Effect of compatibilizer on morphological, thermal and mechanical properties of Starch-Grafted-Polypropylene/Kenaf fibers composites

N H Eszer 1, Z A M Ishak 1*

1 School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus 14300 Nibong Tebal, Penang, Malaysia

*Corresponding author: zafrin.ishak@gmail.com

Abstract. Starch-grafted-polypropylene (starch-g-PP)/kenaf fibres composites were prepared by melt compounding and compression molding. Polypropylene-grafted-maleic anhydrides (MAgPP) were added at different weight contents (1, 3 and 5 wt. %) as compatibilizer. The morphological, thermal and mechanical properties of the composites were characterized using thermogravimetric analysis, scanning electron microscopy, tensile and flexural test. The results indicated that mechanical properties of the composites were improved by addition of compatibilizer. From TGA, the thermal stability of the composites with MAgPP was improved compared with the composites without MAgPP. Finally, scanning electron microscopy of fractured surface revealed better adhesion between the fibers and matrix with presence of compatibilizer.

1. Introduction

With the growing environmental awareness and shortage of natural resource, biodegradable and compostable materials are produced and used in increasing amounts in the areas of life and industry [1,2]. Therefore, the development of biocomposites based on biodegradable thermoplastic starch (TPS) and natural fibers is being widely explored, as an effort to reduce the plastic waste problem. However, the main disadvantages of TPS include unsatisfactory mechanical properties, particularly in wet or dry environments. TPS that were reinforced with natural fiber to improve the mechanical properties of the composites.

Lignocellulosic materials such as henequen, hemp, sisal, kenaf, coir, jute, palm and wood in their natural condition have been widely used as fillers for thermosetting and thermoplastic composites [3]. Lignocellulosic fibers also contribute to the composite with high specific stiffness and strength, a desirable fiber aspect ratio, biodegradability, renewable resources and a low cost per unit volume basis [3]. These fibers are mainly made of cellulose, hemicelluloses, lignin and pectins, with a small quantity of extractives [2]. Aside from such as low density, less machine wear during processing, no health hazards and a high degree of flexibility, kenaf fiber is also easy to be moulded into a product using conventional thermoplastic processing such as extrusion, compression moulding and injection moulding [4]. However, the incorporation of kenaf fiber into conventional polymer composites does not promise fully-biodegradable
characteristics because the matrix phase is not capable of undergoing biodegradation. To produce a fully-biodegradable composite, a combination of natural fiber and biodegradable polymer matrix is needed.

In this study, a commercialized biphasic thermoplastic, Gaialene® (supplied by Roquette, France) was used as a matrix to form an environmental friendly composite with kenaf fibers (KF). Gaialene® is a starch-grafted-polypropylene (starch-g-PP) with the starch/polypropylene ratio of 52/48, which is designed for durable and semi-durable uses. According to the manufacturer, it is over 50% bio-based and the production yields a carbon footprint about 65% lower than that of the cleanest fossil polymers. Addition of natural fibers would also increase the bio-based portion of the material, making it more environmental friendly. In that case, a better interfacial adhesion is obtained between the matrix and filler because kenaf fiber is naturally hydrophilic. The matrix which is thermoplastic starch also is hydrophilic. Moreover, the additions of compatibilizer such as maleic anhydride (MA) between polymer and natural fibers are common solutions used to improve the interfacial adhesion of the composites [5,6]. In previous work, the improvement of tensile properties, hardness, creep stability and tensile impact stress after incorporation of KF into the starch-g-PP were reported by other researchers. In this study, starch-g-PP and kenaf fibers also used as the previous study but with addition of compatibilizer because the interaction between fiber and matrix influence the mechanical properties of the composites. Therefore, compatibilizer was used to improve the interfacial adhesion and mechanical properties of the composites.

2. Materials and methods

2.1 Materials
Starch-grafted-polypropylene with trade name (Gaialene®) was obtained from Roquette, France. Density of the polymer is about 1.28 g/cm³. The polymer was supplied in dry pellet and has melting temperature (Tm) of about 160 ºC used as the matrix of the composites. Commercial maleated polypropylene, MAgPP (OVERAC CA 100) from Arkema with a melt flow index of 10g/10 min and density of 0.909 g/cm³ was used as compatibilizer.

Kenaf fiber (KF) was supplied by Kenaf Natural Fiber Industries Sdn. Bhd. (KFI), Malaysia. In this work, kenaf fibers with 3 mm in length were used. The ash content in kenaf fiber is removed by sieving and washing the fiber. The average density of kenaf fiber is 1.4 g/cm³.

2.2. Compounding conditions
Kenaf fiber was dried in a circulating air oven at 80 ºC for 24 hours. Starch-g-PP also dried in circulating oven at 50 ºC for 12 hours to expel moisture before used for compounding. The kenaf fibers, starch-g-PP and MAgPP pellets were mixed by using an internal mixer with co-rotating double-winged rotors, operating at 175ºC with rotor speed 60 rpm for 7 minutes and the weight percent of the kenaf fibers used was 30 wt.%, the composition were shown in Table 1. The composite compounds were compression moulded at 170 ºC into specimens with dimensions of 120 × 12 × 3 mm³ and 165 × 19 × 3 mm³ for flexural and tensile specimens, respectively, by using a compression moulding machine (model Kao Tieg Gotech). The moulding cycle involved 5 minutes of preheating without pressure, 3 minutes of compression and 5 minutes of cooling.
Table 1. Formulations of the specimens

| Materials designation | Starch-g-PP (wt.%) | Kenaf fibre (wt.%) | MAgPP (wt.%) |
|-----------------------|-------------------|------------------|-------------|
| SGPP                  | 100               | -                | -           |
| SGPP/KF               | 70                | 30               | -           |
| SGPP/KF/1MAgPP        | 69                | 30               | 1           |
| SGPP/KF/3MAgPP        | 67                | 30               | 3           |
| SGPP/KF/5MAgPP        | 65                | 30               | 5           |

2.3. Mechanical testing
Tensile and flexural tests were performed on a Universal Testing Machine (Model Instron 3366). The specimens were kept in desiccators prior to testing to avoid moisture absorption. Tensile and flexural tests were carried out in accordance with ASTM D638 and ASTM D570, respectively with a load cell of 10 kN and crosshead speed was 5 mm/min at room temperature. For tensile test, elastic modulus was evaluated deforming the specimens up to a strain of 1% at a crosshead speed of 5 mm/min. The strain was measured with a gage length of 50 mm. Flexural test were performed in three-points bending mode with span length of 50 mm. At least five specimens were used for each test.

2.4. Thermal testing
Thermogravimetric analysis (TGA) analysis was performed on neat starch-g-PP, starch-g-PP/kenaf fiber composites without and with different MAgPP content in order to investigate the thermal stability of the composites. TGA analysis was carried out using TGA analyzer model Perkin Elmer Pyris 6. 5 – 10 milligrams sample was scanned at a heating rate of 10°C/min from 30 to 620°C in N₂ atmosphere.

2.5. Morphology
Field emission scanning electron microscope (FESEM) (model VPFESEM Supra 35VP) was used to examine morphology of fractured specimens. Prior to viewing the specimens using FESEM, the specimens were sputter coated with gold palladium to avoid electric charging during scanning.

3. Results and discussion
3.1 Mechanical properties
3.1.1. Tensile properties. Figure 1 shows tensile strength of neat starch-g-PP, starch-g-PP/kenaf fiber composites without and with different MAgPP content. The tensile strength of starch-g-PP increase from 10.68 MPa to 15.74 MPa with addition of the kenaf fiber loading. The increase indicated that stress was transferred from the matrix to the fibers [7]. Addition of MAgPP to the starch-g-PP/KF composites resulted further increase in the tensile strength. It can be seen, in Figure 1, tensile strength of the composites increase with MAgPP content up to 3 wt.%. The improvement in the tensile strength is attributed to the increased adhesion between fiber and the matrix that facilitates more stress transfer through bonding to the fibers. The interface adhesion is due to the presence of MAgPP which reacted with the hydroxyl group present in the kenaf fiber surface. With further increasing MAgPP content, the tensile strength of the composites is slightly decreased, which is mainly attributed to the plasticizing effect of MAgPP molecules in the composites.

The modulus of the composites was affected by fibers, matrix and their interface. The tensile modulus of starch-g-PP was improved with addition of kenaf fiber, which is known that fibers act as rigid filler that increases stiffness. Tensile modulus is significantly increased with an increment of 232% at 30 wt.% of fiber loading. It is well documented that, due to its relative high tensile modulus KF notably increases the
tensile modulus of most polymer matrices [8-9]. From Figure 2, it is noted that the elongation at break decreased remarkably with addition of KF. It is understandable that the incorporation of KF with a relatively low elongation at break (1.6%) [8] to the starch-g-PP will reduce the overall elongation at break. However, slightly improvement of the tensile modulus and elongation at break of the composites with the MAgPP content is due to the increase of the interface adhesion.

![Figure 1. Tensile strength and modulus of neat starch-g-PP, starch-g-PP/kenaf fiber composites without and with different MAgPP content.](image1)

3.1.2. Flexural properties. The flexural strength and flexural modulus for starch-g-PP/kenaf fiber composites without and with different MAgPP content was presented in Figure 3. The flexural strength of starch-g-PP increases from 19.52 MPa to 30.14 MPa with addition of kenaf fiber. The trends for flexural strength of the composites with MAgPP content are similar to the tensile strength of the composites. The flexural strength of starch-g-PP/kenaf fibre composites with 3% MAgPP content increased from 30.14 MPa to 37.08 MPa. The improvement is related to the better interface between the fiber and the matrix. The flexural modulus of starch-g-PP was improved with addition of kenaf fiber, which is known that fibers act as rigid filler that increases stiffness. Flexural modulus is significantly increased with an increment of 335 % at 30 wt.% of fiber loading. The slightly improvement of the flexural modulus of the composites with the MAgPP content is due to the increase of the interface adhesion.

![Figure 2. Elongation at break of neat starch-g-PP, starch-g-PP/kenaf fiber composites without and with different MAgPP content.](image2)
Figure 3. Flexural strength of neat starch-g-PP, starch-g-PP/kenaf fibre composites without and with different MAgPP content.

3.2 Thermal properties

The influence of MAgPP on the thermal stability of starch-g-PP/kenaf fibers composites were evaluated by TGA, and the results are shown in Figure 4. The characteristic thermal parameters of the thermal degradation are listed in Table 2. For neat starch-g-PP, exhibit three main mass loss steps, i.e. a first one below exhibit 250 °C; a second one located between 270 and 400 °C and the last one occur beyond 400 °C. As reported by some authors, [10-11] the mass loss below 250 °C is due to the evaporation of adsorbed water and plasticizers contained in the thermoplastic starch. The second mass loss is attributed to the degradation of starch compounds corresponding to a maximum degradation temperature of 350 °C [10]. The main degradation products of starch result mainly from crosslinking of glycosidic units after dehydration leading to unzipping of chains and formation of laevoglucosan, which further decomposes predominantly into furfural, formic acid and formaldehyde and also to other volatile products at low concentration [12]. The last degradation step is relative to the decomposition of the PP phase. As a result, aliphatic saturated and unsaturated products are generated involving dienes, alkanes (C_{12}, C_{13} and C_{14}) and alkenes.
Further, the thermal decomposition of starch-g-PP/KF composite is sharply lower than neat starch-g-PP indicating that introduction of the kenaf fibers reduces the thermal stability. The incorporation of KF in starch-g-PP matrix decreases the values of $T_{10\%}$ and $T_{50\%}$ corresponding to the degradation temperature at 10 and 50% mass loss, respectively. This can be explained by the lower stability of KF compared to the matrix, due to the presence of hemicelluloses that are very sensitive to thermal degradation at low temperature mass loss, respectively. The final decomposition temperature of the composite with MAgPP addition is increased compared with that of the composite without MAgPP. The decrease in percentage weight losses shows the slight improvement in thermal stability with the addition of MAgPP compatibilizer. This is due to the chemical bond between MAgPP with starch-g-PP matrix and kenaf fiber could enhance the interfacial adhesion.

### 3.3 Morphology

Two distinct phases are clearly noticeable in the biphasic neat starch-g-PP matrix, as shown in Figure 5 A and B. The continuous phase is polypropylene, while the dispersed phase is thermoplastic starch (TPS). It can be seen that TPS particles are homogenously dispersed in the PP matrix, and both phases are well bonded to each other [13,14]. The good compatibility between them could be attributed to the chemical affinity between TPS component in starch-g-PP and KF. In fact, both constituents contain hydroxyl groups and ether links in the glucose units and polysaccharides, which might enable the formation of hydrogen bonds [13].

It is well known that, without effective wetting on the fiber, strong interfacial adhesion cannot be achieved, and the lack of interfacial interactions results in poor mechanical properties for the composites.
Therefore, the SEM studies support the tensile and flexural testing results discussed in the previous section. The morphologies of the fractured surfaces of tensile specimens of neat starch-g-PP, starch-g-PP/KF composites without and with 3% MAgPP were investigated by SEM. The results are shown in Figure 5. From the images, there is a difference in the adhesion between starch-g-PP matrix and kenaf fiber. Figure 5C shows the fractured surface of the composites without MAgPP. The fibers were pulled out with relatively clean fiber surface and without the resin on fiber surface that is an indication of low adhesion between them. The kenaf fibers also not in close contact with the starch-g-PP. However, for the composites with MAgPP (shown in 5D and F), the gaps between the fiber and the matrix become small.

On the other hand, the starch-g-PP/MAgPP matrix and kenaf fibers are intimately bonded together. It is also observed that the matrix is pulled out together with the fiber during tensile fracture, which further substantiates adhesion between the fiber and the matrix. The maleic anhydride of the MAgPP compatibilizer can interact with the starch phase of the matrix. Maleic anhydride can react with the numerous hydroxyl groups of the starch which is mainly constituted of amylose and amylopectine. Maleated polyolefins compatibilizer was proven to effectively improve the interfacial adhesion between lignocellulosic fillers and polyolefins [15,16]. Moreover, the interaction between the kenaf fibers and starch-g-PP/MAgPP matrix can be attributed to the formation of hydrogen bonds in the interfacial region, for instance, between the hydroxyl (\{-OH\}) groups of cellulose or its counterpart lignin in kenaf fibers with the anhydride groups in the MAgPP matrix. Figure 6 shows plasticizing effect of starch-g-PP/KF with different MAgPP loading. From Figure 6C, the plasticizing effect for starch-g-PP/KF/5MAgPP obvious compared to starch/KF/1MAgPP and starch-g-PP/KF/3MAgPP.
Figure 5. SEM micrographs of fracture surface of tensile specimen (A) 1.00 KX and (B) 5.00 KX neat matrix, (C,E) starch-g-PP/KF (D,F) starch-g-PP/KF/3MAgPP

Figure 6. SEM micrographs of fracture surface of tensile specimen (A) starch-g-PP/KF/1MAgPP (B) starch-g-PP/KF/3MAgPP (C) starch-g-PP/KF/5MAgPP

4. Conclusions

MAgPP was used as a good compatibilizer for starch-g-PP/KF composites. The influence of different MAgPP content on the properties of the composites was studied. The mechanical properties of the composites were improved with the addition of MAgPP. Starch-g-PP/KF composite with 3 wt% MAgPP has tensile strength of 18.44 MPa and flexural strength of 37.08 MPa. The thermal stability of the composites increased with the addition of MAgPP. SEM examination on the tensile fractured surface of the compatibilized composites revealed the formation of the good fiber-matrix interfacial adhesion between KF and starch-g-PP matrix.

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