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EVA/starch/POE composite for footwear material: How the chemical composition affects its properties compared to standards

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ABSTRACT

The usage of biodegradable foam material in footwear components has positive impacts on environmental sustainability when disposed into landfills. This study was aimed to investigate the effects of polyolefin elastomer (POE) on its properties of foamed EVA/cassava starch composites compared to standards. Foamed EVA/cassava starch composites were prepared by mixing EVA, cassava starch, and additives using a two-roll mill laboratory scale. Content of POE was varied 10-20 phr. The ratios of EVA/cassava starch were varied from 90/10; 80/20; 70/30; and 60/40. Effects of POE were characterized its density, tensile properties, tear strength, permanent set, abrasion resistance, flex resistance, morphology, and biodegradability. It was found that the increase of POE content in EVA/starch composites increased the density and abrassion resistance, but decreased the tensile strength, elongation at break, and permanent set properties. The best formula of foamed EVA/cassava starch/POE composites for footwear materials contains EVA 80 phr, starch 20 phr and POE 20 phr with density 0.983 g/cm^3, tensile strength 22.27 kg/cm^2, elongation at break 645.67%, tear strength 9.42 N/mm, volume loss 88.907 mm, no crack when flexed 150 kcs. These results met the requirements of SNI 0778:2009-Sol Karet Cetak for quality classification 3 of outsoles. The foamed composite containing POE20 has denser morphology than POE10, while the addition of POE has no significance in weight loss after burial test.

Keywords: EVA, modified starch, outsole material, polyolefin elastomer.

INTRODUCTION

Polyolefin Elastomer (POE) is an elastic polymer-modified from ethylene and α-olefins. Polyolefin Elastomer (POE) has excellent properties, such as superior elasticity, strong tensile strength, excellent thermal stability, aging resistance, weather resistance, resistance to ozone, resistant to chemical media, low density, easy processability, and low cost. Therefore it is widely used for impact modifier (Kim *et al*., 2017; Yang *et al*., 2020a; Yang *et al*., 2020b).

Polymer foams are used extensively in a wide range of industries, including footwear, automotive, electronic, sports equipment, and packaging industries. One of the most widely used polymers for foam used in the footwear industry is ethylene-vinyl acetate (EVA). In the footwear industry, EVA foam has commonly used as outsole, insole, and midsole shock-absorbing material. Ethylene-vinyl acetate copolymer EVA resin has excellent flexibility, rubber elasticity, excellent transparency and surface gloss properties, excellent aging resistance, and resistance to ozone strength. EVA foam material is a lightweight material, soft, comfortable, good resilience, chemical corrosion resistance, and relatively inexpensive (Ferreira *et al*., 2018; Guo *et al*., 2021). However, the mechanical properties of single EVA foam materials often can not meet the requirements of sports shoes. To improve the performance and the biodegradability of material foaming, the starch modifiers are added (Hamadache *et al*., 2019; Zhang *et al*., 2014; Rodriguez-Perez *et al*., 2012).

The addition of POE to increase the quality of the foams in the foamed polymer materials has been reported by Wang *et al*. (2016), Gong *et al*. (2018), and Liu (2018). However, there was no report in detail about the effects of POE content on these properties of EVA/cassava starch composite. Therefore, in this study, EVA/cassava starch composites with POE were prepared, and the effects of POE content on these properties of EVA/cassava starch composite were investigated. The combination of EVA and polyolefin elastomer that crosslinked expected provides a material with stronger mechanical properties, but still maintains its softness and toughness, so it can be used as a footwear material. This study was aimed to investigate the effects of POE on the properties of foamed EVA/cassava starch composites compared to standards.

MATERIALS AND METHODS

Materials

Rubber grade EVA (Levapren 500) with vinyl acetate (VAc) content of 50 wt%, Indonesia tapioca flour (trade name Orang Tani), and polyolefin elastomer (POE) were purchased from local suppliers. The commercial-grade of chemicals such as dicumyl peroxide (DCP) as a crosslinking initiator, glycerol and water as a starch plasticizer, $CaCO_3$ (filler), azodicarbonamide (ADCM) as a foaming agent, ZnO as an activator, stearic acid as a co-activator, Zn stearic as a lubricant were purchased from a local supplier. The compost and effective microorganism 4 (EM4) were purchased from a local market.

Methods

Modification of cassava starch

Firstly, cassava starch was modified by mixing the starch with water and glycerol at ratio of starch, glycerol, water were 60:25:15, respectively. These materials were mixed thoroughly by using a high-speed mixer at 350-500 rpm until attaining a homogeneous powdered for 45 minutes. The mixture then was kept for 2 days in a plastic bucket to plasticize and swell the granular starch molecule.

Preparation of foamed EVA/cassava starch composites

Foamed EVA/cassava starch composites were prepared by mixing EVA, cassava starch, and additives using a two-roll mill laboratory scale. The composites were developed according to the formulation in Table 1. Content of POE was varied 10-20 phr. The ratios of EVA/cassava starch were varied from 90/10; 80/20; 70/30; and 60/40. After completion of the mixing process, the composites were rested for 24 h at 25 ºC before subsequent processes. Subsequently, these foamed EVA/cassava starch composite were molded into a sheet using an electrically heated hydraulic press at 165 ºC, 150 kg/cm^2 for 15 minutes (for 2+0.1 mm thickness) and 20 minutes (for 6+0.1 mm thickness).

Characterization

Tensile strength, elongation at break, and tear strength were tested on a Universal Tester (UTM, Tinius Olsen-H25K). Specimens for tensile strength and elongation at break were manufactured according to ISO 37:2017(E) using dumbbell type 2 samples. The test was performed at laboratory temperature (23 ± 2 °C) at a crosshead speed of 500 mm/min. The tensile strength of the test piece was measured using the angle test piece according to ISO 34-1:2015 (E). In all cases, the values shown were averages from three measurements.

The density was tested by comparing sample masses in air and water using an Electron Density Meter (Mirage EW200SG) according to ISO 2781:2018 (E) Method A. The abrasion resistance test was performed using an ISO-compliant rotary drum abrasion resistance tester (Bareiss). The test was conducted using a cylindrical test piece with a diameter of 16±0.2 mm and a height of 6 mm based on ISO 4649:2017. The results of the abrasion resistance test were expressed as relative volume loss compared to a polished sheet calibrated with a standard reference mass.

The 50% permanent set (permanent elongation) test was characterized according SNI 0778:2009 using a permanent set tester. The flex resistance was tested using a Ross flexing machine as the flex followed by 150 kcs according to SNI 0778:2009. The morphology of the compound swollen from EVA/modified starch was determined by the video measurement system (ARCS-SI 901).

The biodegradation test was carried out using the burial method in compost soil. The biodegradability of foamed EVA/modified starch compounds was assessed by Weight Loss Percentage (WLP) according to ASTM D5988-

Table 1. Composition of EVA/cassava starch foamed composites.

Materials	Ratio (phr)							
EVA	90	90	80	80	70	70	60	60
starch	10	10	20	20	30	30	40	40
POE	10	20	10	20	10	20	10	20

*phr: parts per hundred parts of resins by weight. Another additives was fixed as $CaCO_3$ = 1 phr, ZnO = 3 phr, Zn stearate = 0.5 phr, Stearic acid = 2 phr, DCP = 0.5 phr, ADCM = 5 phr.

18. The mixture was cut into a dumbbell shape (dumbbell type 2 sample). These dumbbell samples were buried in plastic pots containing compost enriched with Effective Microorganisms 4 (EM4). The compost contained of fertilizer, charcoal husks, sand, soil, and coconut. Samples were buried in compost at a depth of 10 cm from the surface to be exposed to microbial attack in the compost. The test period was 14 days and lasted 48 days. The WLP formula used equation (1).

$$WLP\ (\%) = [(W_0 - W_1)/W_0] \times 100\% \quad (1)$$

Where WLP (%) indicated the rate of weight loss of the sample. W_1 meant the weight of the sample after deterioration. W_0 indicated the weight of the sample before deterioration.

RESULTS AND DISCUSSION

Density

Effect of POE on the density of the foamed EVA/starch composites were presented in Figure 1. The density of foamed EVA/starch composites increased along with the increase of POE content (Figure 1) at various EVA/starch ratios. This may be caused by the increased viscosity of the composite when the POE content increased. According to Hemmasi *et al*. (2011), the increased viscosity would inhibit the foam from rising and therefore the density of the foamed composites would increase. When associated with Figure 6, the morphology of the foamed composite containing POE 20 (Figure 6b, 6d, 6f, and 6h) was denser than the foamed composite containing POE 10 (Figure 6a, 6c, 6e, and 6g). The density of POE was in the range of 0.886 to 0.912 g/cm^3. The density values of the composite containing POE 20 at the composition of the EVA/starch ratio of 90/10, 80/20, 30/70, and 50/40 were 0.777, 0.893, 0.887, and 0.883 g/cm^3 respectively. The maximum density value of sole material according to SNI 0778: 2009 Sol Karet Cetak is 1.4 g/cm^3, and Figure 1 presented that the density of all foamed EVA/starch composites met the requirements of the Indonesia National Standard SNI 0778:2009-Sol Karet Cetak.

Tensile Properties

The effect of POE on the tensile properties (tensile strength and elongation at break) of foamed EVA/starch composites was shown in Figure 2. Figure 2a showed that POE 20 phr (POE20) gave the optimum tensile strength value for the composite containing EVA 80 phr, while POE 10 phr (POE10) gave the optimum tensile strength value for the composite containing EVA 70 phr. The tensile strength values for composites with EVA/starch ratio 80/20 with POE content of 10 phr and 20 phr were 16.5 kg/cm^2 and 22.27 kg/cm^2, respectively. This meant that POE20 increased the tensile strength by 34.97%. Composite with EVA/starch at ratio 70/30 with POE content of 10 phr and 20 phr respectively were 21.53 kg/cm^2 and 13.37 kg/cm^2, meaning that POE20 decreased in tensile strength value by 37.9%. The decreased in tensile strength at the higher starch concentration (30-40 phr) was due to the low compatibility between POE and the EVA/starch composites. This showed that the more starch molecules which could occupy the intermolecular space of the EVA chain, the interaction of EVA and starch became more significant than the interaction of POE with EVA/starch composites as a matrix, which resulted in easy brittleness if exposed to tension.

According to ISO/TR 20880:2007 Footwear – Performance requirements for components for footwear – Outsoles, the tensile properties (tensile strength and elongation at break) are not required. However, according to the Indonesian National Standard (SNI), the tensile properties became a requirement for molded rubber sole not for the foamed outsole. According to SNI 0778:2009 Sol Karet Cetak, a minimum tensile strength value for quality classification 3of outsoles are 50 kg/cm^2. Therefore, the tensile strength of the resulting foamed EVA/starch composites did not meet the Indonesian National Standard SNI 0778:2009 requirements. Ke *et al*. (2011) reported that the tensile strength of EVA material for sneaker sole with EVA/starch ratios of 90/10 and 80/20 was 1.6 and 2.2 Mpa (16 and 22 kg/cm²), respectively, this value was similar to the results of this study.

POE20 showed slightly higher elongation at break value than POE10 at various EVA/starch ratios (Figure 2b). This showed that POE can increase the EVA/starch matrix ductility. The same result was obtained by Wu *et al*. (2015) with the study of polypropylene/ethylene–octene copolymer (PP/POE) blends. The maximum elongation at break value (697.67%) was presented by the composite containing POE 10 and EVA 70 phr. According to SNI 0778:2009 Sol Karet Cetak, the minimum elongation at break value is 150%. From Figure 2b, it can be seen that the elongation at the break of all the foamed EVA/starch composites met the requirements of SNI 0778:2009 Sol Karet Cetak.

Tear Strength

Effect of POE on the tear strength of foamed EVA/starch composites were presented in Figure 3. POE10 presented an increase in the tear strength value of foamed EVA/starch composites compared to POE20. The maximum tear strength value (10.39 N/mm) of foamed EVA/starch composites was shown by the composite containing POE20 and EVA/starch ratio 80/20. The tear strength values of the composite containing POE10 at the composition of the EVA/starch ratio of 90/10, 80/20, 30/70, and 50/40 were 7.98, 10.39, 8.39, 8.83, respectively.

According to ISO/TR 20880:2007 Footwear – Performance requirements for components for footwear – Outsoles, the minimum tear strength is 8,0 N/mm (for density ≤ 0.9 g/cm³) or 6.0 N/mm (for density > 0.9 g/cm³), therefore the tear strength of almost all the resulting foamed EVA/starch composites met the requirements of ISO/TR 20880:2007 Footwear – Performance requirements for components for footwear – Outsoles, except composite with 90/10 of EVA/starch ratio contains both POE10 and POE20.

Permanent Set

A permanent set of 50% is the amount of permanent change in length of the material that occurs when a material is stretched at 50%

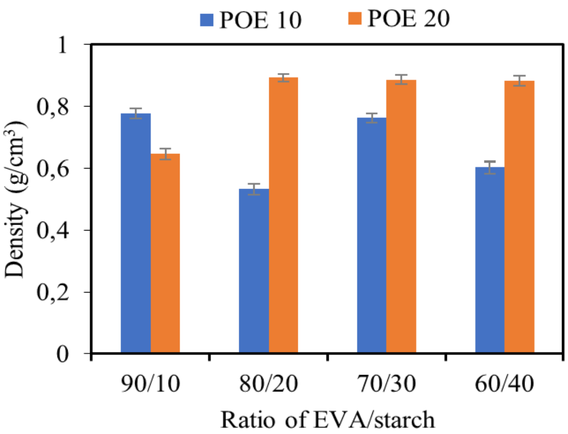


Figure 1. Effect of POE on the density of the foamed EVA/starch composites.

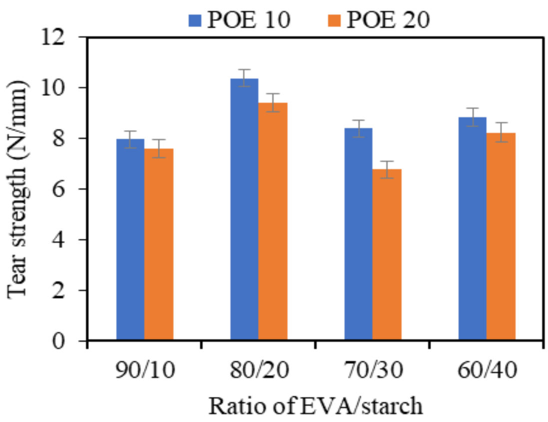
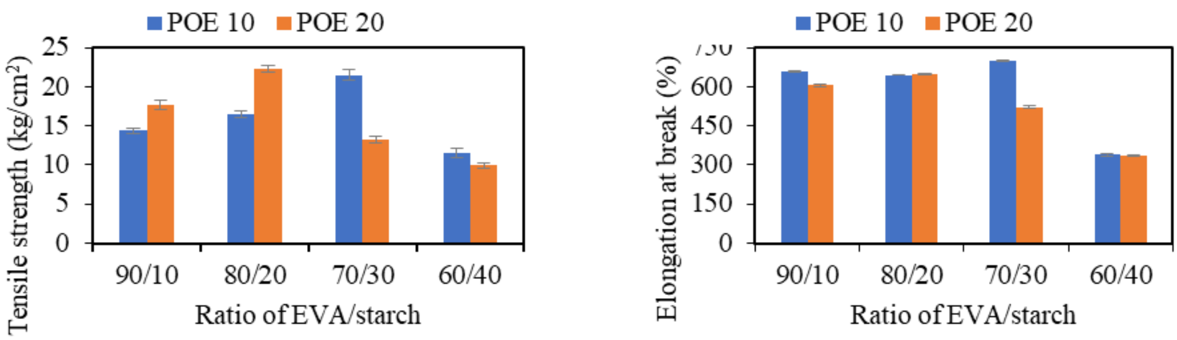


Figure 3. Effect of POE on the tear strength of foamed EVA/starch composites.



(a) (b)

Figure 2. Effect of POE content on tensile strength (a) and elongation at break (b) for the foamed EVA/starch composites.

elongation for a specified time. The effect of POE on the permanent set of foamed EVA/starch composites was shown in Figure 4. It showed that POE20 increased the permanent set of foamed EVA/starch composites.

POE10 slightly decreased the 50% permanent set value of foamed EVA/starch composites (Figure 4). The maximum and the minimum 50% permanent set value of foamed EVA/starch composites containing POE 10 were 9.27 and 6.62 N/mm. The value of 50% permanent set for rubber sole required by SNI 0778: 2009 is a maximum of 6%. Therefore, the permanent set value of the foamed EVA/starch composites did not meet the Indonesia National Standard SNI 0778:2009 requirements.

Abrasion Resistance

Abrasion resistance is expressed as a relative volume loss of the composites. Composites that have smaller volume loss indicate better abrasion resistance. Figure 5 showed the effect of POE on the abrasion resistance of foamed EVA/starch composites.

POE20 slightly decreased the volume loss value of foamed EVA/starch composites (Figure 5). The minimum volume loss value of foamed EVA/starch composites (88.907 mm) was shown by composite that containing POE20 with EVA starch ratio 80/20. This was attributed to the good compatibility between POE and EVA/starch composites. The composites with more starch molecules that fill the intermolecular spaces of the EVA chain had more significant interaction between starch and EVA than the interaction of POE with EVA/starch composites thus it was easily break when exposed to friction. The volume loss value of foamed EVA/starch composites that containing POE20 with EVA starch ratio 80/20 met the requirements of SNI 0778:2009-Sol Karet Cetak. The volume loss required by SNI 0778:2009-Sol Karet Cetak is maximum 350 mm^3.

Flex Resistance

Flexion property indicates the resistance to successive folding and unfolding movements during testing. The flexing resistance of the foamed EVA/cassava starch composites was presented in Table 2. Flex resistance requirements according to SNI 0778:2009-Sol Karet Cetak is no crack. Table 2 showed flexing resistance of the foamed EVA/cassava starch composites containing POE10 and POE20 produced in this study met the requirements of SNI 0778:2009. Therefore, POE10 and POE20 gave a positive effect on the flex resistance of foamed EVA/cassava starch composites.

Morphology

Figure 6 illustrated the differences in foamed composite morphology at different POE content and ratio of EVA/starch ratio. For composites containing POE20, a more aggregated dispersion with enlarged particles was observed than for composites containing POE10. It indicated poor compatibility between the EVA/starch matrix and POE due to EVA being hydrophilic and POE being hydrophobic chemically. Hence, these were not compatible with each other. The effect of POE addition into the composite was the morphology of the foamed composite containing POE20 (Figure 6b, 6d, 6f, and 6h) became denser than the foamed composite containing POE10 (Figure 6a, 6c, 6e, and 6g).

Biodegradability

Effect of POE on the weight loss of foamed

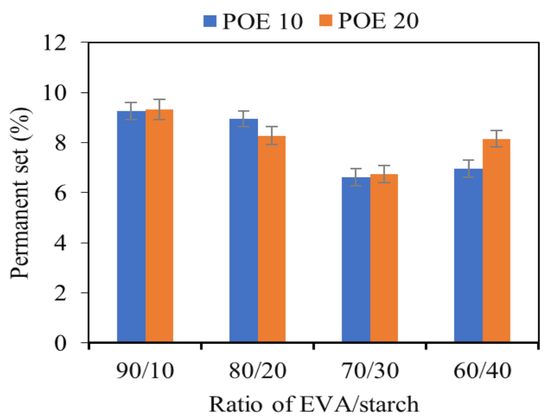


Figure 4. Effect of POE on the permanent set of foamed EVA/starch composites

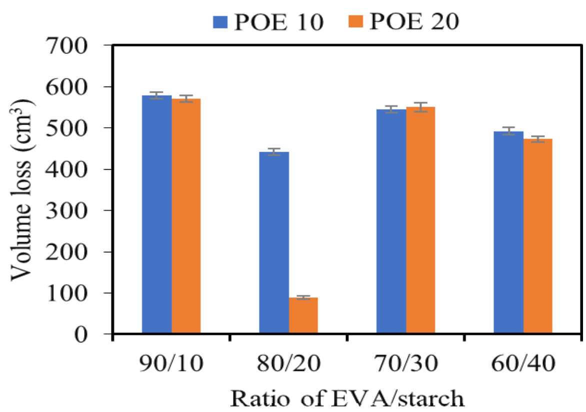


Figure 5. Effect of POE on the abrasion resistance of foamed EVA/starch composites.

Table 2. Flexing resistance of the foamed EVA/cassava starch composites.

Testing parameter	Ratio of EVA/starch/POE							
	90/10/10	90/10/20	80/20/10	80/20/20	70/30/10	70/30/20	60/40/10	60/40/20
Flexing resistance for 150kcs	No crack	No crack	No crack	No crack	No crack	No crack	No crack	No crack

EVA/cassava starch composites at different modified starch content after compost burial test was shown in Figure 7. The weight loss of all samples increased with increasing burial time, with the fastest weight loss occurred in the first 14 days. This showed that the longer the composite was buried, the more biodegradable components can be decomposed by microorganisms. Overall, the largest weight loss was in F3P1 (EVA/starch 70/30, POE10). Rodriguez-Perez *et al.* (2012), Macedo and Rosa (2015), and also Sessini *et al.* (2019) stated that thermoplastic starch has been reported to deliver better biodegradability. Based on Figure 7, F3 has a greater weight loss than F4. This can be caused by the trapping of starch in the EVA-POE blends that made microorganisms

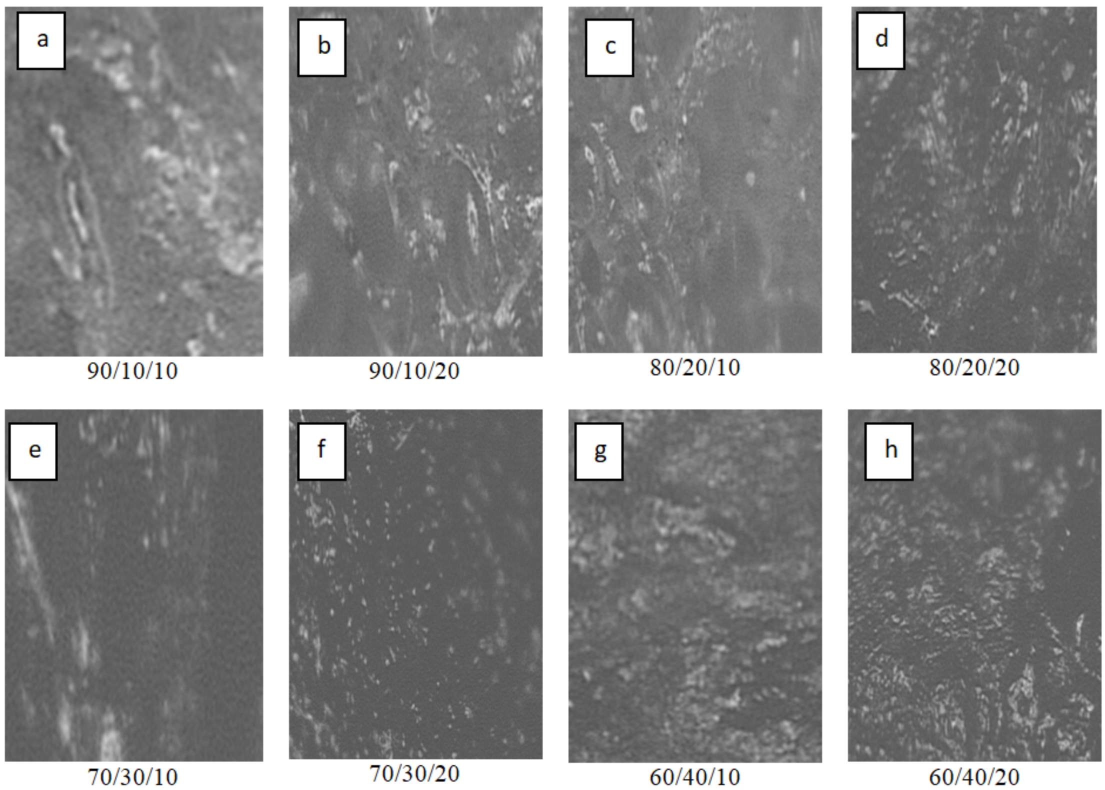


Figure 6. Morphology image of the EVA/modified starch/POE expanded compounds with different modified starch content.

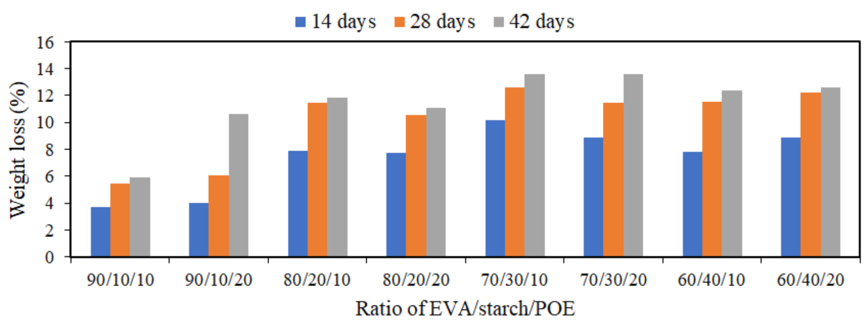


Figure 7. Effect of POE on the weight loss of foamed EVA/cassava starch composites at different modified starch content after compost burial test.

difficult to digest. In general, the addition of a POE of 10 or 20 did not have a significant impact on weight loss.

CONCLUSIONS

In this research, foamed EVA/starch composite for footwear material was developed. The increasement of POE content in EVA/starch composites increased the density and abrassion resistance, but decreased the tensile strength, elongation at break, and permanent set properties. The best formula of foamed EVA/cassava starch/POE composites for footwear materials was 80/20/20 which contained EVA 80 phr, starch 20 phr and POE 20 phr resulted density 0.983 g/cm³, tensile strength 22.27 kg/cm², elongation at break 645.67%, tear strength 9.42 N/mm, volume loss 88.907 mm, no crack when flexed 150 kcs. These results have met the requirements of SNI 0778:2009-Sol Karet Cetak for quality classification 3 of outsoles. The foamed composite containing POE20 has denser morphology than the foamed composite containing POE10, while the addition of POE did not have a significant impact on the weight loss of foamed EVA/starch composites.

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REFERENCES

ASTM International. (2018). *ASTM D5988-18 Standard test method for determining aerobic biodegradation of plastic materials in soil*. PA, USA: ASTM.

BSN (Badan Standardisasi Nasional). (2009). *SNI 0778:2009 Sol karet cetak*. Jakarta, Indonesia: BSN.

Ferreira, E. J., Dias, M. M. & Schneider, E. L. (2018). Analysis of non-uniform expansion behavior of injected EVA. *Academic Journal of Polymer Science*, *1*(4), 61–65. https://doi.org/10.19080/AJOP.2018.01.555569

Gong, W., Fu, H., Zhang, C., Ban, D., Yin, X., He, Y., He, L. & Pei, X. (2018). Study on foaming quality and impact property of foamed polypropylene composites. *Polymers*, *10*(12), 1375. https://doi.org/10.3390/polym10121375

Guo, Y., Hao, X., Liang, G. (2021). Modification and properties of eva foamed material with hemp stem powder. *Journal of Physics: Conference Series*, *1759*, 012013. https://doi.org/10.1088/1742-6596/1759/1/012013

Hamadache, H., Djidjelli, H., Boukerrou, A., Kaci, M., Jofre-Reche, J. A., & Martín-Martínez, J. M. (2019). Different compatibility approaches to improve the thermal and mechanical properties of EVA/starch composites. *Polymer Composites*, *40*(8), 3242–3253. https://doi.org/10.1002/pc.25179

Hemmasi, A. H., Khademi-Eslam, H., Pourabbasi, S., Ghasemi, I., & Talaiepour, M. (2011). Cell morphology and physicomechanical properties of HDPE/EVA/rice hull hybrid foamed composites. *Bioresources*, *6*(3), 2291–2308.

ISO (International Standard Organization). (2015). *ISO 34-1:2015(E) Rubber, vulcanized or thermoplastic — Determination of tear strength — Part 1: Trouser, angle, and crescent test pieces*. Geneva, Switzerland: International Standard Organization

ISO (International Standard Organization). (2017a). *ISO 37:2017(E) Rubber vulcanized or thermoplastic – Determination of tensile stress-strain properties*. Geneva, Switzerland: International Standard Organization.

ISO (International Standard Organization). (2017b). *ISO 4649:2017 Rubber, vulcanized or thermoplastic — Determination of abrasion resistance using a rotating cylindrical drum device*. Geneva, Switzerland: International Standard Organization.

ISO (International Standard Organization). (2018). *ISO 2781:2018(E) Rubber, vulcanized or thermoplastic — Determination of density (Method A)*. Geneva, Switzerland: International Standard Organization

Ke, Y., Cheng, S., Zhang, Q., & Liu, C. (2011). *EVA material for sneaker sole and preparation method thereof*. China patent CN102134349B.

Kim, D. Y., Kim, G. H., Lee, D. Y., & Seo, K. H. (2017), Effects of compatibility on foaming behavior of polypropylene/polyolefin elastomer blends prepared using a chemical blowing agent. *Journal of Applied Polymer Science*, *134*, 45201. https://doi.org/10.1002/app.45201

Liu, L. (2018). Comparison of shock absorption performance of basketball shoe with different sole structures. *Leather and Footwear Journal*, *18*(1), 45–52. https://doi.org/10.24264/lfj.18.1.6

Macedo, J. R. N., & Rosa, D. S. (2015). Effect of fiber and starch incorporation in biodegradation of PLA-TPS-cotton composites. *Key Engineering Materials*, *668*, 54–62. https://doi.org/10.4028/www.scientific.net/KEM.668.54

Rodriguez-Perez, M. A., Simoes, R. D., Roman-Lorza, S., Alvarez-Lainez, M., Montoya-Mesa, C., Constantino, C. J. L., & de Saja, J. A. (2012). Foaming of EVA/starch blends: Characterization of the structure, physical properties, and biodegradability. *Polymer Engineering and*

Science, *52*(1), 62–70. https://doi.org/10.1002/pen.22046

Sessini, V., Arrieta, M. P., Raquez, J. M., Dubois, P., Kenny, J. M., & Peponi, L. (2019). Thermal and composting degradation of EVA/Thermoplastic starch blends and their nanocomposites. *Polymer Degradation and Stability*, *159*, 184–198. https://doi.org/10.1016/j.polymdegradstab.2018.11.025

Wang, S., Ameli, A., Kazemi Y., Kong, T., Park, C. B., & Naguib, H. E. (2015). Decoupling the effects of cell size and relative density on electrical conductivity in polystyrene/MWCNT nanocomposite foams. FOAMS® Conference (Sept.10-11, 2015)

Wu, J., Chen, C., Wu, Y., Wu, G., Kuo, M. C., & Tsai, Y. (2015). Mechanical properties, morphology, and crystallization behavior of polypropylene/elastomer/talc composites. *Polymer Composites*, *36*(1), 69–77. https://doi.org/10.1002/pc.22914

Yang, F., Pan, L., Ma, Z., Lou, Y., Li, Y., & Li, Y. (2020). Highly elastic, strong, and reprocessable cross-linked polyolefin elastomers enabled by boronic ester bonds. *Polymer Chemistry*, *11*, 3285–3295. https://doi.org/10.1039/D0PY00235F

Yang, F., Wang, X., Ma, Z., Wang, B., Pan, L., & Li, Y. (2020). Copolymerization of propylene with higher-olefins by a pyridylamidohafnium catalyst: An effective approach to polypropylene-based elastomer. *Polymers*, *12*, 89. https://doi.org/10.3390/polym12010089.

Zhang, Y. F., Zheng, Y. Y., Liu, Y., Xiao, Y. Y. (2014). The preliminary research on EVA sole foaming materials with wet grafted starch. *Functional Materials*, *44*(15), 2253–2257. https://doi.org10.3969/j.issn.1001-9731.2013.15.027