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Mechanical and degradability properties of polyethylene/ PBL composites in a wet-dry controlled environment

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Abstract

Several blends of polyethylene (PE) and powdered breadfruit leaf (PBL) were prepared in an internal mixer at a temperature above the glass transition of PE without additives. Formulations were based on PE/PBL ratio of 100/0, 90/10, 85/15, 80/20 and 75/25 on a dry weight basis. The effects of PBL content on the composite mechanical properties was evaluated in terms of tensile, flexural and hardness Rockwell test. The results showed increase of elastic and flexural modulus of the composites with increasing PBL contents. The tensile strength, yield strength, yield strain and hardness decreased with increasing PBL contents in the composites. The flexural strength slightly decreased with the presence of the PBL but independent on the percentage of the PBL particles. Degradability of the composites was investigated using wet–dry cycle test. It was found that the composite with higher content of PBL showed higher degradation rate. The morphological change was observed by scanning electron microscope (SEM). The results show morphological change of the composites was started from the surface composites mainly on the biodegradable PBL.

1. Introduction

Polyethylene (PE) is widely used for packaging and single used appliances [1]. A large amount of post consumer PE product discarded causes environmental problem. The development of totally biodegradable materials seems to be more difficult because of their limited industrial application. Hence, we tried on a partially PE replacement by biomaterial. By mixing polymers with biomaterials, which are degradable, the degradation rate is enhanced as a result of the increase in polymer surface created after biomaterials degradation. Therefore, the development of bio-based material from polyethylene (PE) can be achieved by blending it with biodegradable fillers, which can reduce the volume of plastics by partial degradation. Thermal plastic starch (TPS) is a renewable, biodegradable and hydrophilic polymer which could be used as a filler in blend with PE to promote the degradable process of the material after its use. The production of starch-based bioplastic is simple, and they are widely used for packaging applications [2].The suitability of rice and corn-based thermoplastic starch for packaging applications have been extensively studied [3]. The required characteristics of the bioplastics are achieved by fine-tuning the quantities of the fillers. For industrial applications, the starch-based plastics are regularly mixed with eco-friendly polyesters.

Blends of PE/starch have been investigated [4-8]. The results showed that PE/starch tensile strength was lower than tensile strength of PE and it was decrease with increase of starch contents. However, the degradation properties are increased with increase of starch contents [9-13]. They found that the mechanical properties of PE/starch blends were decreased with an increase of starch content [9-10]. Bio-based materials based on conventional polymer and thermoplastics starch have been studied, however, their industrial application is still limited. The mechanical, biodegradable and thermal properties of PE/starch blends were studied at different starch content [11-13]. Research to develop and expand usability of polymer-starch based materials is in progress [10,14-15]. They found that more than 50% weight of the starch/plastics composites degraded in soil for 5 month. Starch plays significant role in degradation initiation for the starch/plastic blends.

Other studies on the use of non food biodegradable filler have been reported on lignin/polyethylene blends [16-24]. The tensile strength of lignin/PE blends increase and elongation decrease with the increase of lignin [16-17]. The lignin/PE blends shows better thermal stability [18-19]. Rice husk/PE blends resulted bending & tensile strength decrease with increase of rice husk filler [20-24], but the modulus was increased [20-22]. Studies on the use of biodegradable cellulose/PE blends have been done to modify hydrophobicity of the blends [25-26]. The change in hydrophobicity will then affect thermal & barrier properties of the blends. Cellulose surface modification to improve miscibility of cellulose/PE blends have been done using cellulose acetat butyrat (CAB) [27] and using cellulose nanocrystals (CNCs) [28]. They found that blends miscibility increase on the cellulose - amorphous PE.

It was well known that PE is hydrophobic, while natural biomaterial is hydrophylic. Solving incompatibility between hydrophobic PE and hydrophylic biomaterials is crucial for improving performance of the blends. Some methods have been reported to improve interfacial adhesion between hydrophilic wood flour and hydrophobic PE [29–30]. When maleat anhydride was added to the high density polyetyelene (HDPE)/ wood flour composites, tensile strength and flexural strength increase ca.157% & 146 % compared with the composites prepared without maleat anhydride, respectively. Plastics composites with pineapple leaf fiber [31-32] and palm leaf fiber [33] have been also reported. Maleat anhydride shown good complatibiliser, thus increase mechanical properties of the composites [31]. Tensile strength and flexural strength increase with increase in fiber content [32, 33].

Bio-based materials based on conventional polymer and thermoplastics have been studied, however, their industrial application is still limited. Consideration of environmental issues suggest that the biomass (and waste) can be beneficial in term of both lower energy consumption and overall emission. Non –fiber leaves for polymer composites production is hardly reported even though *Posidonia oceanica* dead leaves for PLA reinforcement [34] and leaves of sweet cherry were reported [35]. To the best of our knowledge, the use of breadfruit leaves for filler in composites is not published yet. Breadfruit tree is easily grows in Indonesia and widely found all over the country. Breadfruit is consumed at any stage of ripeness and serves in the form of steamed, fried breadfruit, or chips. The breadfruit leaves are believed as a good herb for kidney failure treatment, lowers cholesterol levels as well as lowers risks of heart disease [36]. However, breadfruit leaves are mostly still unutilized/ discarded.

The main objective of this work is to study the potential of waste material breadfruit leaf as a biodegradable filler/ agent in the polymer composites and compare their mechanical properties and durability in a wet–dry controlled environmental. In addition, the effect of leaf loading contents on the durability on the above mentioned properties were studied. The most important of this study is to promote the degradation of polyethylene by adding the waste leaf. During its lifetime and as wastes, the polymer composites are exposed to sunlight, heat, oxygen as well as moisture. It is of great importance to investigate the composite durability. Therefore, the simulated condition was carried out during this study.

2. Material and Methods

2.1. Material

Materials used and composites preparation were same as in our previous study [37]. Dead breadfruit leaves were collected in 2015 from North Bandung (7ºNL, 108ºEL) area, West Java. The dead breadfruit leaves were water washed and dried at room temperature. The leaves were then crushed and shaker sieved for 140 mesh (identical hole of 105 µm). Powdered breadfruit leaves (PBL) were oven–dried in Nabertherm at 105 ºC for at least 24 h. Water content was kept below 1% before melt blending. Composition of PBL is shown in Table 1.

It shows that PBL contained lower cellulose, higher lignin, and rich with extractive compared with wood and non–wood resources [38, 39]. This composition is in good agreement with previous study of which *Capsicum frutescens* contains 16 and 18% extractive when extracted in water and ethanol, respectively [40]. The cellulose and lignin were not isolated from the PBL and no further treatment before blending to be composites, except drying. Such a preparation lead us to get a natural filler which is fairly inexpensive. Lignin and cellulose, besides being a biodegradable material also role as reinforcement in the plastic composites.

Table 1: Composition of PBL

Composition	Weight (%)	Method of analysis
Cellulose total	27.1	T 203 cm–99
Lignin	35.9	SNI 0492:2008
Extractives	9.5	SNI 8401:2017
Ash	34.8	SNI 0442:2009

Figure. 1 shows that the PBL are random form and grain size. The coarse and cracky morphology of the PBL grain will facilitate an intrusion of melting PE during the blending process.

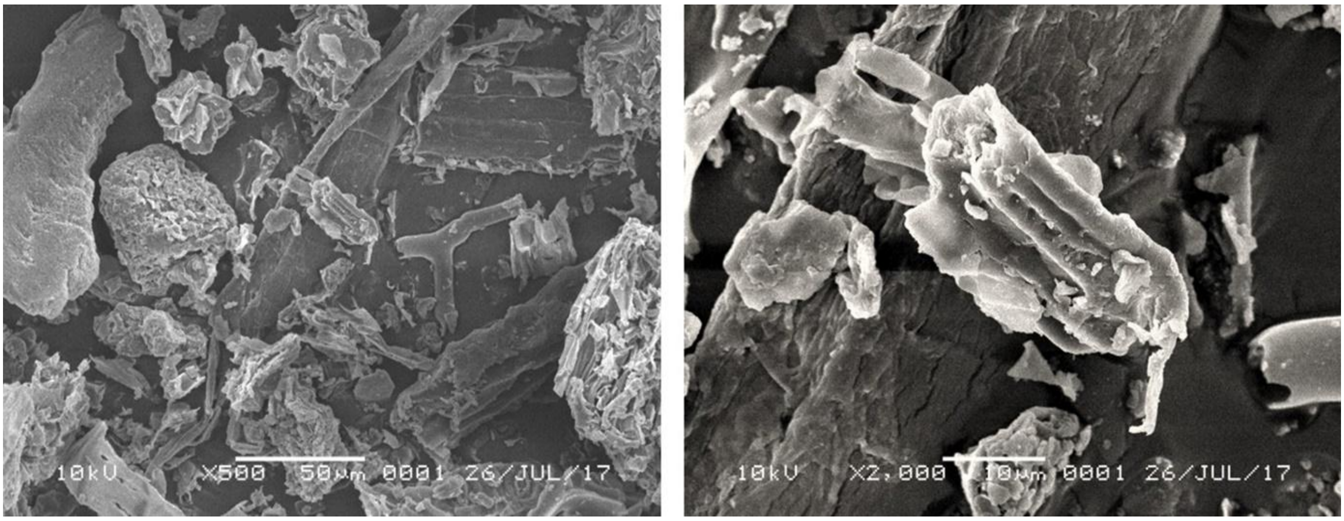

Figure 1: Micrograph of the PBL

Polyethylene (PE) was purchased from PT. Chandra Asri Petrochemical, Tbk. Indonesia. Lot number MI–LLD 45–12 with melting temperature was 123 °C measured by Differential Scanning Calorimetry (DSC 214 Polyma Netzsch) at a heating rate of 5 °C/min, containing undisclosed composition of conventional thermal stabilizer.

2.2. PE/PBL composites preparation

PBL–based composites with different leaves content (0, 10, 15, 20 and 25 w/w) were melt blended using an Internal Mixer (Labo Plastomill Model 30R150, Toyo Seiki Ltd. Japan, Capacity of 60 ml) at the set up temperature of 135 °C. The screw rotation was kept at 50 rpm, for mixing time of 8 min. The composite sheets were prepared from the melt blended samples using a hand–press (Gonno, ram stroke diameter 152 mm, capacity 37 ton). Pressing temperature was set at 130 °C. The melt blended samples were pressed in such a way till the end of the processing pressure of 50 kg/cm^2. After pressing for around 8 min, the sheets were dried–quenching using cold press. The rectangular sheets of ca. 120 x 120 x 0.23 mm were cut into dumbbell for tensile test. The specimen for hardness and flexural characterization were prepared in a dimension of 80 x 20 x 3 mm.

2.3. Wet-dry exposure

The wet–dry test was carried out using an Adhesive Endurance Tester (AET), Toyo Seiki Ltd., to examine durability and degradability of the composites. Samples were clipped at the one end and the other end was free. Specimens were then hanged–up vertically in the chamber of AET. The faucet water was used to soak the samples in the equipment. One cycle treatment was determined as soaking in water at room temperature for 1 h followed by hanging–up at air 60 ^oC for 1h, respectively. Mechanical properties were evaluated after 30 cycles with cycle interval of 15 cycles for 150 cycle exposure.

2.4. Characterization

Tensile properties were measured using Universal Testing Machine, Orientec Co. Ltd, Model UCT–5T. The composite sheet was cut into dumbbell according to ISO 572–2 type 5A. Dumbbell specimens were conditioned at 23 ^oC and 50 % relative humidity for not less than 48 h before testing. The testing speed was of 5.0 mm/min. Flexural properties were measured using the same equipment with tensile properties, based on ASTM D 790 – 10. Loading nose and supports have cylindrical surfaces with radii of 5 mm. Measurement was performed following procedure B since the samples did not break after the strain more than 5 %. The rate of crosshead motion was 13 mm/min.

Rockwell Hardness Testing Machine, Matsuzawa Mrk–M was used to measure the hardness of samples based on ASTM D 785 – 08, using ball indenter of 12.7 mm diameter. The minor and major loads were 10 and 60 kg, respectively. The hardness reading was taken 15 s after releasing major to minor loads. Five specimens were tested for every property under each composite formulation.

The PBL distribution/ dispersion and interfacial bonding between the polymer matrix PE and PBL on the composites were investigated using a Scanning Electron Microscope JSM IT–300, supplied by JEOL Co., Ltd., Japan. A gold sputtering technique was applied to coating samples in order to obtain good micrograph. The micrographs were taken at acceleration voltage of 10 or 15 KV. Samples were observed on the surface (outer) and on inner parts. The inner parts of samples were prepared by cryo–fractured.

3. Results and discussion

3.1. Tensile, flexural and hardness properties

To describe the mechanical properties of different PE and PE/PBL composites, their tensile, flexural and hardness were determined. Sample codes (PE, A1, A2, A3 and A4) and their composites composition are listed in Table 2. Table 2 shows that the elastic modulus is in general increased with increasing PBL percentage, and they are higher than elastic modulus of pure PE. These data indicating considerable reinforcing effects of the PBL (which rich with cellulose & lignin) on the composites. Similar results have been shown by Nourbakhsh [41] and Idowu [42] who studied wood– polypropylene composites.

Table 2: The average measured values of mechanical properties in terms of tensile, flexural and hardness of the PE and PE/PBL composites

Sample code	**Composition (wt.%)**		**Elastic Modulus (MPa)**	**Tensile Strength (MPa)**	**Yield Strain (% GL)**	**Flexural Strength (MPa)**	**Flexural Modulus (MPa)**	**HRR**
	PE	**PBL**						
PE	100	0	361.6	12.8	15.2	14.50	518.6	28.5
A1	90	10	392.2	11.5	12.5	14.02	555.5	12.2
A2	85	15	420.5	11.2	9.6	13.96	585.4	11.0
A3	80	20	440.8	11.2	7.5	14.11	616.9	6.9
A4	75	25	446.7	10.8	6.3	13.84	670.2	4.0

The tensile strength of PE composites decreases with increasing PBL composition. This can be explained by taking into account the adhesion of PBL–PE is smaller compare with the cohesion among PE molecules. The tensile strength reduces as the content of PBL increases owing to poor stretch transfer from the uncompatibilized PE matrix to the filler, besides the PBL filler in the composites is discontinuos phase. These PE/PBL composites have the greater tensile strength compare with that of natural additive starch/ lignin LDPE blends prepared by others [43]. The tensile strength of the blends with natural additives is 6.8 – 7.2 MPa or 64% of the tensile strength of LDPE alone [43].

The elongation at breaking of PE/PBL composites is shown in Table 2. For all the composites, the elongation at breaking is shorter than that of pure PE and it is decreased with increasing PBL content in the composites. This suggests that the more brittle characteristic of composites with the higher PBL content. The higher PBL contents resulting less homogeneous and larger discontinuous phase composites.

Their flexural modulus is higher than that of pure PE. The flexural modulus increased with increasing of PBL content in the composites. The highest flexural modulus is the 670 MPa that is composite with 25% PBL contents.

The flexural strength of PE/PBL composites was shown in Table 2. Even the test performed with the strain rate of 0.10 mm/mm/min (*procedure* B, ASTM D790-10), the samples did not yield or broken within the required 5% strain limit. According to the standard, the flexural strength should be determined as the flexural stress at the strain of 5%, and the testing or loading specimen were terminated. The flexural strength of PE/PBL composites for all PBL composition was lower than that of pure PE, but seems to be independent of the PBL contents. The flexural testing show that the composite did not broken at 5% strain, indicating the composite are not brittle. These composites promising applicability for packaging materials, even though the yield strain on the tensile test show significant decreased.

In order to evaluate the hardness of the PE/PBL composites, the specimen were loaded with a ball indenter of diameter 12.7 mm. The initial load (minor load) was 10 kg and the major load was 60 kg. The Rockwell hardness scale R (HRR) was determined 15 second after releasing major load to minor load. Table 2 shows the average hardness of the PE/PBL composites decreased with the increased of PBL contents. These facts could be attributed to the poor interfacial adhesion of PE matrix and the PBL filler. The lower PBL contents may resulting composites mixture more homogeneous. Physical condition of PBL is powder which no bonding among the powder grain, so that do not have HRR. The PBL spread in the composite as discontinuous phase. The HRR reduces as the content of PBL increases because very poor back stress from the filler during loading indenter on the HRR measurement.

3.2. Composites morphology and biodegradability

In plastic composites, it is essential to study the morphology of the final product because most of plastic composites properties, especially its mechanical properties, depend on it. In most cases, the major component of the composites form the continuous phase, whereas the minor component is the dispersed phase. As the volume fraction of the minor component increases, at a certain value, depending on the nature of the polymers and the processing conditions, continuity of both polymer phases may be obtained. It was observed that PBL was always dispersed phase, independent on the percentage. Thus, in the PE/PBL composites, the PBL is expected to be the dispersed phase. Figure 2 shows the inner part (cryo-fractured) of PE and the composites before and after exposing 150 cycles. In the figures, textures before and after exposure are not clearly differentiable. The texture of PE seems smoother than the textures of the composites. The texture PBL fillers can be clearly seen in the inner composite micrograph due to the weak interfacial bonding between the filler and PE matrix. It can be seen that PBL dispersed phase is not homogenous and their interfacial adhesion with PE continuous matrix is poor. The more uniform dispersion of PBL in the PE matrix can be observed in composites with the lower contents of PBL. Fig 2 (right) shows the inner part of the sample after 150 cycles of exposure. It can be observed that the morphology is very similar with that of Figure 2 (left) suggesting that degradation not yet reach the inner part of the samples.

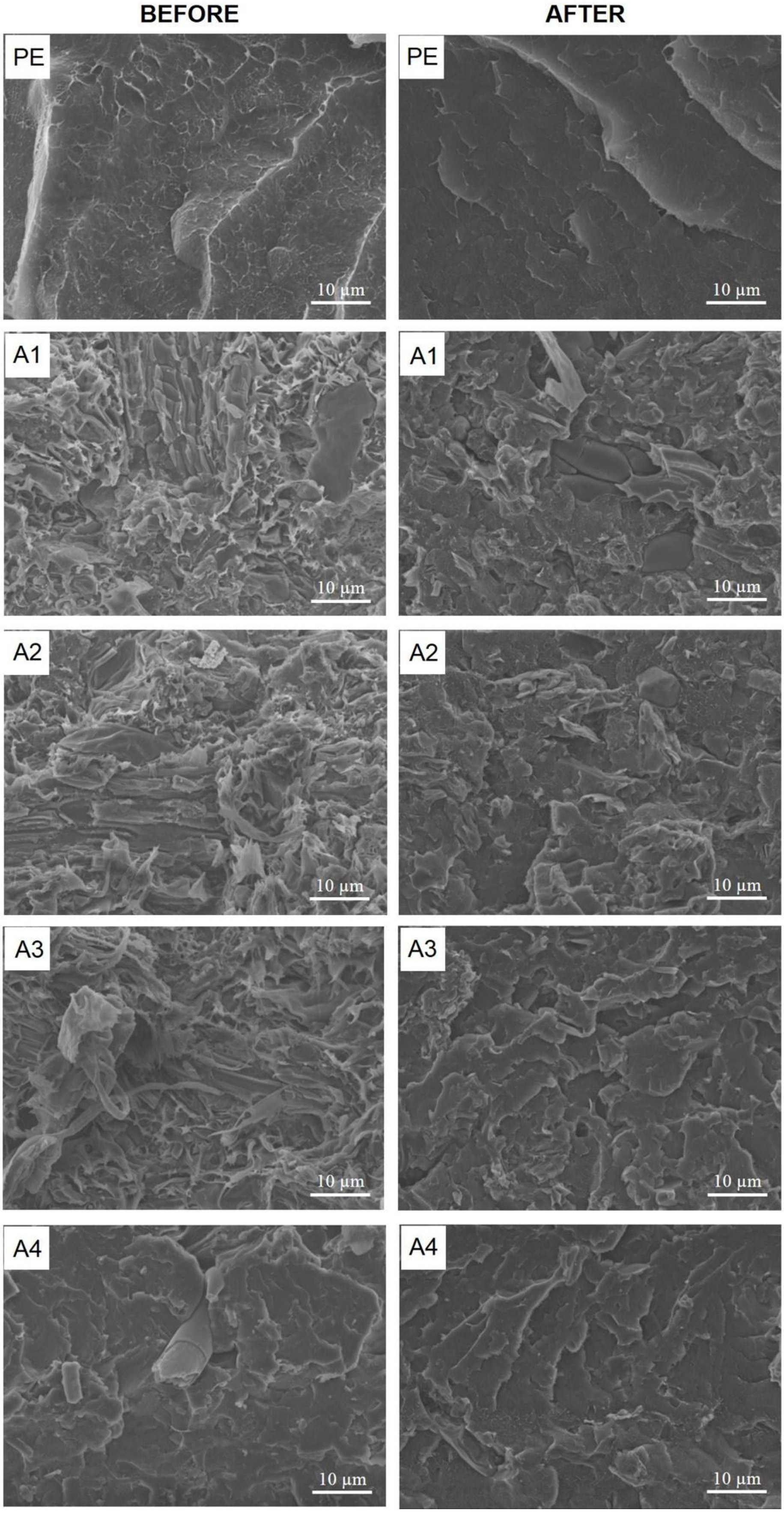

Figure 2: Inner morphology of PE and the Composites: before exposure (Left) and after 150 cycles exposure (right).

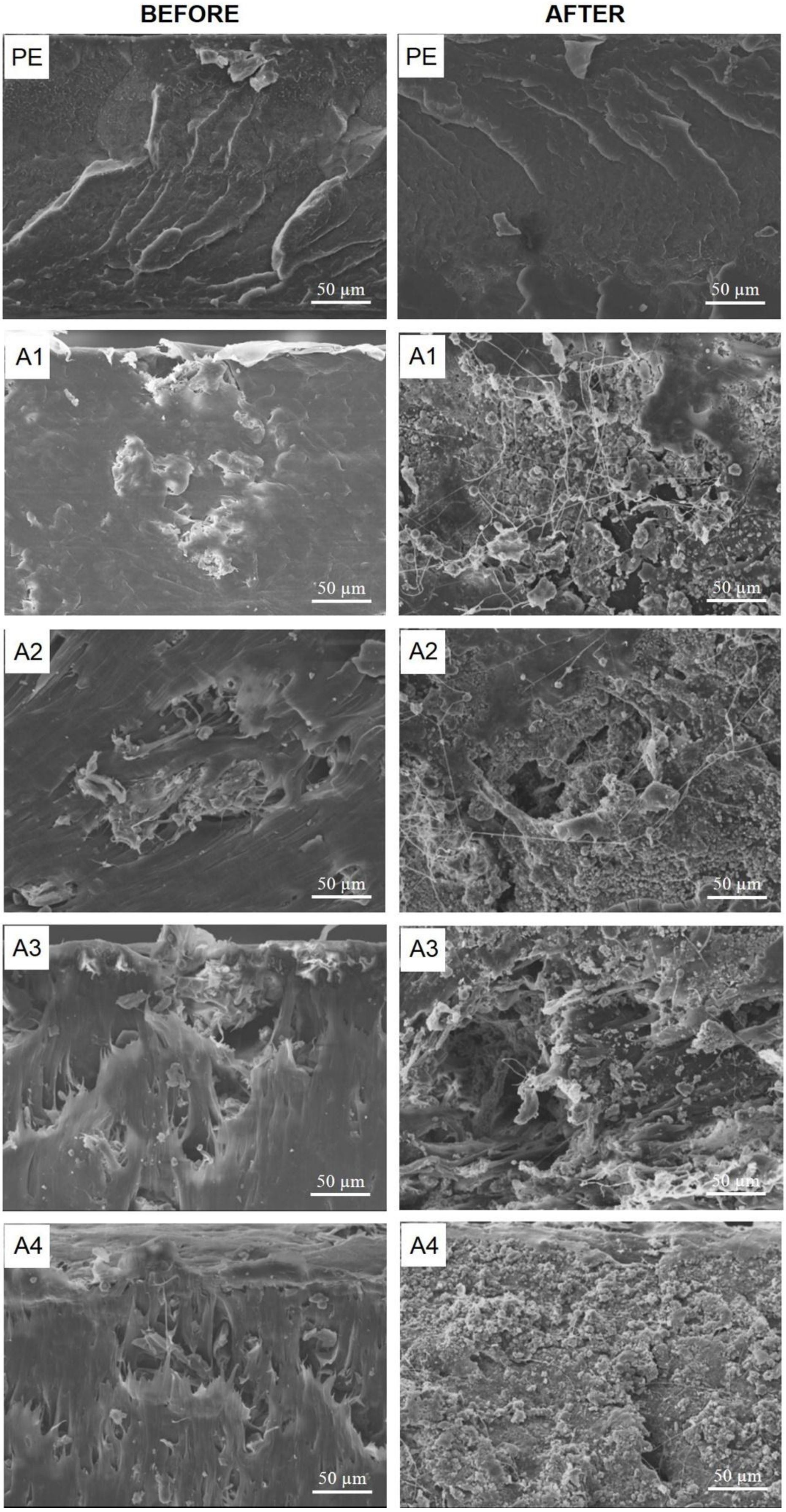

Figure 3: Surface/outer morphology of PE and the Composites: before exposure (leftside) and after 150 cycles exposure (rightside)

The morphology of the surface samples, before and after 150 cycle exposure is shown in Figure 3. Figures 3 (PE, left) and 3 (PE, right), show almost same micrograph features, indicating the PE morphology remained unchanged after 150 cycle exposure. Figure 3 (left: A1 – A4) shows the sample surface before exposure. In these micrographs, interfacial boundary of PE and PBL is not so clearly observed. However, the feature of micrograph in Figure 3 (right: A1 – A4) looked coarser and interfacial PBL particles more obviously seen after 150 cycle of exposure. They looked ununiformed and coarse morphology. The morphology appear as PBL detached or degraded from the PE matrix. The detached and or degraded PBL from the composites leave pores in the matrix. The porous PE matrix stimulates degradation and composting of the composites samples. Figure 3 shows degradability composites was occurred in the surface composites after exposure of 150 cycles. Thus, Figures 2 and 3 confirmed that degradation of the composites was started from the surface of samples and it might be provoked by water absorption of the PBL filler.

3.3. Mechanical degradability

3.3.1. Tensile deterioration

Fig. 4 shows the degradation test experimental data for the composites of before and after wet–dry exposure. The elastic moduli decrease drastically for the first 30 cycles and almost unchanged during the next cycle time until 150 cycles. It can be noted that pure PE and the composites have a similar elastic modulus characteristic degradation tendency. These observations were in agreement with the findings reported in the work by Kaczmarek and Oldak [44] and Oldak et al. [45]. They found that with a very small amount of cellulose (5–15%) in polyethylene (PE) composites, it may not improve its biodegradability. The biodegradability in PE films will only have the pronounced effect if it contains 30% cellulose and more.

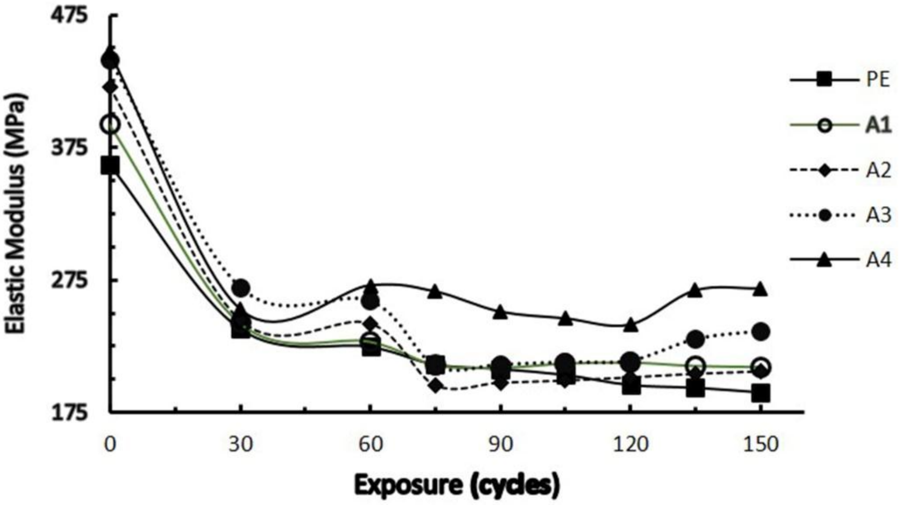

Figure 4: Elastic modulus of PE and the composites during wet-dry exposure

In the early stage of exposure, water absorption by the filler may occurred intensively, so that sample composites become softer and decrease its elastic modulus. For the next 60 to 150 cycle exposure, the elastic modulus does not change significant compare with that of 30 cycles. These facts may arise from the water absorption has been saturated while the PE matrix still good condition. In PE matrix, a change of crystal–amorphous may occurred during all cycle exposure [46]. Elastic modulus of pure PE seems minor decrease along 30 – 150 exposure cycles may attributable to stability of crystal–amorphous structure [47]. Figure 5 shows tensile strength of PE and the composites during wet–dry exposure. Tensile Strength decreases along the exposure cycles. The decrease of the tensile Strength was significant during the first 30 cycle exposure. In the first 30 cycles exposure, water may immediately absorbed by the composites. The absorbed water will affect interfacial adhesion and stress between the matrix and PBL materials. Consequently, the tensile strength of the composites decreased. In case of pure PE, water absorption was almost zero but effect quenching from dry (hot) to wet (cool) may produce amorphous structure. In addition, various parameters influence the mechanical properties of fiber–reinforced composites including the fiber aspect ratio, fiber–matrix adhesion, stress transfer at the interface and mixing temperatures.

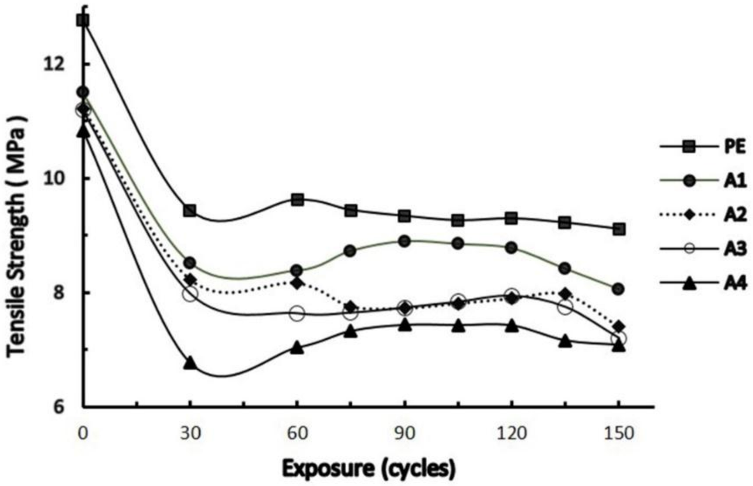

Figure 5: Tensile strength of PE and the composites during wet-dry exposure

Figure 6 shows the yield strain a slight increase from 0 to around 105 exposure cycles. The increasing of yield strain demonstrates as if no degradation of yield strain during these cycles period. Yield strain then decreases at 120 to 150 exposure cycles, however, they still higher than their zero cycles. PE was no much affected by the soaking in water since PE is hydrophobic. The exposure cycles were more dominant affected on view of hot–cold as annealing and quenching temperatures. In general, quenching will produce amorphous structure of PE.

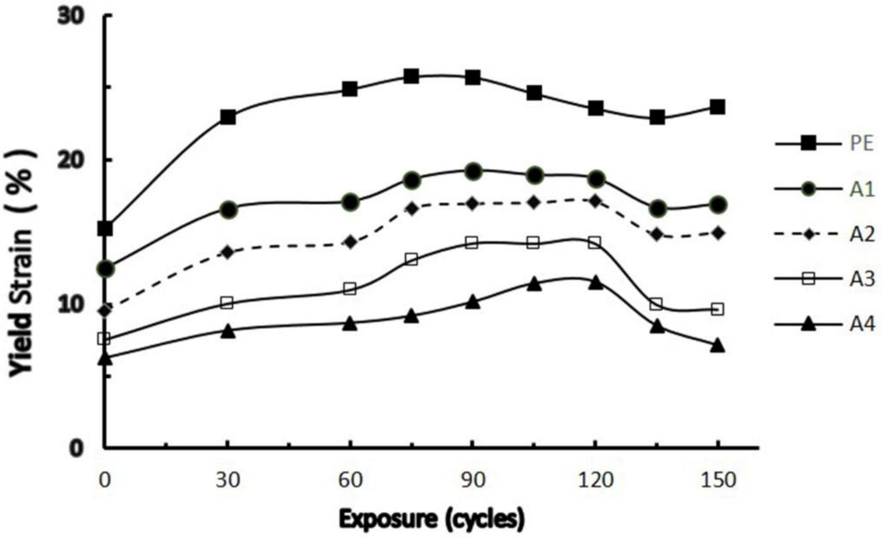

Figure 6: Yield strain of PE and the composites during wet-dry exposure

3.3.2. Flexural deterioration

The effect of exposure cycles on the flexural strength for PE/PBL composites are presented in Figure 7. Flexural Strength increase up to 60 exposure cycles, then it decreases till 150 exposure cycles. Different from the trend results of tensile properties, the exposure cycles results in slight increase in flexural strength properties of the composites. The slight increase in flexural strength achieved can be attributed to the increase crystallinity of the matrix PE. These exposure cycles also induce water absorption to the composites, however. The water absorption will deteriorate compatibility interfacial adhesion between the matrix and fillers. Araujo et.al. [48] have been investigated interfacial adhesion and surface modification of cellulose. They found that these two factors can increase Young’s modulus and break stress of the cellulose composite. Simultaneous change crystallinity and the interfacial interaction supposed to be dominant factors affected the mechanical properties (flexural strength). Flexural strength values are found to be much higher in composites at exposure of 60 cycles. The flexural strength of the composites reached the maximum values exposure of 60 cycles, but its maximum at 75 cycles for sample A1 (lowest PBL contents) and A3. These facts may leads to interpretation that increasing crystallinity was more dominant factor affecting flexural strength in the early exposure. As it can clearly be seen from Figure 7, with increase in exposure from 60 to 150 cycles, the flexural properties are considerably decreased.

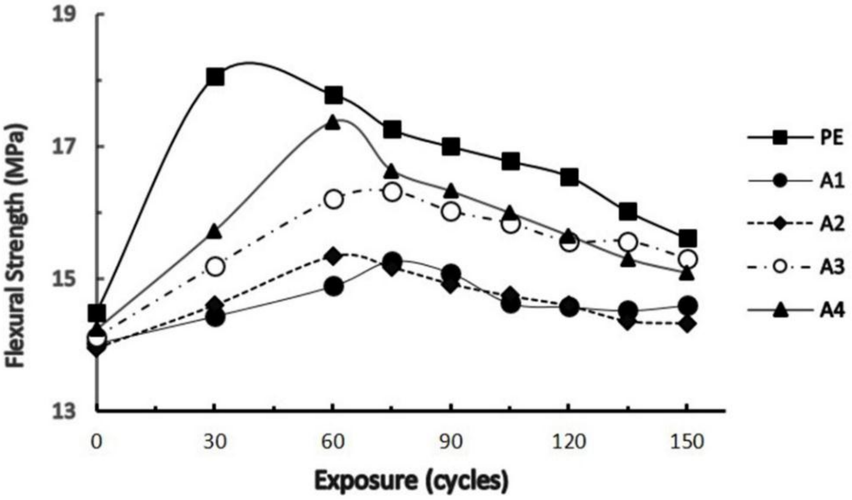

Figure 7: Flexural strength of PE and composites after exposure cycles

The effect of exposure cycles on the flexural modulus for PE/ PBL composites are presented in Figure 8. In general, the flexural modulus decreases after the exposures. The decreasing of flexural modulus means the samples becoming more elastic flexure. Similar with the tendency results of tensile properties, the exposure cycles results in slight decrease in flexural modulus properties of the composites. The slight decrease in flexural modulus achieved can be attributed to absorbance water of cellulosic fillers (leaves materials) and to deteriorate interfacial adhesion between the matrix and fillers.

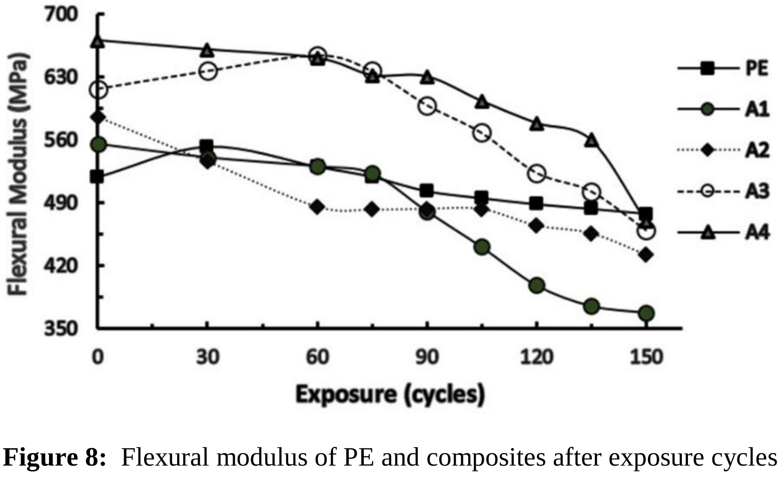

Figure 8: Flexural modulus of PE and composites after exposure cycles

3.3.32. Hardness deterioration

Figure 9 reports the result of hardness measurement function of the exposure of the composites. For composites before exposure, with increasing PBL lignocellulosic contents hardness decreased linearly. This may be due to the decrease in stiffness of the respective composites. The increases contents of PBL particles reduced interfacial area of contact between the PBL particles and the PE matrix, and hence diminishes the potential of a given PBL particles to be able to bond with the matrix. Mechanical performance of PBL particle composites depends on many factors including the nature of the constituent, particle/matrix interface, the construction and geometry of the composites and test conditions. The hardness of PE and the composites were fairly stable along the exposure cycles. These facts can be attributed to resistance of the composites is comparable to resistance of PE along the exposure cycles. The hardness degradation of the composites was not as pronounce as degradation in tensile properties in this exposure may resulted from the different thickness of the test specimen. Hardness specimen thickness was 14 times thicker than that of tensile. Water absorption in which induces degradation was started from the surface of the test specimen. Since the degradation occurred on the composite surfaces, and in the middle sample may remain unchanged, so that the hardness only slight decreased during these exposure cycles.

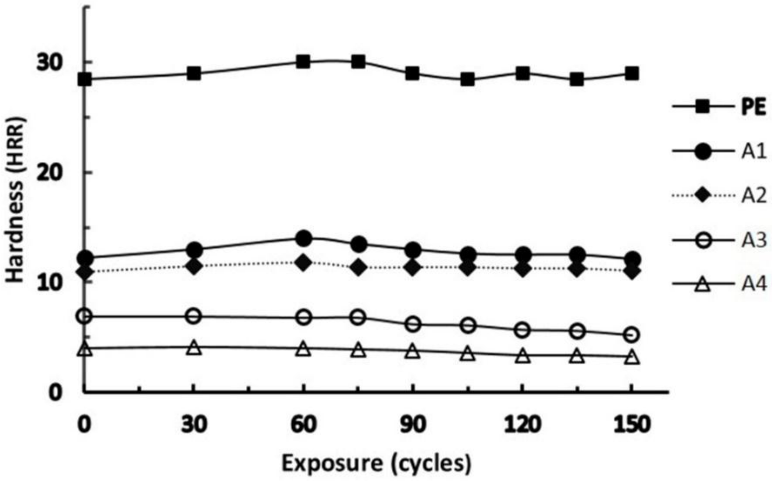

Figure 9: Hardness of PE and composites after exposure cycles

Conclusion

The effect of PBL on the mechanical properties of PE/PBL composites was found to depend on the PBL contents on the composites. Except the flexural and elastic moduli, all mechanical properties were found to decrease with increase in PBL loading. It appears that PBL, besides for being a biodegradable material, can also act as modulus reinforcement filler. The highest biodegradation rate was achieved with the highest PBL content. Based on the results of this investigation, it is possible to blend the non–degradable PE matrix with PBL in order to improve its biodegradability. The degradability of PE/PBL composites was confirmed by worsening interfacial adhesion of PE matrix – PBL filler and changes in mechanical properties. PBL could be considered as a potential source of low cost and biodegradable material for composites.

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