

SYNTHESIS OF EVA-g-MA AND ITS EFFECTS ON TENSILE PROPERTIES AND MORPHOLOGY OF ETHYLENE VINYL ACETATE COPOLYMER/BAMBOO FLOUR AND POLYPROPYLENE/ BAMBOO FLOUR COMPOSITES

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ABSTRACT

Thermoplastic composites reinforced with natural fillers (WPCs) have been being attracted many attentions in recent years. The biggest challenges for WPCs production have to face is the poor adhesion and interaction between the components in the composites. This study investigates the technique to overcome these challenges without the treatment and surface modification of natural additive fillers. The obtained experimental results showed that using maleic anhydride grafted ethylene vinyl acetate copolymer (EVA-g-MA) with 1.16 wt.% of MA could enhance the adhesion and interaction of bamboo flour (BF) with EVA and polypropylene (PP) matrices. The improvements of those properties were reflected in tensile properties and morphological structure of EVA/BF composite and PP/BF composite with the presence of EVA-g-MA. Tensile strength of EVA/BF and PP/BF composites at the same 50 wt% of BF, increased by 67 % and 12 %, respectively when EVA-g-MA was introduced.

Keywords: compatibiliser, wood plastic composites, ethylene vinyl acetate, polypropylene, bamboo flour.

1. INTRODUCTION

Thermoplastic composites reinforced with natural fillers have been gaining many attentions in recent years. These materials have outstanding properties such as environment-friendly behaviours, low density, easy to recycle [1-2]. Consequently, they can be widely applied for decking, siding, indoor building material and so on [3]. However, the use of wood to prepare these composites faces the environmental problem associated with the exploitation and protection of forest. Recently, wood flour has been gradually replacing by bamboo flour in wood plastic composites (WPCs). Bamboo is well known as one of the fastest growing trees in the world with a maturity cycle of 3-4 years [4-5]. Besides, bamboo has high mechanical properties in comparison with the other fibers. Therefore, bamboo flour (BF) is considered as one of the best reinforcing fillers for WPCs.

The biggest challenges for above WPCs production has to face is the quite poor adhesion between bamboo flour and plastic matrix. These issues are often solved by treating BF with alkaline solution or modifying its surface with surfactants in order to improve the compatibility and adhesion between plastic matrices and BF. Sukmawan et al. used BF which were treated with alkaline solution to enhance adhesion with poly (lactic acid) (PLA) [6]. In another work, the mechanical properties of PLA/BF composite were improved by using lysine-diisocyanate (LDI) as a coupling agent to modify the surface of BF [7]. However, the use of solvents in the surface modification of BF is difficult to apply for WPCs manufacture in the industrial scale due to high cost and environmental pollution by solvent release. Therefore, the usage of compatibilizers for manufacturing WPC can help to reduce the demand for solvents and environmental impacts associated with chemical bamboo treatment. Sanjay K. Chattopadhyay et al. utilized polypropylene grafted maleic anhydride (PP-g-MA) as a compatibilizer for polypropylene/bamboo flour composite to improve the adhesion between filler and matrix [8]. In Viet Nam, Bui Chuong and co-workers also indicated that the application of PP-g-MA or maleic anhydride grafted polyethylene copolymer (PE-g-MA) could improve the mechanical properties of WPCs obtained from PP and PE with natural fillers such as bamboo, jute, pineapple, etc.[9-10].

In general, compatible materials such as PE-g-MA or PP-g-MA are commonly used for composites based on polyolefin (PP, PE...) resins, however the application of graft-copolymers from ethylene vinyl acetate copolymer (EVA) for WPCs production have not much been mentioned. This study focused on the synthesis of EVA-g-MA graft copolymers and investigated the interaction and adhesion between EVA-g-MA and BF as well as their effects on the tensile characteristics and morphologies of EVA/BF and PP/BF composites.

2. MATERIALS AND METHODS

2.1. Materials

Ethylene vinyl acetate copolymer (EVA) containing 18 wt.% of vinyl acetate and density of 0.93 g/cm³ was purchased from Honam company (South Korea). Maleic anhydride (MA), purity 99 % and dicumyl peroxide (DCP) were purchased from Merck (Germany). The BF (moisture content < 8 %) of *Dendrocalamus barbatus* (North Vietnam) with diameter of 150 μm was provided by VNDD Ltd. (Vietnam). Acetone, purity 99.7 % and xylene, purity 99.7 % were supplied by Duc Giang chemical company (Vietnam).

2.2. Sample preparation

2.2.1. Synthesis of EVA-g-MA graft copolymers

The EVA-g-MA graft copolymers were synthesized by melt mixing method in an internal mixer (Haake Rheomix 610). The processing temperature, rotor speed, and time mixing were held at the same parameters for all samples. Predetermined amounts of EVA, DCP and MA (as indicated in Table 1) were charged into the mixing chamber which was preheated to constant temperature of 150 °C, the rotor speed was set at 50 rpm. After 5 minutes of mixing, graft copolymers were taken out of the chamber, quickly cut into pieces and cooled down to room temperature.

Table 1. Weights of components for EVA-g-MA preparation.

Sample code	EVA (g)	AM (g)	DCP (g)
EVAg1	45	0.45	0.045
EVAg2	45	0.90	0.090
EVAg3	45	1.35	0.135
EVAg4	45	1.80	0.180

2.2.2. Preparation of EVA-g-MA/bamboo flour composites

EVA-g-MA/BF composites were prepared by mixing different EVA-g-MA copolymers with BF by melt mixing in the Haake Rheomix 610 at 150 °C and rotors speed of 50 rpm for 5 minutes. The ratio weight of EVA-g-MA/BF was kept constant of 80/20 for all samples, as shown in Table 2. After mixing, the molten products were taken out of the chamber and hot pressed at 170 °C with the pressure of 5 MPa into 2-mm thickness sheets. The samples were then cooled down and stored at room temperature for at least 24 hours before characterization.

Table 2. EVA-g-AM/BF composites (wt./wt. of 80/20) with different graft copolymers.

Samples code	EVAgMA copolymer /weight (g)	BF (g)
EVAg1BF	EVAg1 /39.74	9.93
EVAg2BF	EVAg2 /39.74	9.93
EVAg3BF	EVAg3 /39.74	9.93
EVAg4BF	EVAg4 /39.74	9.93

2.2.3. Preparation of EVA/BF composite and PP/BF composite

Table 3. The composition of EVA/BF composites and PP/BF composites.

Samples code	EVA (wt.%)	PP (wt.%)	EVAgMA (G) (wt.%)	BF (wt.%)
EVA/G/BF30	66	-	4	30
EVA/G/BF40	56	-	4	40
EVA/G/BF50	46	-	4	50
EVA/G/BF60	36	-	4	60
EVABF30	70	-	-	30
EVABF40	60	-	-	40
EVABF50	50	-	-	50
EVABF60	40	-	-	60
PP/G/BF30	-	66	4	30
PP/G/BF40	-	56	4	40
PP/G/BF50	-	46	4	50
PP/G/BF60	-	36	4	60
PPBF30	-	70	-	30
PPBF40	-	60	-	40
PPBF50	-	50	-	50
PPBF60	-	40	-	60

EVA/BF and PP/BF composites with different BF contents (30, 40, 50 and 60 wt.%), using 4.0 wt% EVA-g-MA (G) as a compatibiliser were produced in melting state in a internal Haake mixer at rotor speed of 50 rpm for 5 minutes. The processing temperatures for composites production were 150 °C and 175 °C respective to EVA/BF and PP/BF composites. The composition of these composites were listed in Table 3.

2.3. Characterization methods

2.3.1. Determination of MA grafted content in EVAgMA by chemical titration

Removal process of residue MA from EVA-g-MA: A certain amount of EVAgMA copolymer was dissolved in xylene at concentration of 5 wt.% under magnetic stirring at 60 °C for 2 hours. After homogeneous solution was obtained, residue MA was removed from EVA-g-MA by precipitating the solution into excess 20-fold volume of cold acetone, the precipitant was collected and then washed 3 times with acetone, and finally dried in vacuum at 50°C for 24 hours to obtain precipitated EVA-g-MA.

The MA grafted content in EVA-g-MA copolymers was determined by acid-base titration method, as follows: Complete dissolution of 0.3g precipitated EVAgMA in 20 mL xylene at 60 °C for 2 hours, then two drops of 1wt.% phenolphthalein/ethanol solution as an indicator were added into the solution. An excess volume of 0.1N KOH/ethanol (V_{KOH}) was dropwise into the solution to get stable pink color for 30 min under continuous stirring. The unreacted KOH was neutralise by adding dropwise of 0.1N HCl/ethanol solution (V_{HCl}) into reacting solution until pink color disappeared.

The graft content can be calculated according to the formula:

$$\% \text{ grafting ratio} = \frac{m_{MA}}{m_{EVAg-pre}} = \frac{(V_{KOH} - V_{HCl}) \times 0.1 \times 98}{2 \times m \times 1000} \times 100$$

2.3.2. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were recorded using a NEXUS 670 (United States) at the Institute for Tropical Technology with the resolution of 4 cm⁻¹ and 32 scans in the wave number range of 4000 - 400 cm⁻¹. For FTIR sampling, graft copolymers EVAgMA were dissolved in xylene and casted into film with thickness about 20 μm. FTIR of BF was carried out by mixing BF with KBr and pressed into a small disc. Whereas, EVAg3BF was analyzed by using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).

2.3.3. Mechanical properties

Mechanical properties: tensile strength, elongation at break of the composites were measured by using Zwick Z2.5 instrument (Germany) according to DIN 53503, with cross-head speed of 50 mm/min at room temperature. Each sample was measured three times to obtain average results.

3. RESULTS AND DISCUSSION

3.1. The formation of EVA-g-MA graft copolymers

Figure 1 shows FTIR spectra of neat EVA and precipitated EVA-g-MA graft copolymers (EVAg1, 2, 3, 4) which were respectively modified with 1, 2, 3, and 4 wt.% of MA. In FTIR spectrum of neat EVA, C-H stretching vibrations (ν) can be observed in the 3000 - 2800 cm^{-1} range. The peaks at 1739, 1467 and 1371, 1242 cm^{-1} are assigned to C=O stretching, CH_2 in-plane bending (δ_{ip}), CH_3 bending (δ), C-O stretching, respectively (abbreviated as: $\nu(\text{C}=\text{O})$, $\delta_{\text{ip}}(\text{CH}_2)$, $\delta(\text{CH}_3)$, $\nu(\text{C}-\text{O})$) [11].

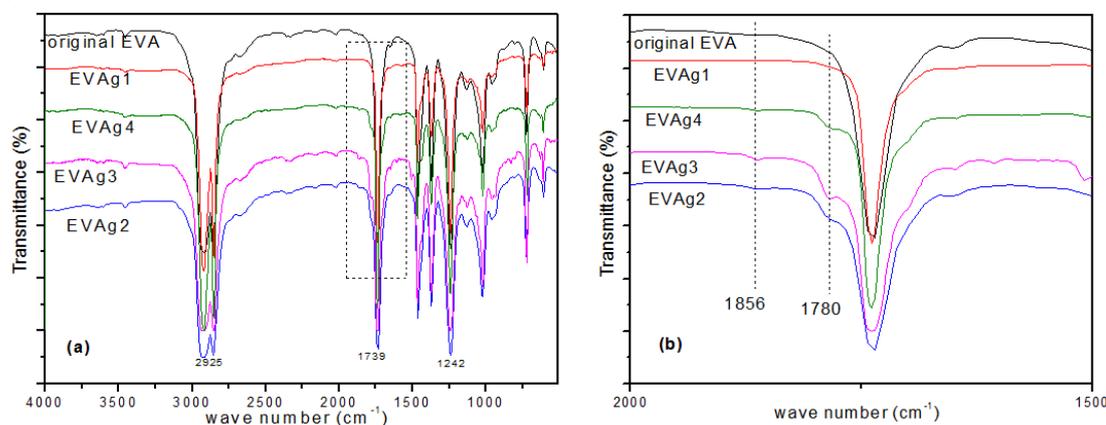


Figure 1. (a) FTIR spectra of original EVA and EVAgAM with different AM content; (b) Zoomed FTIR spectra in region from 1500-2000 cm^{-1} .

In FTIR spectra of EVAg2, EVAg3 and EVAg4 graft copolymer samples, there were new peaks at 1856 cm^{-1} and the shoulders at 1780 cm^{-1} which were attributed to symmetrical and asymmetrical stretching vibrations of C=O of cyclic anhydride when MA was grafted in EVA. This can be clearly observed on the zoomed spectra at the region of 2000 – 1500 cm^{-1} (Fig. 1b). It is worth to mention that MA monomers were grafted on EVA macromolecules. The above peaks was not observed in spectrum of EVAg1 copolymer, it may be due to amount of MA grafted on EVA was too small [12, 13].

Table 4. MA grafted content (wt.%) in EVAgAM.

Sample	EVAg1	EVAg2	EVAg3	EVAg4
MA grafted content (wt.%)	0.28	0.75	1.16	0.98

In addition, it is noticeably that peak intensity of C=O of cyclic anhydride rised as grafted MA content increased. This result is consistent with MA grafted content in EVAgMA by acid-base titration and is presented in Table 4. The content of grafted MA strongly increases with the MA amount introduced into EVA and reaches to the highest value of 1.16 % for EVAg3. However, a slight decrease in the MA grafted content was seen for EVAg4. The decrease is probably due to the competition between grafting and self-polymerizing reactions, which reduced the grafting efficiency as AM content added into EVA is too much [14].

3.2. Investigation of the interaction between EVA-g-AM and BF

Figure 2 (a) and (b) exhibit FTIR spectra of BF and EVAg3BF. Figure 2 (a) is FTIR spectrum of BF showing the peaks at 3420, 1626 cm^{-1} , which can be attributed to the absorption

bands of OH group. The peaks at 2901, 1426, 1384 cm^{-1} and 717 are characteristic of methylene groups in WF. Besides, the vibration of C-O bonds in WF is exhibited at 1053 cm^{-1} .

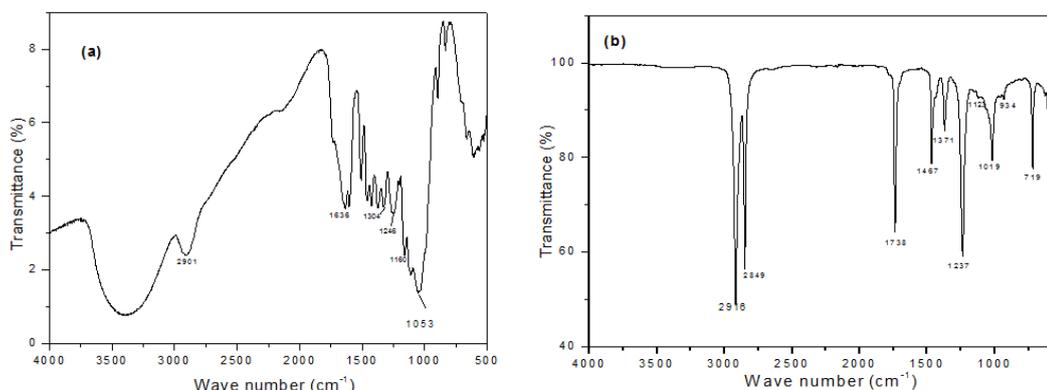
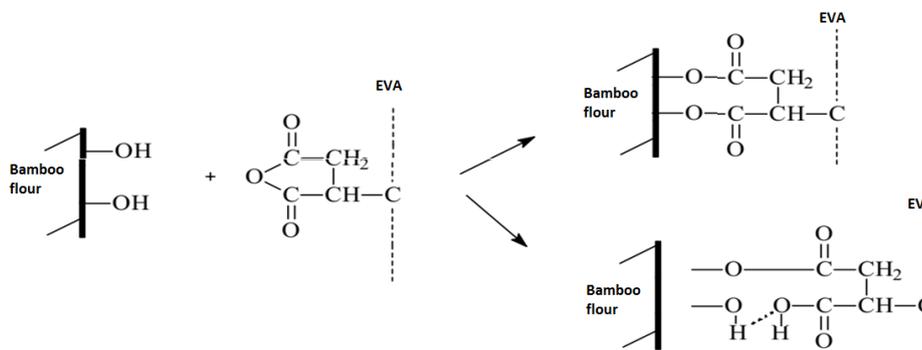


Figure 2. FTIR spectra of BF(a) and EVAg3BF composite (b).

Figure 2 (b) shows some peaks assigned for both BF and EVAg3. In comparison with EVAg3 (as shown in Figure 1), the C-O stretching shifted from 1242 cm^{-1} to lower wave number at 1237 cm^{-1} , it may be due to interaction between EVA and BF which is similar to the results obtained when adding PP-g-AM into PP/BF composites [8]. The interaction between EVA-g-MA with BF includes hydrogen bond between hydroxyl groups on BF surface with C-O-C or carboxyl groups in EVA-g-MA. Besides, during the melt mixing EVA-g-MA and BF, the esterization reaction between hydroxyl on BF surface and anhydride groups in EVA-g-MA may occur as followed [8]:



To prove the role of EVA-g-AM in the improvement in the interactions of EVA with BF, the tensile properties of EVA/BF and EVA-g-MA/BF composites were tested and shown in Table 5. The tensile strength of original EVA is about 14.2 MPa. With the same addition of 20 wt.% BF, tensile strength and elongation at break of both EVA/BF and EVA-g-MA/BF composites decreased. The elongation at break of all composites reduced more than half compared to EVA. However, elongation at break of EVA-g-MA/BF decreased more significantly than that of EVA/BF composites and the reduction increases with the increasing content of MA grafted on EVA. The decrease in tensile strength of EVA/BF composites occurred more sharply, fell down to 6.06 MPa in the comparison with EVA-g-MA/BF composites. Tensile strength of the composites using grafted EVA even increases with the rise of MA grafted content and reaches up to 9.07 MPa for EVAg3BF composites, 49.7 % higher than

that of EVA/BF composites. This increase can be explained by the presence of MA that improves the interaction and adhesion between EVA matrix and BF filler as mentioned above. The highest increase in tensile strength seen in EVAg3BF can be attributed to the greatest improvement of the interaction and adhesion between EVA matrix and BF as the MA content grafted on EVA reached the maximum value, which is confirmed in above section. Obviously, thanks to the grafting MA on EVA molecules, the interaction and adhesion between EVA and BF is enhanced, thus the mechanical properties of the obtained composites are improved. This suggests that EVAgMA can be used as a compatibilizer for the olefin composites reinforced with natural additive filler such as BF.

Table 5. Tensile strength and elongation at break of EVA-g-AM/BF (80/20) composites.

Sample	Tensile characteristics	
	Tensile strength (MPa)	Elongation at break (%)
EVA	14.20	640
EVABF	6.06	330
EVAg1BF	6.60	291
EVAg2BF	7.55	288
EVAg3BF	9.07	266
EVAg4BF	9.00	256

3.3. Effect of EVA-g-AM on tensile properties and morphologies of EVA/BF and PP/BF composites

Table 6. The effect of EVA-g-MA on tensile characteristics of EVA/BF and PP/BF composites.

BF content (wt.%)	Tensile characteristics							
	Tensile strength (MPa)				Elongation at break (%)			
	PP/BF	PP/G/BF	EVA/BF	EVA/G/BF	PP/BF	PP/G/BF	EVA/BF	EVA/G/BF
0	28.02	28.02	14.20	14.20	145.12	145.12	640	640
30	22.63	23.25	5.93	9.31	4.43	4.02	332	291
40	16.69	18.71	6.31	11.00	3.43	2.30	230	200
50	15.01	17.80	7.42	12.32	1.80	1.78	47	30
60	15.24	17.06	7.05	11.24	1.76	1.62	11	18

To evaluate the effectiveness of mechanical improvement for WPC material, EVAg3 (G) was used as compatibilizer for preparing EVA/BF and PP/BF composites with various BF contents. Tensile strength and elongation at break of EVA/BF and PP/BF composites are shown in Table 6. In term of elongation at breaks, there is a dramatic decrease for all samples as BF

content increases. Particularly, elongation at break of PP/BF and PP/G/BF composites are not much different and these values are lower than 5 % for all PP/BF composites.

For EVA/BF composites, the elongation at break of EVA/G/BF composites are lower than that of EVABF composites. This decrease can be explained by the presence of EVA_g3 (G) which helps to improve the adhesion of matrix and filler and that might restrict EVA molecular mobility under the impact of tensile stress.

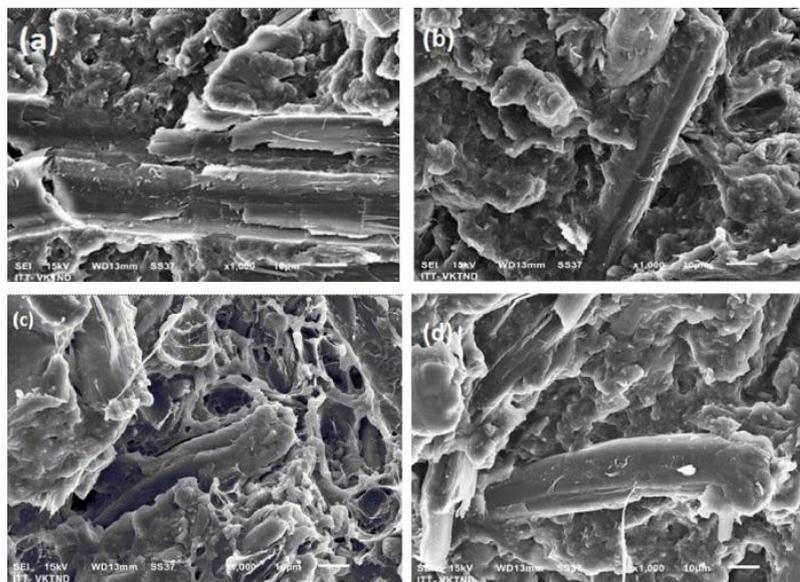


Figure 3. The SEM fractured surface images of (a) EVA/BF composite; (b) EVA_g/BF composite; (c) PP/BF composite and (d) PP/G/BF with same 50 wt.% of BF content.

With BF addition, the tensile strength of PP/BF composite showed a gradual downtrend from 28.01 MPa for neat PP to 15.24 MPa for composites filled 60 wt.% of BF. This may be due to the difference in hydrophobicity of BF and PP resin, leading to the poor interaction and adhesion of BF with PP matrix. However, a much less decrease in tensile strength was also seen for the PP/G/BF composites containing 4 wt.% EVA_g3. At 60 wt.% of BF content, the tensile strength of PP/G/BF composite was about 17.06 MPa and increase by 12 % in comparison to the PP/BF composite. For EVA/BF composites, the introduction of BF reduced the tensile strength of EVA. However, there is a slight increase in tensile strength for EVA/BF composites with the BF content. At 50 wt% of BF content, the tensile strength of the composites reached a peak of 7.42 MPa and then slowly decreased to 7.05 MPa as BF content ascended 60 wt.%. In the case of EVA/G/BF composites, tensile strength has been strongly improved thanks to the presence of EVA_g3. Similarly, EVA/G/BF sample reaches to the highest value of 12.32 MPa, about 1.67 times higher than EVA/BF composites at the same 50 wt.% of BF. This means that there is a good adhesion between the matrix and the filler at the interfacial phase, resulting in the higher tensile strength for EVA/G/BF samples. EVA_g3 plays a role of a compatibilizer with higher performance for EVA/BF composites than PP/BF composite. It is clearly understood due to higher polarity of EVA in comparison with PP.

Figure 3 shows SEM fractured surface images of EVA/BF composites and PP/BF composites. In Figure 3(a) and (b), there is no void appeared between EVA resin and BF. This means that the adhesion between the matrix and the fillers is relative good. It is worth noting that

the same morphologies were observed for the EVA/BF composite without the compatibilizer. This can be explained that interaction between the polar functional groups of EVA and hydroxyl groups on BF surface is sufficient to create the interfacial adhesion and to form the continuous structure at the interphase of EVA and BF.

In Figure 3 (c), the gaps at interface of PP matrix and BF are shown, this suggests that the adhesion and interaction between PP matrix and BF is quite poor. For the PP/G/BF composite, these gaps disappeared (Fig.3.d). This indicates an improvement of the compatibility between PP and BF due to the addition of EVA-g-MA.

4. CONCLUSIONS

Graft copolymer EVA-g-MA was successfully produced by melt mixing with the highest content MA grafted on EVA reaching 1.16 wt.%. The presence of MA improved the interaction between EVA-g-MA and BF, thus, enhanced tensile properties of EVA-g-MA/BF composites. The addition of EVA-g-MA into EVA/BF and PP/BF composites formed the good adhesion at the interface of polymer matrix and BF filler and helped to significantly improve the tensile properties of these composites. These results proved that EVA-g-MA could be used as a compatibilizer for WPCs production.

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