

Improvement of Thermo-Mechanical Properties of Short Natural Fiber Reinforced Recycled Polypropylene Composites through Double Step Grafting Process

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Abstract. This study focused on the effect of a compatibilizer addition, maleic anhydrides (MAH) on mechanical, thermal and water absorption properties of oil palm empty fruit bunches (EFB) fiber reinforced recycled polypropylene (rPP) biocomposites. The double steps grafting process were conducted by incorporated MAH on both rPP and EFB to improve the surface adhesion between these materials, to result in a good mechanical properties as well as biocompatibility to nature. The chemical test was carried out using FTIR (Fourier Transform Infra-Red) spectroscopy technique to evaluated grafting process. The mechanical test was investigated and found that the addition of 10 phr MAH to both rPP and EFB improved mechanical strength of the biocomposites higher than another formulas. In this study, thermal properties of biocomposites also characterized. Water absorption (WA) analysis showed the presence of EFB fiber increased the water uptake of the material.

1. Introduction

Natural fiber reinforced polymer has been interested to developed due to their advantages such as excellent mechanical properties, biodegradable, renewable, lightweight, economical and environmentally friendly [1,2]. Moreover, developing of natural fiber reinforced polymer was motivated by an environmental issue which required green material for sustainability [3]. Polypropylene was hydrophobic polymer materials which mostly used in several applications such as packaging, interior automotive panels, aerospace and others [4,5]. To improve their properties, fiber reinforcing materials, such as natural fiber was introduced. However, it is difficult to obtain good adhesion between hydrophilic cellulose and hydrophobic polypropylene due to their different polarity. This problem will lead the final product has poor mechanical properties due poor ability to stress transfer from matrix polymer to fiber [6]. Additionally, cellulose fiber has highly hydrophilic which lead strong hydrogen bonding between the fiber, thus resulted in poor dispersion of fiber in the matrix and weak interfacial interaction between fiber and matrix [3,7].

The previous researchers have been modified the natural fiber surfaces to improve their adhesion between polymer and fiber. This step is one of promising strategy to obtain high strength materials. The

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grafting agents have been used by previous researcher, i.e. silane compound [8], acrylic acid [9], maleic anhydrides [10, 11] and others. Jiang et al. [8] was modified the fiber surface with [3(2-aminoethyl) aminopropyl] triethoxysilane on the polyurethane/carbon fiber (CF) composites preparation and improve tensile strength up to 42% compare to composites without grafting agent. Suharty et al. [9] used acrylic acid as grating agent on the recycled-polypropylene (rPP)/rice husk powder (RHP) biocomposites to obtain high mechanical properties. Acrylic acid grafted polypropylene (PP-g-AA) was also introduced by Suharty et al. [12] on the manufactured rPP/kenaf fiber (KF) biocomposites, resulted high mechanical properties. Arao et al. [13] added maleic anhydrides grafted polypropylene (PP-g-MAH) on PP/CF composites, obtained an improvement of interfacial share strength up to 119% compared to PP. The PP-g-MAH grafting agent has polar maleic group which can forming ester linkage with hydroxyl group of natural fiber. In addition, polypropylene backbone of PP-g-MAH will be form one phase with polypropylene chain [3].

In our previous research [10], has been successfully manufactured rPP/short empty fruit bunch fiber (sEFB) with the presence of PP-g-MAH. However, the MAH grafting process was only performed on polypropylene chain. Thus, in this research was conducted two steps grafting process which are both in rPP and sEFB. This research was focused on the effect of two steps grafting process on thermo-mechanical properties of rPP/sEFB biocomposites.

2. Experimental

2.1. Materials

Recycled polypropylene (rPP) from waste plastic bottle water which collected from Surakarta, Indonesia was used as matrix polymer. Short natural fibers was oil palm empty fruit bunches (EFB) which obtain from LIPI Serpong, Indonesia. Compatibilizer maleic anhydride (MAH) was obtained from Merck. Other chemicals such as benzoyl peroxide (BPO, Merck) and divinyl benzene (DVB, Merck), xylene (PT. Brataco, Indonesia), toluene (Merck), acetone (Merck), ethanol (Merck), N,N-dimethyl formamide (DMF, Merck), hydroquinone (purchase from UMS Surakarta) were used without purification.

2.2. Preparation of MAH grafted EFB (EFB-g-MAH)

The grafting of EFB fiber was prepared according to Rozman et al. [14] method. The EFB fiber was chopped about 2-5 mm and immerse in a mixture solution of toluene, ethanol and acetone with ratio 4:1:1 about 3 hours. The fibers were filtered and dry about 16 hours in temperature 105 °C. In the different place was prepared variation concentration of maleic anhydride (5, 10, 15 and 20 phr w/w) by dissolved it in DMF. Afterward, hydroquinone (5% w/w to MAH) was added to MAH solution. The solution was added drop-wise into three round neck bottom flask contained 50 grams of EFB. The mixture was refluxed about 1 hour at 80 °C. Grafting product t-EFB-g-MAH was washed using acetone to remove unreacted MAH. The product was dried about 16 hours at 105 °C to obtain EFB-g-MAH. The raw material and the final product was characterized using FTIR.

2.3. Fabrication and testing of rPP/EFB biocomposites

Table 1. showed a formulation in the manufacturing of rPP/sEFB bio-composites. Fabrication of rPP/EFB biocomposites was conducted using solution method and radically reaction. About 20 grams of rPP was dissolved in boiling xylene. The previous optimum amount of MAH (10% w/w), benzoyl peroxide and divinyl benzene were added after rPP successfully melted. After 5 minutes, the EFB-g-MAH was added and stirred for 1 hours. The rPP/sEFB bio-composites was dried for 24 hours at room temperature and fabricated using hot press hydraulic machine.

Table 1. The formulation of rPP/EFB biocomposites.

Materials	Formulas (phr)						
	F1a	F1b	F2a	F2b	F2c	F2d	F2e
rPP	100	100	70	70	70	70	70
EFB	-	-	30	-	-	-	-
EFB-g-MAH5	-	-	-	30	-	-	-
EFB-g-MAH10	-	-	-	-	30	-	-
EFB-g-MAH15	-	-	-	-	-	30	-
EFB-g-MAH20	-	-	-	-	-	-	30
MAH	-	10	-	10	10	10	10

Thermal properties was analyzed using Simultaneous Thermal Analyzer (STA) Lineises PT-1600. The sample was recorded in the range of 30-600 °C with the heating rate of 10 °C/minute. Before analysis, the sample was dried in an oven at 50 °C for 1 hour.

Mechanical properties of biocomposites were evaluated by following ASTM D638-02a method. The tensile test was performed using mechanical testing machine Ray-Ran M500-50CT with crosshead speed of 10 mm/minute.

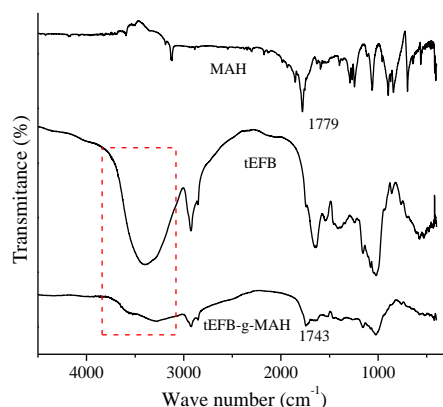
Water adsorption was carried out by measure the mass of sample after immersed in water for 1 hour. The samples before testing were weighed and recorded as initial weight (W_o). After immersion for 24, 48, 72, 96 and 120 hours, the samples were weighed again and recorded as final weight (W_i), then determined the percentage of water absorption capacity (% WA) by equation 1.

$$\%WA = \frac{(W_i - W_o)}{W_o} \times 100\% \dots\dots\dots(1)$$

3. Result and Discussion

3.1. Functional group analysis

The grafting product of EFB fiber was characterized using FTIR technique. Fig 1 showed FTIR spectra of EFB and EFB-g-MAH. A strong absorbance band at 1743 cm^{-1} in EFB-g-MAH spectrum was corresponding to the carbonyl group of MAH. The appearance of this absorbance band indicated that grafting process was successfully achieved. The low peak intensity of hydroxyl group after after grafting was affect by ester linkage formation. The hydroxyl group of EFB was react with anhydride group of MAH to form an ester linkage.

**Figure 1.** FTIR spectrum of MAH, EFB and EFB-g-MAH

3.2. Mechanical properties of the biocomposites

Mechanical properties of some composites with and without compatibilizer maleic anhydride had been showed in Fig 2. It was noted from our previous work that the uncompatibilizing rPP/tEFB (F2a) biocomposites have lower tensile strength compared to others formula, 24.67 MPa. Surface treatment of EFB fiber by the addition of MAH was able to improve the mechanical properties. By using of 10% MAH into EFB fiber was able to increase tensile strength up to 84 % compared to ungrafted EFB fiber. The presence of MAH in EFB fiber improved their surface adhesion with hydrophobic polypropylene matrix. Good adhesion between filler and matrix caused that optimum stress transfer from matrix to fiber was achieved. Consequently, the tensile strength value of the biocomposites will be increased. However, the tensile strength by the addition of 15 and 20 phr of MAH was slightly decreased. It indicated that surface modification of EFB with maleic anhydride has optimum state at 10 phr MAH addition.

Elongation data is one of indicators to determine the elasticity of materials. The higher value of materials elongation indicated that it has high elasticity. From the data, by introduced MAH in composites system was not only improve their strength, but also their elasticity. The F2a composites has elongation under 20%, however, almost composites contained MAH had elongation above 20%.

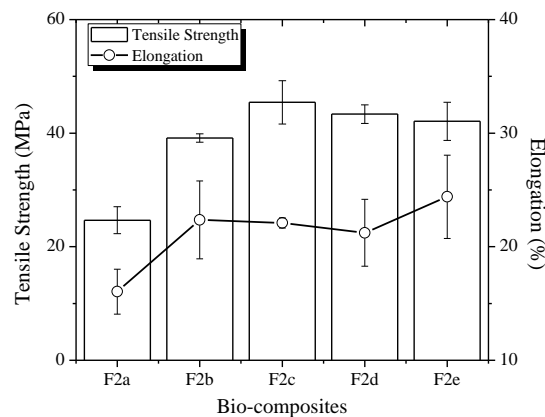


Figure 2. Tensile strength and elongation of the biocomposites

3.3. Thermal properties

Thermal properties of untreated and grafted fiber on rPP/tEFB biocomposites has been shown in Fig 3. Weight loss of rPP/tEFB bi-composite in the first degradation was about 74%. However, after surface grafting was applied in the tEFB fiber, the weight loss of bio-composite was reduced to about 59%. This indicated that by surface treatment on EFB fiber improved the thermal stability of biocomposites. Good interaction between fiber and matrix will improve the bond strength of the composites, thus it was impact on the improving of thermal stability. Different thermal analysis (DTA) thermograph showed that the second degradation temperature of biocomposite contained EFB-g-MAH10 slightly increased compared to untreated fiber, which was 445 °C. The possible reason for this phenomena is the fiber has hydrophilic properties will lead the fiber has high hydrogen bonding formation. The internal hydrogen bonding between hydroxyl groups in tEFB fiber with MAH groups was higher than without MAH groups. Thus, it required high energy to degrade the fiber with the presence of MAH.

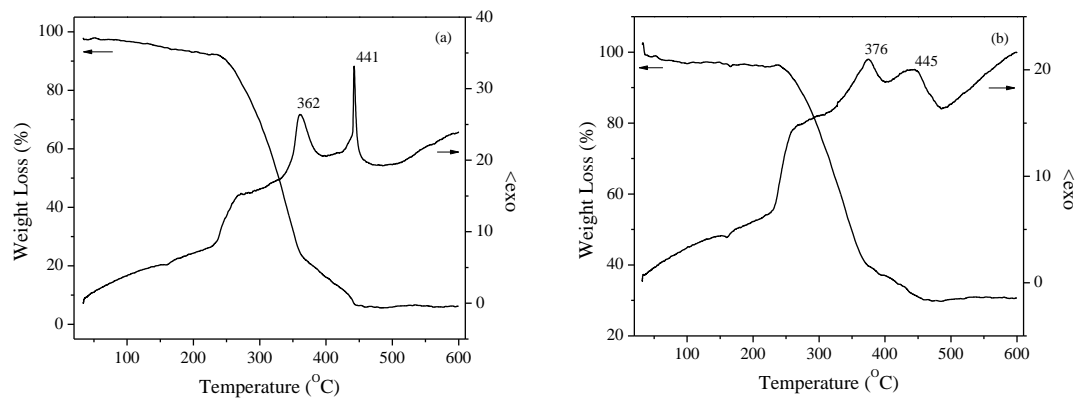


Figure 3. TGA graph of (a) rPP/EFB and (b) rPP/EFB-g-MAH10 biocomposites

3.4. Water absorption properties

Water adsorption behavior of unmodified rPP/EFB and rPP/tEFB-g-MAH10 biocomposites was showed in Fig 4. The rPP/EFB-g-MAH10 biocomposites displayed an increasing of water adsorption by soaking for 48 hours. Afterward, the composite reached saturation adsorption at immersion time of 72 and 96 hours, about 8.5%. It was occurred due to their limited water uptake ability which caused by good distribution and interaction between matrix and the fiber and resulting in the improvement of interfacial adhesion with the presence of compatibilizer agent [15]. This good interaction resulted in low void content in the biocomposites, while the void content was one of water adsorption factors. Also, good interaction between matrix and the fiber will lead the fiber difficult to interact with water. By comparing to unmodified rPP/tEFB bio-composites, the water adsorption value increased with the increasing of immersion times, while after immersing at 24, 48, 72 and 96 hours, the biocomposites was allowed to adsorb the water up to 4.3%, 13.1%, 21.7% and 23.9%, respectively. In rPP/EFB biocomposites, saturation adsorption was not actually reached even after 96 hours immersion times. Water adsorption was influenced by several factors such as fiber content, void content, fiber orientation, surface protection and many others [3, 16].

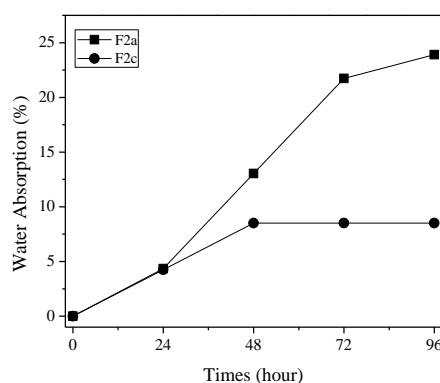


Figure 4. Water adsorption of rPP/EFB and rPP/EFB-g-MAH10

Cellulose fiber has hydrophilic in nature, it means that, they was easy to absorb the water due to the hydrogen bonding between an organic compound and water molecules. Without compatibilizer agent, the matrix and the fiber has poor interaction and lead to produce the void site. Consequently, it was able to entrap the water molecules [17]. Moreover, high polar fiber fraction was easy to absorb the water and increase the composites weight. It can be concluded that water adsorption behavior of some biocomposites materials was dependent on the presence of free hydroxyl group on the surface of fiber

[18]. Thus, by the addition of MAH into the fiber, esterification between anhydride group and hydroxyl group occurred. As the result, the free hydroxyl group on the fiber surface decreased.

4. Conclusion

The grafting of both short natural fiber and polypropylene on the rPP/EFB composites have significantly influence on both mechanical and thermal properties. Surface grafting of short natural fiber with 10 phr maleic anhydride is the optimum composition on the composites preparation due to they has high mechanical properties compared to another formula. In another cases, the presence of MAH also decreased the water adsorption of the composites.

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