows the loss of C-O groups from cellulose during the sample photooxidation (Figure 4). It can be observed that the peak at 1023 cm^{-1} is significantly decreased after 30 days of weathering without stabilizer Tinuvin. However, C-O absorbance in the sample prepared with 0.25 phr of stabilizer is higher in comparison to the sample without the stabilizer due to the stabilizer's protective action. Therefore, after the initial small production

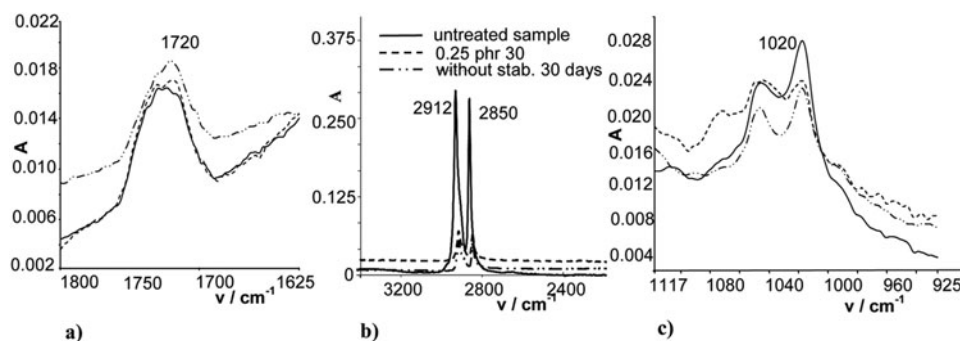


Figure 2. FTIR spectra of HDPE/WF composites after weathering: (a) carbonyl groups in HDPE; (b) diminishing of characteristic peaks for HDPE; (c) carbonyl groups in cellulose.

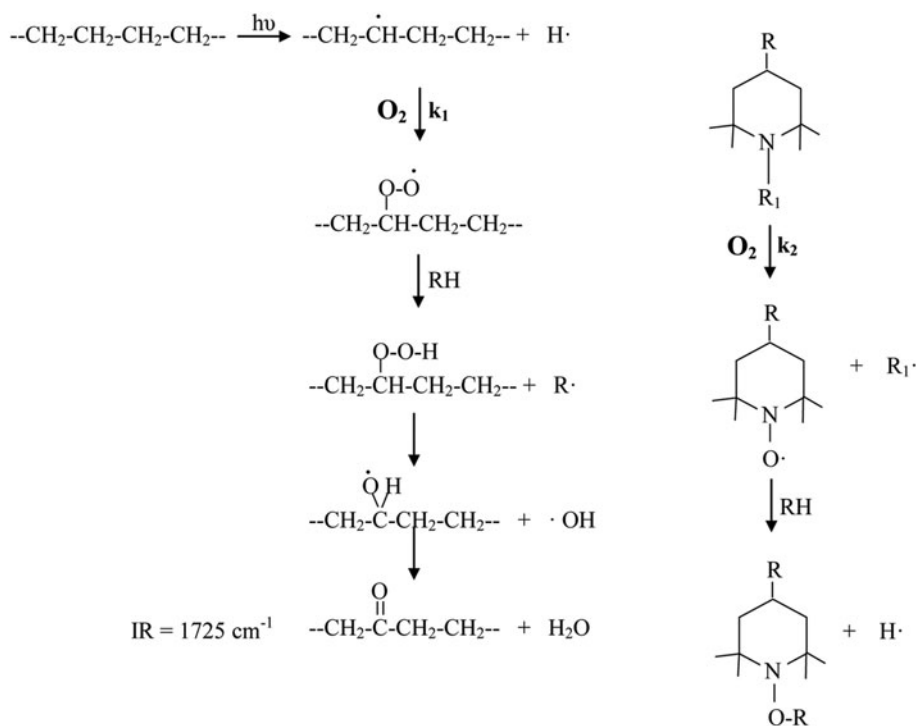


Figure 3. Polyethylene degradation and mechanism of HALS stabilizer.

of hydroperoxides, the polyethylene degradation is dominated by the formation of carbonyl as well as vinyl species. Recombination of polymer radicals formed by degradation results in the formation of vinyl groups.^[13] All obtained results indicate significant changes in the chemical structure of the studied HDPE/WF composite when degradation is not prevented

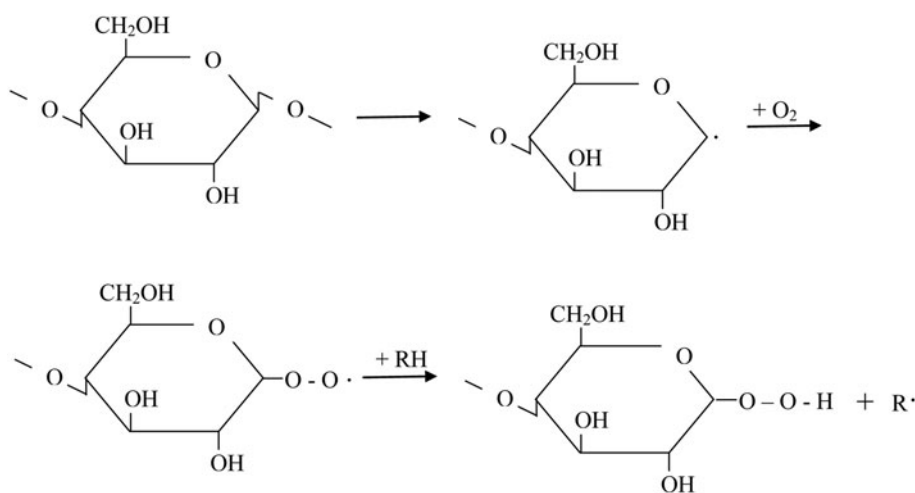


Figure 4. Cellulose degradation.

by the Tinuvin stabilizer. As discussed above, the modifications of the IR spectra of HDPE polymer after weathering are mostly caused by the formation of carbonyl groups at about 1720 cm^{-1} (Fig. 2a), while the formation of other groups reported in the literature, such as γ -lactones at 1780 cm^{-1} , hydroperoxides/alcohols at 3420 cm^{-1} , and unsaturation at 910 , 965 , 990 , and 1640 cm^{-1} , is negligible.^[14]

Thus, carbonyl groups' formation (Fig. 2) is an effective parameter for monitoring the photooxidation degree of polyethylene and can be presented as carbonyl index (CI), calculated according to the equation^[15]:

$$\text{CI} = \text{absorption at } 1720\text{ cm}^{-1} / \text{absorption at } 2020\text{ cm}^{-1} (\text{internal thickness band}) \quad (2)$$

A higher value of carbonyl index indicates a higher degree of polymer degradation. According to the results in Figure 5, the most stabile composites are those prepared with 0.25 and 0.5 phr of UV stabilizer. Furthermore, it can be seen that, after 30 days of UV treatment, CI values increased 114% for the composite without UV stabilizer and only 38% for the composite with 0.25 phr of UV stabilizer.

For a more precise study of composites' UV degradation, wood component aging is also characterized. The wood index (WI) in HDPE/WF composites has been calculated according to Eq. (3).^[16] It is defined as a ratio of peak absorbance for C-O groups in cellulose at 1023 cm^{-1} to peak absorbance at 2912 cm^{-1} , multiplied by 100:

$$\text{WI} = (A_{1023}/A_{2912}) \times 100 \quad (3)$$

The results are presented in Figure 6 and show that degradation of wood component can be successfully monitored through the changes in FTIR spectra. WI values are presented in dependence of Tinuvin stabilizer concentration for the untreated samples and those after 30 days of UV treatment.

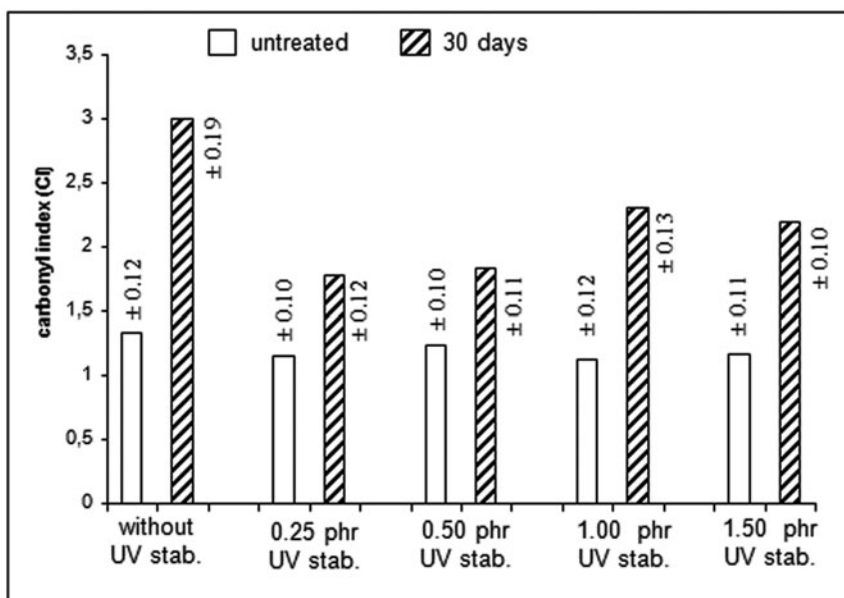


Figure 5. Carbonyl index of HDPE/WF composites.

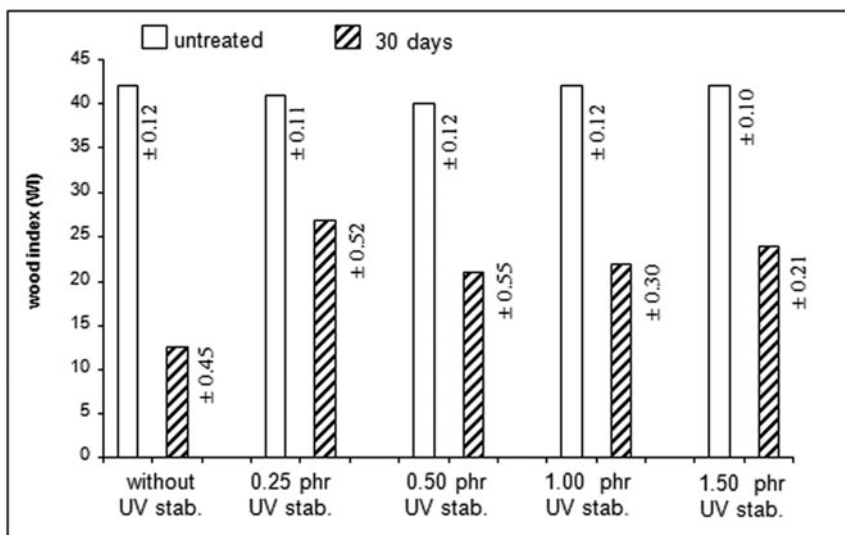


Figure 6. Wood index of HDPE/WF composites.

It can be observed that, after weathering, the wood index for all studied composites is decreased due to the loss of C-O groups in cellulose. It is seen that WI values after 30 days of UV treatment are decreased by 72% for the composite without the UV stabilizer and 37% for the composite with 0.25 phr of the UV stabilizer. It is interesting to note that the composites with higher content of UV stabilizer (1 and 1.5 phr) did not show better resistance to thermo- and photodegradation, as was expected. The best result shows the sample prepared with 0.25 phr of the UV stabilizer.

The weathering resistance of neat polyethylene of commercial grades has been related to the photooxidation reactions, which occur preferentially close to the surface of the specimen, so it can be concluded that the use of the stabilizer for WPC outdoor application is needed in most cases to ensure their prolonged use.^[12] It should be pointed out that obtained results characterize degradation mostly on the surface of the composite, while the degradation is supposed to be significantly less present in material bulk. Furthermore, due to UV lightening during weathering, discoloration of the WPC surface also occurs.^[17] The preservation of surface characteristics is important for aesthetic reasons, so the presence of a light stabilizer like Tinuvin is necessary in WPCs' preparation.

Scanning Electron Microscopy

In order to further study HDPE/WF composites' photodegradation, degradation analysis by scanning electron microscopy was performed. Micrographs of the surfaces of studied HDPE/WF composites before degradation are shown in Figure 7. It seems that, before weathering, the composite surface is relatively smooth because no degradation is present and HDPE polymer covers the wood particles. There are almost no voids (Fig. 7) and it can be concluded that HDPE encapsulation of wood is successful. It is assumed that such good structure is achieved due to increased interface adhesion between the wood flour and polymer matrix using a diisodecyl phthalate plasticizer (DIDP) in the composites' preparation. Before the preparation of HDPE/WF composites, the HDPE polymer was treated with DIDP suspension to enable the plasticizer to cover the polymer surface. In

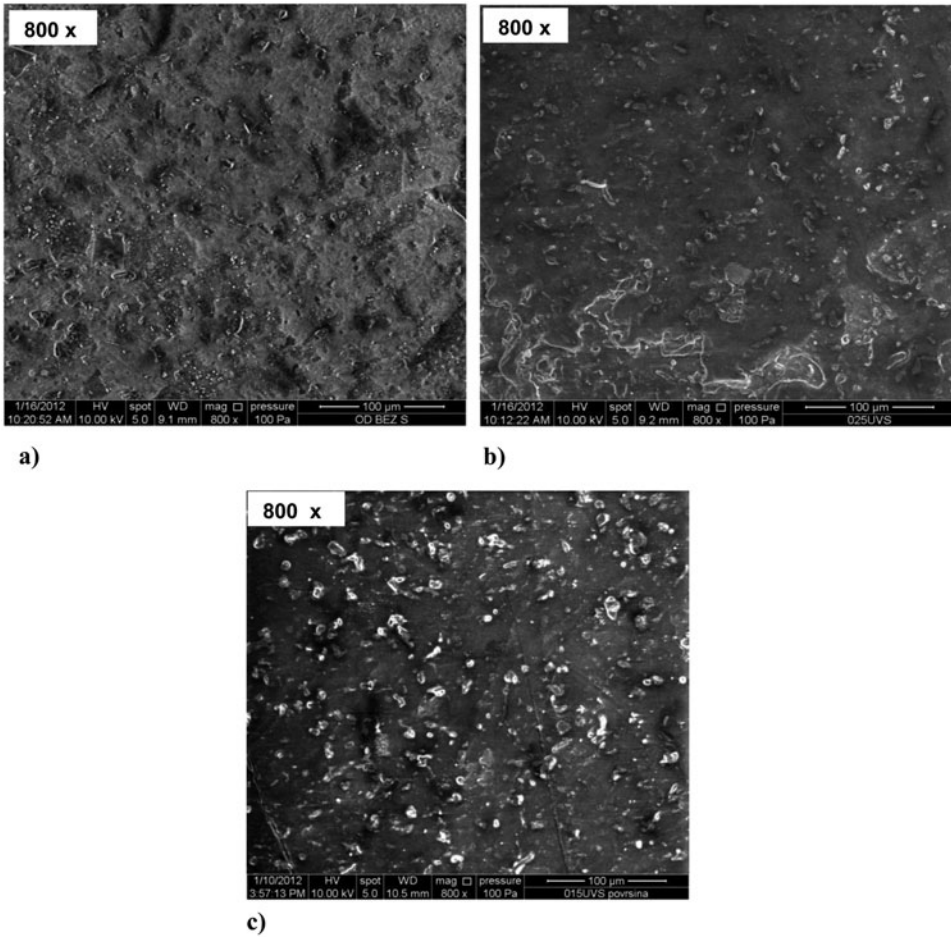


Figure 7. SEM micrographs of the untreated samples: (a) without stabilizer; (b) 0.25 phr of UV stab.; and (c) 1.5 phr of UV stab.

this way, the better adhesion of wood flour on the polymer matrix is achieved.^[18] It is important to remark that the preparation of the WPC samples plays an important role in their final quality. The injection molding can be considered to be a better procedure for WPC preparation. Such a process helps to avoid the appearance of undesirable defects in WPC structure (internal air voids) in the samples due to the release of gases during extrusion. After weathering, the surface characteristics of composites are changed and the results are given in Figure 8. It can be seen that the surface of HDPE/WF composites is damaged and the appearance of cracks on the surface in lengths up to 10 μm can be noticed. As UV treatment progresses, wood becomes degraded and more brittle, so microcracks in the HDPE matrix occur. Analyzed decreased wood index after UV treatment confirms a loss of wood from the composite surface. This is the consequence of thermal and UV treatment, which caused material degradation and formation of microcracks on the matrix surface due to the fracture of wood particles. The protrusion of wood particles from the HDPE matrix occurred as a result of degradation.^[16] This can be explained by the fact that, as aging progresses, those wood particles occupy a larger volume, creating a pressure which causes

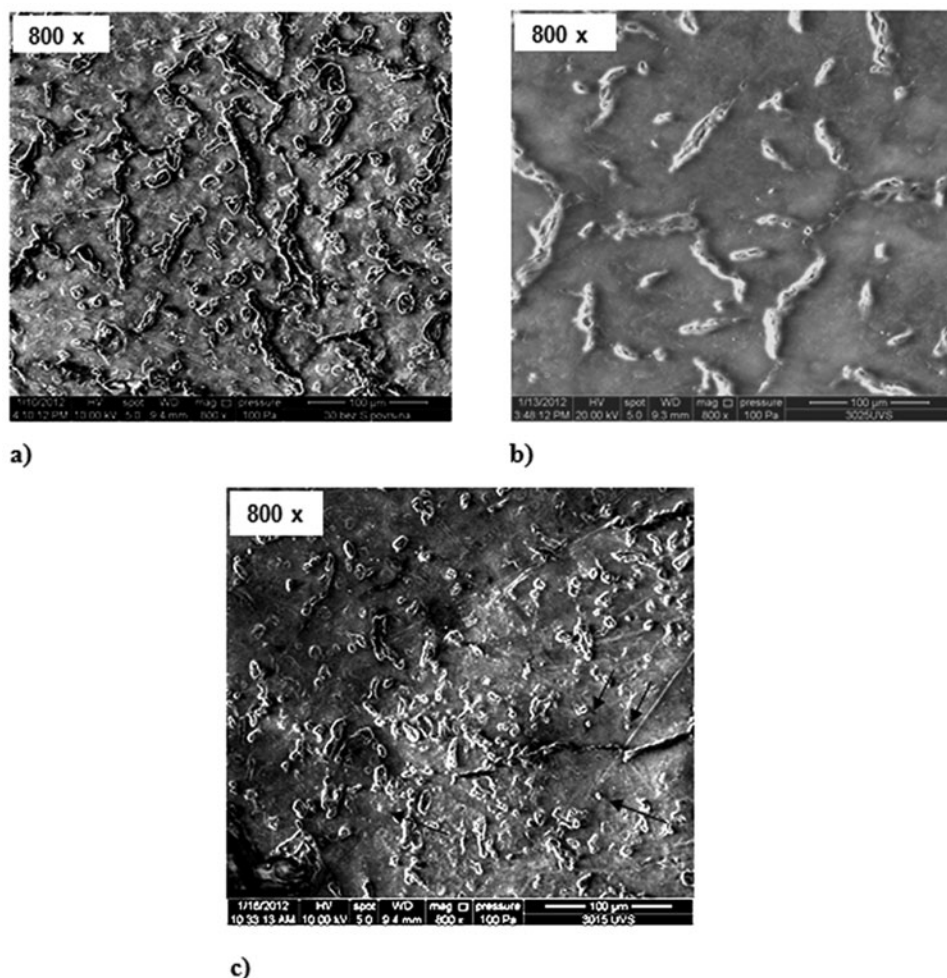


Figure 8. SEM micrographs of the samples after 30 days of UV treatment: (a) without stabilizer; (b) 0.25 phr of UV stab.; and (c) 1.5 phr of UV stab.

the fracture of the polymer matrix and the formation of microcracks on the surface. These results also match the conclusion obtained by FTIR, which implies that degradation of the wood component in the composite was dominant while the HDPE matrix is less susceptible to degradation. Therefore, the more intensive degradation of cellulose and lignin is already confirmed by FTIR analysis. Furthermore, from Figure 8a it is evident that the surface of the composite prepared without the stabilizer is the most degraded, while the surfaces of the samples prepared with the UV stabilizer (Figs. 8b and 8c) show only partial changes and much less degradation. Thus, the composite with 0.25 phr of Tinuvin shows larger cracks, but the total surface area of the sample is less affected by degradation, while the sample with 1.5 phr has a significantly higher proportion of degraded surface area. From that, it is concluded that the sample with only 0.25 phr of Tinuvin stabilizer shows the best resistance to degradation. The higher efficiency of the UV stabilizer, which is present in lower concentration (0.25 phr), is explained by its better dispersion in the composite. When Tinuvin stabilizer is added in higher concentration (1.5 phr), the presence of stabilizer

aggregates can be observed (white spots in Figure 8c). Aggregates are of higher size than in the composite in micrograph 8b. Observed good dispersion of the stabilizer in blends with 0.25% of Tinuvin affects successful inhibition of HDPE/WF surface degradation and inhibition of cracks' appearance due to achieved blend stabilization. It can be concluded that it is very important to ensure the lowest possible degradation of HDPE/WF composites using an optimal amount of stabilizer, which prevents the progression of cracks and grooves at the surface. Otherwise, such fractures and loss of wood from the composite surface could lead to material defects (weak points) and profoundly influence the mechanical properties of material.

Water Absorption Degree

Due to widespread outdoor application, a very important characteristic of HDPE/WF composites is the degree of water absorption (α). It is necessary to maintain the lowest possible value of water absorption to gain HDPE/WF composites' dimensional stability. The water absorption degree for studied samples is listed in Table 2. It is obvious that water absorption degree increases with time of UV treatment for all studied samples. It is interesting to observe that the WPC samples absorbed maximum water content in the first 24 hours; there were no significant changes in prolonged duration of moisture tests. The increase of the water absorption is explained mostly by degradation of the wood component in composites. The low increase of α values with time of UV exposure indicates degradation of composites on the surface, not in the bulk. Such behavior is expected due to surface degradation, which progresses with time and causes the microcracks in the composite that become more porous and a higher content of water is absorbed. The significantly higher value of the water

Table 2
Water absorption degree for HDPE/WF samples

Sample	0 days	10 days	20 days	30 days
24 h, water absorption degree α /%				
Without stabilizer	6.39 \pm 0.61	7.73 \pm 0.75	7.79 \pm 0.65	7.90 \pm 0.45
0.25 phr UV stab.	1.23 \pm 0.12	1.27 \pm 0.15	1.42 \pm 0.12	1.45 \pm 0.13
0.50 phr UV stab.	3.47 \pm 0.20	4.51 \pm 0.21	4.25 \pm 0.18	4.18 \pm 0.17
1.00 phr UV stab.	3.04 \pm 0.10	4.48 \pm 0.15	4.70 \pm 0.15	5.29 \pm 0.16
1.50 phr UV stab.	3.26 \pm 0.12	4.09 \pm 0.14	4.76 \pm 0.15	5.05 \pm 0.12
48 h, water absorption degree α /%				
Without stabilizer	6.33 \pm 0.52	7.69 \pm 0.25	7.70 \pm 0.62	7.92 \pm 0.25
0.25 phr UV stab.	1.19 \pm 0.11	1.21 \pm 0.11	1.40 \pm 0.10	1.40 \pm 0.10
0.50 phr UV stab.	3.41 \pm 0.18	4.50 \pm 0.11	4.21 \pm 0.18	4.16 \pm 0.15
1.00 phr UV stab.	3.00 \pm 0.09	4.42 \pm 0.10	4.68 \pm 0.14	5.30 \pm 0.12
1.50 phr UV stab.	3.20 \pm 0.12	4.04 \pm 0.14	4.79 \pm 0.15	5.01 \pm 0.10
120 h, water absorption degree α /%				
Without stabilizer	6.35 \pm 0.50	7.71 \pm 0.23	7.72 \pm 0.54	7.89 \pm 0.21
0.25 phr UV stab.	1.20 \pm 0.11	1.24 \pm 0.12	1.40 \pm 0.12	1.41 \pm 0.10
0.50 phr UV stab.	3.45 \pm 0.13	4.42 \pm 0.10	4.19 \pm 0.14	4.15 \pm 0.10
1.00 phr UV stab.	3.00 \pm 0.10	4.33 \pm 0.13	4.65 \pm 0.14	5.28 \pm 0.17
1.50 phr UV stab.	3.24 \pm 0.10	4.08 \pm 0.14	4.75 \pm 0.10	5.02 \pm 0.12

absorption degree in regard to the other samples shows the sample without the Tinuvin stabilizer. For example, after 30 days of treatment, 7.9% of water was absorbed. On the contrary, all composites with the Tinuvin stabilizer show significantly lower water absorption (i.e., higher stability), indicating hydrophobic behavior of the Tinuvin stabilizer. In particular, low water absorption degree shows the sample with Tinuvin stabilizer concentration of 0.25 phr, even after 30 days of UV treatment ($\alpha = 1.45\%$). After the same time of UV treatment, the value of water absorption for the sample prepared with 1.50 phr of UV stabilizer is 4.76%. This is explained by the fact that water absorption also depends on wood particles and stabilizer arrangement in the polymer matrix. Furthermore, the higher aggregation of wood particles would also contribute to higher water absorption, because of the formation of dispersed homogenous domains with larger size. The wood component is hydrophilic and has considerably larger affinity to water absorption than the polymer hydrophobic matrix. Due to better stabilizer dispersion, the sample with stabilizer content of 0.25 phr shows the lower water absorption degree than the sample prepared with the higher quantity of stabilizer. Another factor for the prevention of WPCs' susceptibility to swelling is the use of the plasticizer DIDP in WPC preparation, which enhances hydrophobicity of HDPE, and it is expected that it would result in a decrease of water absorption.^[18] Thus, overall composite structure is a key factor in the quantity of water that is going to be absorbed.

From the results, it can be seen that Tinuvin stabilizer concentration of 0.25 phr contributes to optimal and successful dispersion in the composite and greatly affects the overall HDPE/WF composite properties. The acceptable water absorption degree for WPCs is below 1%,^[19] so the sample with 0.25 phr Tinuvin almost meets the requirements.

Differential Scanning Calorimetry

DSC measurements were used to record the changes in the crystallinity of HDPE/WF composites after weathering, due to the well-known fact that the changes in material structure caused by degradation will result in property changes. From the results in Table 3, it can be seen that for all the samples there are two melting (T_m) and two crystallization (T_c) temperatures. The T_{m1} is assigned to melting of some fraction of depolymerized HDPE caused by UV treatment (fraction of degraded HDPE with lower molecular masses). This melting peak has lower intensity and occurs in the temperature range from 112 to 116°C for all samples. The T_{m2} is assigned to the HDPE polymer and its values are from 132 to 136°C. The occurrence of two melting and crystallization temperatures, even for untreated samples, can be explained by a slight degradation of the sample during its preparation (high temperatures during WPCs extrusion and further formation by molding).^[20]

Furthermore, it can be observed that, after UV treatment, there is no significant change in melting temperatures for all studied samples. A slight discrepancy in T_m is seen with the addition of Tinuvin stabilizer, indicating some changes in composite structure. It was assumed that a small fraction of degraded chains with lower molecular masses, formed by chain scission, would melt at lower temperature.^[20] Because of the high temperatures used in polymer processing, degradation occurs related to thermal stress in combination with mechanical stress during processing in an extruder.^[21] The results of T_m point out that, even after 30 days of UV treatment, the polymer component shows high photostability and that the surface degradation does not have the effect on bulk properties of the HDPE/WF composite. The slight increase of T_{c1} values after weathering indicates changes in the structure of the composite due to a degradation process that takes place in composites, already discussed by FTIR and SEM. The changes in polymer chain structure can be more clearly seen through the crystallinity degree, which is calculated according to Eq. (4) and

Table 3
Melting temperature, crystallization temperature, melting enthalpy and crystallization degree of the studied samples

Sample	T _{m1} / °C	T _{m2} / °C	T _{c1} / °C	T _{c2} / °C	ΔH _m / Jg ⁻¹	X _c /%
	Untreated sample					
Without stabilizer	114.9 ± 4.2	133.1 ± 4.2	84.3 ± 3.4	116.7 ± 5.5	83.8	40.88 ± 2.41
0.25 phr UV stab.	116.6 ± 2.3	135.3 ± 3.2	80.4 ± 4.1	115.4 ± 5.1	95.9	46.78 ± 1.22
1.5 phr UV stab.	112.7 ± 4.1	132.6 ± 3.1	76.7 ± 2.3	115.6 ± 2.4	77.1	37.60 ± 2.53
	30 days of UV treatment					
Without stabilizer	115.8 ± 5.2	134.1 ± 2.5	85.1 ± 2.1	115.8 ± 2.4	78.8	38.45 ± 1.22
0.25 phr UV stab.	114.8 ± 1.2	133.1 ± 3.0	82.1 ± 3.1	117.2 ± 2.7	71.8	35.01 ± 2.31
1.5 phr UV stab.	113.4 ± 3.1	133.6 ± 2.0	78.4 ± 2.4	115.3 ± 2.1	116.5	56.84 ± 2.40

results are also presented in Table 3.

$$X_c(\text{HDPE}) = \Delta H_m / (\Delta H_m^0 \times w(\text{HDPE})) \quad (4)$$

where ΔH_m represents the heat quantity obtained by DSC, ΔH_m^0 is molar enthalpy of 100% crystalline polymer melting (293 J/g for HDPE), and $w(\text{HDPE})$ is the amount of HDPE in samples.^[22] Results show that with prolonged time of UV treatment, a significant decrease in crystallinity for all composites is observed. This is explained by the higher concentration of formed polymer radicals with different functional groups (carbonyl, carboxyl, hydroxyl, vinyl) as a result of depolymerization induced by exposure to weathering conditions. Such groups disable the fine order of polymer chains and the crystallinity degree decreases.^[22]

Thermogravimetric Analysis

Thermogravimetric analysis is one of the thermal techniques suitable for estimation of the polymeric materials' stability. Namely, due to the influence of high temperatures, polymers decompose and lead to the formation of various low molecular products. TGA is a method that provides good insight into the behavior of polymer materials during oxidation or thermal degradation. It can be used for the prediction of their behavior during the actual exposure to atmospheric conditions. In this experiment, it is expected that TGA results will give us information about the changes in material structure caused by degradation and the response to the use of a UV stabilizer. Thermal stability of prepared wood-plastic composites was studied by thermogravimetric analysis in a nitrogen atmosphere at a heating rate of 5°C/min. Analysis showed that the decomposition of HDPE/WF composites occurs in two steps (Table 4). The first step of thermal decomposition is approximately from 200 to 350°C. This step corresponds to the degradation of hemicellulose, lignin, and cellulose. Kim et al. and Fabiyi et al.^[23,24] stated that the degradation of hemicellulose, lignin, and cellulose occurs between 180 and 350°C, 250 and 500°C, and between 275 and 350°C, respectively. Furthermore, the second degradation step is attributed to the degradation of the HDPE matrix and occurs at about 400 to 470°C. During the WPC decomposition, higher thermal stability is achieved for the sample with 0.25 phr of Tinuvin stabilizer.

Table 4
TGA results of HDPE/WF composites

Time of UV aging	Without stabilizer		0.25 phr UV stab.		0.50 phr UV stab.	
Days	T ₉₅ / °C	T _{max} / °C	T ₉₅ / °C	T _{max} / °C	T ₉₅ / °C	T _{max} / °C
0	225.6 ± 1.1	450.5 ± 2.0	259.6 ± 0.7	450.5 ± 0.5	230.6 ± 2.7	448.6 ± 2.1
10	230.8 ± 2.1	450.0 ± 1.6	259.3 ± 0.9	450.0 ± 1.2	235.4 ± 0.9	446.4 ± 0.8
20	243.8 ± 1.4	450.4 ± 2.2	259.1 ± 1.0	450.3 ± 2.5	237.6 ± 1.6	450.2 ± 0.4
30	231.5 ± 1.2	450.1 ± 1.8	247.5 ± 0.8	450.1 ± 2.8	235.3 ± 2.2	451.5 ± 1.4
	1.00 phr UV stab.		1.50 phr UV stab.			
Days	T ₉₅ / °C	T _{max} / °C	T ₉₅ / °C	T _{max} / °C		
0	244.3 ± 2.2	449.4 ± 0.4	240.3 ± 2.1	449.6 ± 0.5		
10	245.9 ± 1.4	448.2 ± 0.8	219.6 ± 1.8	447.7 ± 0.7		
20	238.3 ± 0.5	450.6 ± 1.2	228.3 ± 1.5	449.6 ± 1.3		
30	228.2 ± 1.0	449.4 ± 0.8	227.2 ± 1.3	450.4 ± 2.1		

Table 4 contains the results of the initial decomposition temperature (T_{95}) and the maximum loss rate temperature (T_{max}) of the studied samples. T_{95} and T_{max} are two of the essential parameters for the estimation of the polymer materials' thermal stability. The results show that the lowest susceptibility to thermal degradation shows the sample prepared with 0.25 phr of stabilizer. Namely, T_{95} of untreated sample prepared with 0.25 phr stabilizer is about 260°C, while the T_{95} of the sample prepared with 1.5 phr of stabilizer is approximately 240°C. The decrease of T_{95} indicates lower thermal stability of the composites due to their disturbed structure caused by UV exposure. Furthermore, the results show that the maximum loss rate temperature (T_{max}) is approximately equal for all studied samples because, at this stage, it mostly decomposes the HDPE matrix. Obtained TGA results also showed that the wood component is more susceptible to UV degradation and that the stabilizer mostly prevents HDPE degradation. It can be concluded that the stabilizer's good and uniform dispersion in wood plastic composites is the key factor for the properties' preservation and the composite's stability.

Conclusion

WPC is a very promising, sustainable, and environmentally friendly material, containing no toxic chemicals. In order to overcome the problem of polymer incompatibility between matrix and wood, WPCs were prepared with plasticizer DIDP, which changes HDPE surface properties, enhances WPC extrusion, and decreases water absorption degree.

The results show that UV treatment of HDPE/WF composites leads to degradation of the composites' surface. A wood component is more susceptible to degradation than the HDPE matrix and the stabilizer activity is mostly directed to HDPE preservation. Furthermore, it can be concluded that the optimal concentration of the stabilizer in WPC is 0.25 phr.

When the optimal concentration of the Tinuvin stabilizer is used, it becomes finely dispersed in the HDPE matrix. In contrast, a higher concentration of stabilizer (1.50 phr) induced aggregation in composites and contributed to the deterioration of their properties. Thus, good stabilizer dispersion directly influences enhancement of WPCs' properties and enables higher resistance to aging. Furthermore, lower water absorption occurs due to stabilizer hydrophobic properties. The obtained results imply that the carefully chosen composition of wood plastic composites plays an important role in their overall properties and stability. These findings can have obvious consequences for WPCs' outdoor durability assessment and application.

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