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Influence of Zinc Oxide Nanoparticles on Flame Resistance in Wood Plastic Composites

Utjecaj nanočestica cinkova oksida na vatrootpornost drvno-plastičnih kompozita

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT • The interest in wood plastic composites (WPCs) has increased in recent years. The utilization of environmentally friendly materials has been of great significance due to the overwhelming pressure on nature. As a widely used material, plastic is, however, easily combustible due to its structure. In this study, WPCs were reinforced with zinc oxide (ZnO) nanoparticles. The effect of higher content of ZnO nanoparticles (1, 3, 5, 10%) on WPCs thermal stability and fire performance was investigated. Thermogravimetric analysis (TGA) clearly demonstrated that nanoparticles acted as a shield, which inhibited heat transfer and increased the degradation temperature thanks to covering the surface of materials. Free radicals accelerated the thermal degradation of neat-HDPE (high-density polyethylene) by oxidative reactions, while ZnO nanoparticles reduced the degradation velocity. Moreover, the increase in nanoparticle content significantly affected the residue. The fire performance of WPCs was also investigated by the limit oxygen index (LOI) test. While neat-HDPE flamed with dripping, ZnO nanoparticles made flaming difficult for WPCs. Therefore, the LOI values increased with increasing nanoparticle content up to 28.5 %, which indicated the need for more oxygen. The improvement reached up to 54 % compared to neat HDPE. Moreover, the char forming was also improved, which helped enhance the fire resistance. The scanning electron microscope (SEM) investigation indicated that nanoparticles were well dispersed in the matrix. However, the tendency to agglomerate increased with the increase of concentration. The ability of carbonization of wood fiber surface during the combustion also contributed to improving thermal stability and fire performance.

KEYWORDS: ZnO nanoparticles; LOI test; TGA analysis; thermal resistance; WPC

SAŽETAK • Zanimanje za drvno-plastične kompozite (WPC) posljednjih je godina poraslo. Upotreba ekološki prihvatljivih materijala ima veliko značenje zbog golemog pritiska na okoliš. Plastika je široko rasprostranjen i vrlo često upotrebljavan materijal, ali je zbog svoje strukture lako zapaljiva. U ovom su istraživanju drvno-plastični kompoziti ojačani nanočesticama ZnO. Istraživan je utjecaj većeg udjela nanočestica cinkova oksida (ZnO) (1, 3, 5 i 10 %) na toplinsku stabilnost i vatrootpornost WPC-a. Termogravimetrijska analiza (TGA) jasno je pokazala da nanočestice djeluju kao štit koji inhibira prijenos topline i povećava temperaturu razgradnje. Nadalje, slobodni radikali u reakcijama oksidacije ubrzali su toplinsku razgradnju čistog HDPE-a (polietilena visoke gustoće), dok su nanočestice ZnO smanjile brzinu razgradnje. Štoviše, povećanje udjela nanočestica znatno je utjecalo na

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ostatak nakon razgradnje. Vatrootpornost WPC-a također je ispitana mjerenjem graničnog indeksa kisika (LOI). Dok je čisti HDPE gorio uz kapanje, nanočestice ZnO otežale su gorenje WPC-a. LOI vrijednosti rasle su s povećanjem udjela nanočestica do 28,5 %, što je upućivalo na veću potrebu za kisikom. Poboljšanje je iznosilo do 54 % u usporedbi s čistim HDPE-om. Štoviše, poboljšano je i stvaranje pougljenjenog sloja koji je pridonio povećanju vatrootpornosti. Istraživanje pretražnim elektronskim mikroskopom (SEM) pokazalo je da su se nanočestice dobro dispergirale u matrici. Međutim, tendencija aglomeraciji povećala se s povećanjem koncentracije nanočestica. Sposobnost karbonizacije površine drvnih vlakanaca tijekom gorenja također je pridonijela poboljšanju toplinske stabilnosti i vatrootpornosti WPC-a.

KLJUČNE RIJEČI: nanočestice ZnO; LOI test; TGA analiza; toplinska otpornost; WPC

1 INTRODUCTION

1. UVOD

Climate change is increasing the pressure on the environment, driving manufacturers to produce greener products. Today, however, it is not only the desire for green materials that is more important, but also efficiency. The scarcity of raw materials also makes efficiency vital. Composite materials meet these requirements. Composites consist of two or more materials with different properties than the sum of the properties of two components. Wood-based composites are among the most popular composites because of their green label. Wood is a renewable, biodegradable, and abundant material, distinguishing it from other materials. The properties of wood vary between species, within the same species, and even more between different parts of the same tree. However, composites made from wood have homogeneous properties that attract designers, architects, engineers, etc. Today, woodbased composites are evaluated for everything from furniture to structures, car parts to unique designs.

WPCs, one of the wood-based composites, have existed for over 50 years in various applications: decks, fences, railing, garden furniture, doors, and window frames (Kim and Pal, 2010; Klyosov, 2007). Mixing wood and plastic creates a new material with superior properties. Plastic is one of the most remarkable inventions of the 20th century. Its high resistance to outdoor conditions makes it a more practical material against factors such as UV light, moisture, insects, fungi, etc. However, wood does not have the same advantages. On the contrary, it can be easily degraded by biotic and abiotic factors under the right conditions. Therefore, WPCs have become more desirable in recent years due to their high durability, high strength, low cost, noncorrosion, and environmental friendliness. Moreover, they can be considered an alternative material for most industries such as construction, car, architectural and structural design, aerospace, etc. (Erchiqui et al., 2020; Smith and Wolcott, 2006).

Composites are recognized as superior in comparison with their own constituents. However, there is still a need for improvement to overcome the existing shortcomings. Most research has focused on improving WPCs physical, mechanical, and weathering durability. However, the high flame sensitivity of polymer restricted WPC application, mainly indoors and outdoors, due to higher heat during thermal degradation. Heat or temperature differentiations affect WPCs thermal properties (Guo et al., 2019a). Free radicals initiate oxidation reactions during thermal degradation, decreasing the thermal stability of polymers (He et al., 2012). The chain scissions resulted in mass losses with increasing temperature due to thermaloxidative reactions. Eventually, most of the structure is converted to carbon monoxide (CO), carbon dioxide (CO₂), and water (H₂O) (Devi and Maji, 2012). In addition, the polymer threatens structural integrity, especially in structural design, due to its formability at low temperatures.

On the other hand, wood is a biopolymer consisting of cellulose, hemicellulose, and lignin. When exposed to heat or temperature, there are also some changes in the chemical and physical structure of wood. The cross-linked structure makes lignin more resistant to high temperatures, while hemicellulose is vulnerable (Lowden and Hull, 2013). Acetic and formic acid, furfural, and methanol formation occur during high-temperature exposure, which degrades cellulose and hemicellulose amorphous structures (Özgenç et al., 2017). Meanwhile, thermal degradation involves liquefaction, gasification, and pyrolysis (Mohan et al., 2006). Liquefaction gradually decreases and turns into some gases and solids; CO, CO₂, and H₂O, followed by gasification, which starts below 200 °C with non-combustible gases. Combustible gases also begin to accompany the process as the temperature rises, which starts the combustion of the combustible material. This produces char, which breaks down the wood.

The incompatibility between wood and polymer is also a crucial issue for the thermal stability of WPCs, as well as for their physical and mechanical properties. The bond between the polymer and wood flour, which are hydrophobic and hydrophilic, respectively, has a negative effect on the thermal expansion of WPCs (Yang *et al.*, 2005).

The effect of various fillers on the physicochemical and mechanical properties of polymer composites is determined by many factors. Moreover, some studies have also been carried out to improve the thermal stability of WPC with the reinforcement of synthetic fibers. Rasana *et al.* (2019) stated that glass fibers act as a thermal shield and inhibit degradation. The degradation of carbon fibers above 600 °C, which is higher than polyethylene and wood, improves the thermal stability of WPCs (Eibl, 2017; Guo *et al.*, 2019b; Yao *et al.*, 2018). As in previous studies, the thermal degradation of WPCs was retarded with the reinforcement of glass and carbon-woven fabrics (Durmaz *et al.*, 2021). Moreover, some studies also dealt with improving the thermal stability and fire performance of fibers with aerogels (He *et al.*, 2022; Zhang *et al.*, 2023).

Nanotechnology applications have been quite prevalent in recent years. The small size of nanoparticles surpasses their traditional counterparts and remarkably improves the materials properties (De Filpo et al., 2013). Nanomaterials improve the mechanical and physical properties of WPCs, and also significantly improve the thermal stability and fire performance (Chaharmahali et al., 2014). Metal oxide nanoparticles are the preferred nanoparticles for most applications. ZnO nanoparticle is one of the metal oxides evaluated in various applications due to its inherent properties (Franco-Urquiza et al., 2020). Zhao and Li (2006) highlighted that the thermal stability of polypropylene-based WPCs with ZnO nanoparticles was maintained even after exposure to UV light. Devi and Maji (2012) also found that the degradation temperature improved with the thermal shielding ability of ZnO nanoparticles. The small size of the nanoparticles allows them to cover the material surface, inhibiting the free radicals that occur during thermal degradation. As a result, the degradation temperature was improved. Jouyandeh et al. (2019) also found that increasing the content thickens the nanoparticle layer, which acts as an insulator and reduces heat transfer. Moreover, ZnO nanoparticles can absorb UV light between 200-380 nm (He et al., 2009). As in previous studies, ZnO nanoparticles improved weathering resistance with increasing content. The loss of mechanical properties was also reduced with decreasing crack formation (Durmaz et al., 2022).

High thermal stability and fire resistance are essential for the expansion of indoor and outdoor applications of WPCs. The main objective of this study was to improve the thermal strength and fire resistance of HDPE-based WPCs with ZnO nanoparticle reinforcement. For this purpose, the effect of ZnO nanoparticles at high contents on the WPCs thermal stability and fire performance was investigated. The distribution of ZnO nanoparticles was investigated by SEM analysis. The thermal behavior of the reinforced WPCs was investigated using TGA. The LOI test also revealed the fire behavior of the reinforced WPCs.

2 MATERIALS AND METHODS

2. MATERIJALI I METODE

2.1 Materials

2.1. Materijali

The pine wood flour (Pinus sylvestris L.) with 40-60 mesh dimensions as a lignocellulosic filler and HDPE as a thermoplastic polymer were supplied from commercial suppliers (Ucar Plastic, İzmir, Turkey). HDPE is one of the world's most popular plastics due to its resistance to high temperatures, strong chemicals, and UV light. The fine-grain polymer (~200 mesh) was used to obtain a homogenous mixture. The melt flow index (MFI) and density of HDPE were 5.5 g/10 min (190 °C/2.16 kg) and 0.965 g/cm³, respectively. Maleic anhydride grafted polyethylene (Licocene PE MA 4351 Fine Grain) was used as a coupling agent to improve the bonding between the materials. The MAPE softening point and density were 123 °C and 0.99 g/ cm³, respectively. The ZnO nanoparticles with dimensions of 30-50 nm and a density of 5.5 g/cm³ were used as a reinforcement agent (Nanografi, Ankara, Turkey).

2.2 Methods

2.2. Metode

The wood flour, thermoplastic polymer, and nanoparticles were mixed in a mechanical mixer (1200 rev/min) to obtain a homogeneous mixture, according to the scheme in Table 1. Before manufacturing, wood flour was oven-dried until constant weight at 80 °C. Then, the homogeneous mixture was extruded with a single screw extruder (Teknomatik, Turkey). The screw speed was set to 40 rpm. The extruder temperature was from 180 to 195 °C. The extruded samples were cooled in water and pelletized. The pellets were dried at (102 ± 2) °C and hot pressed at 180 °C for 15 min (CemilUsta SSP 125, Istanbul, Turkey). The reinforcement of ZnO nanoparticles decreased the melt flow index of the polymer. The pressure of the hot press was 2.35-

 Table 1 Wood flour, polymer, and nanoparticle content (%)

 Tablica 1. Sadržaj drvnog brašna, polimera i nanočestica (%)

Groups <i>Grupe</i>	Wood/Polymer ratio	Nanoparticle content	
-	Omjer drvo /	Sadržaj nanočestica	
	polimer		
Neat-HDPE	0/100	-	
WPC40	40/60	-	
WPC50	50/50	-	
WPC40-1	40/59	1	
WPC40-3	40/57	3	
WPC40-5	40/55	5	
WPC40-10	40/50	10	
WPC50-1	50/49	1	
WPC50-3	50/47	3	
WPC50-5	50/45	5	
WPC50-10	50/40	10	

2.55 MPa. The dimensions of the panels were 500 mm \times 500 mm \times 4 mm.

2.3 Thermal properties

2.3. Toplinska svojstva

TGA indicates the difference in the weight of samples as a function of temperature or time. DTGA is also obtained by taking the first derivative of TGA curves as a temperature or time function. The WPC samples underwent grinding utilizing an IKA grinder with a 1 mm sieve. The thermal stability of WPCs was determined with Perkin–Elmer STA 6000 thermogravimetric analyzer 4000 (USA). Samples were heated from 30 °C to 600 °C with a heating rate of 10 °C/min under nitrogen gases. Two samples were tested for each group.

The LOI test is one of the most prominent test methods for characterizing the fire behavior of materials due to its ability to analyze small samples. The LOI test determines the minimum oxygen content for the continuing flame combustion of the samples. The LOI test was performed with the Dynisco LOI analyzer (Franklin, USA) (Figure 1) according to ASTM D 2863-19 (2019). The LOI was measured on five samples for each group (with one sample measuring 127 mm \times 12.7 mm \times 5 mm). Each sample was placed in the center of a glass tube in which a mixture of oxygen and nitrogen gas was released. After the gas mixture had expanded the glass tube, the sample was burned with a pilot fire. The sample was monitored during the 50 mm of burning or flaming for 180 s. The higher LOI values indicate resistance to flammability, while the lower LOI values are associated with flammable materials.

2.4 SEM analysis

2.4. SEM analiza

The WPC samples were investigated by a scanning electron microscope (Zeiss, Evo LS10). Before



Figure 1 LOI instrument Slika 1. LOI uređaj

the investigation, WPC samples were dried until constant weight and coated with gold (Emitech, SC7620).

2.5 Statistical analysis

2.5. Statistička analiza

A comprehensive statistical analysis was conducted to explore the data, employing a robust approach involving analysis of variance (ANOVA) followed by post-hoc Duncan testing (significance level set at p < 0.05). This rigorous statistical methodology allowed for a thorough examination of the dataset, and consequently meaningful conclusions could be drawn based on the observed differences among the variables.

3 RESULTS AND DISCUSSION

3. REZULTATI I RASPRAVA

3.1 TGA analysis 3.1. TGA analiza

The behavior of materials against gradual temperature increase is essential for applications. The effect of ZnO nanoparticles on the gradual temperature increase (10 °C/min) was examined by TGA analysis, as seen in Table 2. The degradation of WPCs occurred in three temperature stages, as shown in Figure 2. As the temperature increased, the weight loss of the WPCs increased. First, the moisture released from the samples accelerated after 50 °C, causing a slight weight loss (~3-4 %). The primary degradation (2nd stage) was initiated after 180 °C. It is well-known that the main wood cell wall components, hemicellulose, cellulose, and lignin, begin to degrade above this temperature (Jarukumjorn and Suppakarn, 2009; Rowell, 2012).

It is well known that the thermal stability of wood is lower than that of polymer. Therefore, the first degradation was initiated in the wood cell wall components (Ramesh et al., 2022). Hemicellulose is the most sensitive to thermal degradation among the other cell wall components - degradation of hemicellulose followed by cellulose and lignin. In addition, the increase in wood content has a negative effect on the weight loss of WPCs. As shown in Table 2, the higher the wood content, the higher the weight loss. As the wood content increases, the encapsulation of the wood fibers decreases, which weakens the thermal stability. Meanwhile, the carbonization of wood fiber improves the thermal stability of the polymer due to the thermal shielding effect (Guo et al., 2019a). In addition, the wood content also affects the residue. Wood can contain up to ~ 5 % ash, contributing to the increase in residue.

The degradation temperature of the second stage varied from 175.19 to 204.24 °C, in which hemicelluloses started to degrade first, followed by others. The final degradation stage (above 390 °C) was the decomposition of HDPE. Under the inert atmosphere, the py-

Groups Grupe	Stage Stadij	T onset, ℃	T endset, ℃	T deg., °C	Weight loss, % Gubitak mase, %	Weight onset, % Masa na početku, %	Weight endset, % Masa na kraju, %
Neat-HDPE		327.29	526.47	473	96.70	98.0916	1.395
WPC40	2 nd stage	179.34	398.47	345.64	27.42	98.703	71.286
	3 nd stage	398.47	529.82	473.96	60.72	71.286	10.568
WPC50	2 nd stage	175.19	396.71	344.52	34.17	98.095	63.926
	3 rd stage	396.71	523.27	449.17	51.44	63.926	12.487
WPC40-1	2 nd stage	181.25	398.95	347.4	26.26	98.426	72.169
	3 rd stage	398.95	529.18	474.28	60.36	72.23	11.87
WPC40-3	2 nd stage	188.6	398.95	346.76	26.76	98.469	71.712
	3 rd stage	398.95	530.62	473.32	58.85	71.712	12.867
WPC40-5	2 nd stage	191.31	397.51	347.56	26.87	98.81	71.94
	3 rd stage	397.51	526.94	469.81	57.04	71.94	14.9
WPC40-10	2 nd stage	204.08	395.91	346.28	26.18	98.691	72.51
	3 rd stage	395.91	523.11	468.37	52.69	72.51	19.825
WPC50-1	2 nd stage	189.39	399.74	347.4	31.98	97.887	65.912
	3 rd stage	399.74	530.3	474.44	52.95	65.912	12.959
WPC50-3	2 nd stage	180.93	402.3	349.31	34.71	98.189	63.476
	3rd stage	402.3	529.5	473.16	49.01	63.476	14.469
WPC50-5	2 nd stage	204.24	399.58	346.28	31.64	98.084	66.445
	3 rd stage	399.58	529.98	471.08	48.10	66.445	18.349
WPC50-10	2 nd stage	202.32	404.05	350.75	36.21	96.715	60.509
	3 rd stage	404.05	544.98	466.46	28.89	60.509	31.624

Table 2 TGA values of WPCs**Tablica 2.** TGA vrijednosti WPC-a

rolytic degradation starts the cleavage reactions, resulting in rapid weight loss (Peters, 1979). Therefore, the neat HDPE was easily degraded due to its structure. The DTGA plot also showed the rapid degradation of neat HDPE, as seen in Figure 3. As in the previous study, we found that ZnO nanoparticles limit the interaction with active surface groups by covering the surface (Durmaz *et al.*, 2022). In addition, the nanoparticles cover the materials, which scavenges oxygen from the surface and inhibits scission reactions. The synergistic effect of carbonization of wood and nanoparticles limits the O_2 penetration, creating a barrier to thermal degradation. Therefore, the degradation temperatures were increased due to the heat-shielding role of nanomaterials as well as the carbonization of wood fibers. The increased degradation temperature is crucial because it retards the softening of the matrix and ceases the relaxation process (Xian *et al.*, 2023).

In addition, ZnO nanoparticles inhibited the free radicals that cause thermal oxidative reactions, which reduced the degradation rate and improved thermal stability. Increasing the content of ZnO nanoparticles also



Figure 2 TGA thermograms of WPCs **Slika 2.** TGA termogrami WPC-a



Figure 3 DTG thermograms of WPCs Slika 3. DTG termogrami WPC-a

affected the degradation rate. The nanoparticle layer becomes thicker with increasing nanoparticle content, which increases the heat requirement for free radicals to cause scission reactions. Similarly, Uyup et al. (2019) attributed the higher thermal stability to the higher nanoparticle content. Therefore, the lowest degradation rate was observed for WPC50-10, as shown in the DTGA plot. In addition, HDPE degrades to volatile compounds with no residue above 550 °C (Dorigato et al., 2012). However, the addition of wood and nanoparticles increased the residue, which is essential for fire performance, as discussed below. The highest residue was detected from ZnO50-10. As nanoparticle content increases, they tend to agglomerate, affecting the matrix thermal conductivity, which limits the polymer chain scission reactions (Anu and Pillai, 2022). Therefore, this situation could increase the char residue

for WPC-10. Xu *et al.* (2019) also highlighted the contribution of ZnO nanoparticles to char residue, which limits heat transfer and oxygen penetration.

3.2 LOI test 3.2. LOI test

The effect of ZnO nanoparticles on the fire performance of WPCs was examined by the LOI test. The oxygen is necessary for continuing flaming combustion. Fire-resistant materials also need much more oxygen for flaming combustion than easily combustible materials. As seen in Figure 4, the LOI values of WPCs were between 18.5 to 28.5. Due to its structure, neat HDPE is recognized as a combustible and flammable droplet thermoplastic. Therefore, it can be easily flamed. Free radicals, such as alkyl or alkyl peroxide, are formed due to oxidative reactions during thermal



Figure 4 LOI values of WPCs, with letters indicating significant group differences (p < 0.05) determined by Duncan test **Slika 4.** LOI vrijednosti WPC-a sa slovima koja označavaju značajne grupne razlike (p < 0.05) utvrđene Duncanovim testom



Figure 5 LOI samples **Slika 5.** Uzorci nakon LOI testa

degradation, which initiates polymer chain degradation (He *et al.*, 2012). As the degradation progresses, the free radicals are transformed into CO, CO_2 , and H_2O during degradation. Therefore, the fire resistance of neat HDPE was the lowest. In addition, the conversion to CO, CO_2 , and H_2O during thermal degradation results in low char formation, which reduces the fire performance of the polymer. The reduced char formation also contributes positively to the polymer dripping during the LOI test.

The lignocellulosic materials are critical in reducing the heat release rate, heat release during combustion, and mass loss rate (Borysiak et al., 2006; Kozłowski and Władyka-Przybylak, 2008). Carbonization of wood fiber during carbonization limits O₂ penetration from the surface to the center of the fiber, which improves fire performance. In addition, carbonization of the wood fiber enhances the char formation of WPCs, which limits the dripping of WPCs, as seen in Figure 5. This phenomenon is not neglected for structural applications. The addition of wood flour to the polymer increased the oxygen demand, resulting in higher LOI values. In addition, the polymer penetrates the wood interstices during extrusion. Nanoparticles absorbed by the polymer and deposited in the wood cells provide a barrier that scavenges oxygen from the surface and inhibits oxidation reactions, thereby improving fire performance. The deposited nanoparticles also coat the material, limiting the interaction of components with O₂, which is essential for continued flaming.

The reinforcement with ZnO nanoparticles increased the LOI values up to 28.5 %. Previous studies have also shown that nanoparticles inhibit heat transfer and reduce combustible volatile compounds (Sun *et al.*, 2012; Yin *et al.*, 2022). In addition, the burning drop was improved as the nanoparticles acted as a heat shield. While the combustion behavior of neat HDPE was flaming drips, the reinforced WPCs charred without dripping, which improved the fire resistance. Therefore, the fire classification was upgraded from "flammable or combustible material" to "limited fire retardant of fireresistant material" according to ISO 4589-1 (2017), as a result of reinforced wood fibers and nanoparticles. Adding nanoparticles to WPCs improves fire performance, which is critical for indoor applications.

3.3 SEM analysis 3.3. SEM analiza

The distribution of ZnO nanoparticles in the matrix is crucial in improving fire and thermal performance. Therefore, the structure of WPC samples was investigated by SEM analysis, as seen in Figure 6. SEM images showed that the nanoparticles were welldispersed in the matrix. It was thought that the powder form of polyethylene played a key role in distribution. Mainly, the lowest content resulted in a good dispersion of nanoparticles (white circles). On the other hand, as nanoparticle content increased, the tendency to agglomerate increased (white arrows). As stated in previous studies, the good dispersion of nanoparticles helped to improve the technological properties of WPCs (Durmaz et al., 2022). Likewise, ZnO nanoparticles were well dispersed in the matrix and covered the surface of materials, as clearly seen in the highest content of nanoparticles (Figure 6d, h). As stated above, nanoparticles occurred in thicker layers on the materials with increasing content, which inhibited heat transfer for the scission reaction of the polymer. Therefore, the degradation temperature increased, as explained in the TGA analysis. Moreover, the oxygen penetration was limited. Significantly, the highest nanoparticle content contributed to char formation, which descended the dripping of WPCs during the combustion and improved the fire performance of WPCs.



Figure 6 SEM images of WPCs: a) WPC40-1, b) WPC40-3, c) WPC40-5, d) WPC40-10, e) WPC50-1, f) WPC50-3, g) WPC50-5, h) WPC50-10 (White circles show ZnO nanoparticles, while white arrows show agglomeration of ZnO nanoparticles)

Slika 6. SEM slike WPC-a: a) WPC40-1, b) WPC40-3, c) WPC40-5, d) WPC40-10, e) WPC50-1, f) WPC50-3, g) WPC50-5, h) WPC50-10 (bijelim kružićima označene su nanočestice ZnO, a bijele strelice pokazuju aglomeraciju nanočestica ZnO)

4 CONCLUSIONS

4. ZAKLJUČAK

The petroleum-based polymers and wood are susceptible to thermal degradation. Many prior investigations have predominantly focused on assessing the impact of relatively modest quantities of ZnO nanoparticles in WPCs. However, in this study, we have elevated the thermal stability and fire-resistant characteristics of HDPE-based WPCs by augmenting them with ZnO nanoparticles, with enhancements observed at levels of up to 10%. TGA analysis also clearly demonstrated the thermal behavior of neat HDPE. The gradual increase in temperature leads to the formation of free radicals on the chemical chains of the polymer, which ultimately causes chain scission and mass loss. TGA analysis demonstrated that wood thermal stability was lower compared to polymer. However, the degradation pattern was changed with the addition of wood flour. Although the wood fibers thermally degraded at lower temperatures, the char formation improved the thermal stability. In addition, ZnO nanoparticles cover the surface of materials and insulate them from heat by acting as a heat shield. Therefore, the degradation was slowed down, and the degradation temperature increased. The surface coverage of the nanoparticles also inhibited free radicals, a key factor in the degradation rate. There was a rapid degradation for neat HDPE, while it was very moderate for ZnO nanoparticles.

Oxygen is an essential factor for combustion, as determined by the LOI test for WPCs. Carbonization of wood fiber surfaces inhibits oxygen penetration, which improves fire resistance. Therefore, only wood flour significantly improved the LOI values. In addition, nanoparticle reinforcement also supported insulation and increased oxygen demand. Meanwhile, char formation affected the fire performance. Increasing the wood flour and nanoparticle content increased the char formation, which helped to improve the fire performance. Nanoparticle reinforcement also limited dripping. SEM images indicated that nanoparticles were well-dispersed in the matrix. However, the increase in the nanoparticle content increased the tendency for aggregation. On the other hand, WPCs containing the highest nanoparticles were well covered, which clearly explained why thermal and fire performance improved. Consequently, improving thermal stability and fire performance with ZnO nanoparticles could contribute to improving WPC applications on a large scale. As the application range of WPCs widens, thermal stability is vital for safety in use. The improved thermal resistance makes WPCs safer for many applications, such as siding, decking, playgrounds, gardening furniture, windows, doors, etc.

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