Effect of coupling agent on durian skin fibre nanocomposite reinforced polypropylene

M A Siti Nur E’zzati, H Anuar and A R Siti Munirah Salimah

1Department of Manufacturing and Materials Engineering, International Islamic University Malaysia (IIUM), Jalan Gombak, 53100 Kuala Lumpur, Malaysia

Email:snezzatiapandi@gmail.com

Abstract. This paper reports on the development of a composite-based natural fiber to reduce the reliance on petroleum-based product in order to amplify environmental awareness. The production of Durian Skin Nanofiber (DSNF) was conducted using biological fermentation method via rhizopus oryzae in order to obtain the nano dimension of the particle size. Polypropylene (PP) and DSNF were produced using Haake internal mixer via melt blending technique. The significant effect of maleic anhydride grafted polypropylene (MAPP) on the properties of PP/DSNF nanocomposite was investigated to study its mechanical properties which are tensile strength and thermal stability using thermogravimetric (TGA) and differential scanning analysis (DSC). The tensile property of PP nanocomposites increased from 33 MPa to 38 MPa with the presence of MAPP. The addition of MAPP also increased the thermal stability of PP/DSNF nanocomposite where the char residue increased by 52%. Besides that, the thermal degradation of PP/DSNF and PP/DSNF-MAPP were higher than PP where they exerted higher amount of weight loss at an elevated temperature. The percentage of crystallinity, %Xc, of PP nanocomposites improved with the addition of MAPP by 35% based on the differential scanning calorimetry (DSC) result. The SEM analysis showed that the PP/DSNF-MAPP exerts ductile fracture while PP/DSNF exerts brittle fracture.

1. Introduction

A lot of research has been done to investigate the effect of using natural fibers such as jute and kenaf in producing environmental-friendly composites such that there will be improvement on the degradability. Thus, efforts have been made to replace these types of materials with those that are more environmentally friendly. The prospect of using renewable resources gives a huge impact towards the global sustainability of composite materials and natural fiber development [1]. The interest of reinforcing polymer composites with natural fiber offers lower environmental effect since they give similar attributes as artificial fibers such as carbon and glass [2]. The application of natural fiber composites is limited because of its lower mechanical properties but it can still be used for household products such as plastic bottles, plates, cups, and food containers. As an effort to manufacture eco-friendly products, studies on strengthening thermoplastic and thermostet materials with natural fibers such as coir, bamboo, sisal, and pineapple leaves have been done [3].

One of the most popular seasonal fruits in South East Asia is Durian. Durian is a climacteric fruit belonging to the Bombacaceae family [4]. Durian is considered the king of fruits by the locals from South East Asia countries. Durio zibethinus is a type of durian that is commonly used for...
commercial and economic importance. The skin of a durian contains 15.45% lignin, 13.09% hemicelluloses, and 60.45% celluloses [5],[6]. It was discovered that we can make fiber from durian peel and this has the potential to encourage new studies in natural fiber around the world. The target is to value-add the durian skin that so in the next few years, the durian trashes will be decreased and together it will reduce accumulated trashes in the country.

In this paper, the usage of agricultural waste as reinforcement for polymeric nanocomposites is suitable by combining petroleum-derived polymer matrix with natural fiber waste according to their potential performance in the mechanical properties [7]. Since durian can be found in Malaysia, durian waste can be developed as reinforcement for polymer biocomposite. This will also aid in reducing the durian waste and improve the degradability of polymer biocomposites [8]. The addition of maleic anhydride grafted polypropylene (MAPP) coupling agent can be used to modify the compatibility of nanocomposite [9],[10]. Thus, this study is important to analyze the effect of DSNF on the mechanical and thermal properties of polypropylene nanocomposites. Comparison is also made between PP/DSNF nanocomposite with and without the presence of the coupling agent.

2. Experimental Procedure
Durian skin waste was obtained in Kuala Lumpur, Malaysia. Polypropylene grade 6331 was supplied by Titan Pro Polymers (M) Sdn. Bhd. and maleic anhydride polypropylene (MAPP) was provided by Sigma-Aldrich.

The preparation of durian skin nanofiber (DSNF) started with washing, chopping, grinding, and sieving processes until DSF in the size of over 250 µm was attained. The production of DSNF was conducted using biological fermentation method via Rhizopus Oryzae in order to obtain the nano dimension of the particle size. The Rhizopus oryzae was obtained from expired bread. From there, it was transferred to a potato dextrose agar (PDA) medium. Rhizopus oryzae was allowed to grow within the PDA medium on a petri dish at 37 °C inside the oven. The first step of the fermentation was done by adding 50 ml of PDB solution and 50 ml of distilled water into the flask. The PDB medium contained 20 g per liter of dextrose and 4 g per liter of potato starch. Next, 2 g of DSF was added into the flask. After that, the grown Rhizopus oryzae was added into the flask and covered with an aluminium foil. Then, the flask was shaken thoroughly using an incubator shaker at the speed of 250 rpm for 7 days [11]. After 7 days, the fermented fiber was filtered, washed, and then dehydrated in the oven for a day at 60 °C.

The PP/DSNF and PP/DSNF-MAPP nanocomposite material was done by mixing the sample at 180 °C using Internal Mixer model Haake Polylab System Thermo Scientific. The rotor speed was 50 rpm and mixed for 12 min.

The tensile tests were done to obtain the tensile properties of PP/DSNF and PP/DSNF-MAPP biocomposite. The test was done by following the ASTM D638 standard by using LLOYD universal testing machine where the load was 10 kN and the test speed used was 50 mm/min.

Morphological observation of the tensile fracture specimen was conducted under scanning electron microscope (SEM) Jeol Jsm-5600.

Thermal gravimetry analysis (TGA) was done to analyze the thermal degradation of PP/DSNF and PP/DSNF-MAPP nanocomposite by following the ASTM D3850 standard. TA instruments Q500 were used in this analysis where the samples were heated on a platinum pan under inert atmosphere of nitrogen gas. The samples were heated from 28 °C to 800 °C at a rate of 20 °C /min. Differential scanning calorimetry (DSC) test was done to determine the thermal properties of PP/DSNF and PP/DSNF-MAPP biocomposite such as the crystallization enthalpy and degree of crystallinity. The machine used was Perkin Elmer Pyris Diamond. The samples were heated at a rate of 20 °C/min with the temperature ranging between 40 °C to 300 °C. The percentage of crystallinity, %Xc, was calculated by obtaining the crystallization enthalpy of composite ΔH and the crystallization enthalpy of fully crystalline polypropylene ΔHm. The value for melting enthalpy of 100% crystalline PP was fixed at 207.1 J/g [12].
%Xc = (\Delta H \div \Delta Hm) \times 100\% \text{.........................Eq. 1}

3. Results and Discussion
The tensile strength of neat PP and PP/DSNF-MAPP 2.5% is shown in figure 1. The graph contains the comparison between PP/DSNF without MAPP and PP/DSNF with MAPP. Before the addition of MAPP, neat PP had the highest tensile strength of 32.4 MPa as compared to PP reinforced with 1 wt%, 3 wt%, and 5 wt% DSNF. The tensile strength of PP/DSNF decreased with the increasing amount of fiber loading. This was due to poor interaction of interfacial bonding between the PP matrix and DSNF. This poor interaction is mainly because of the hydrophobicity of PP and hydrophilicity of DSNF. PP has an even electrons distribution which makes it non-polar, thus it cannot attract water [13]. DSNF is a form of cellulose which means that it contains a long chain of hydrocarbon that consists of glucose, thus it has polarity and absorbs water [11]. The effect of MAPP towards the tensile strength of PP reinforced with 1 wt%, 3 wt%, and 5 wt% DSNF were also analysed in figure 1. The addition of 2.5 wt% MAPP increased the tensile strength of PP/DSNF composites with 1 wt% DSNF to 5 wt% DSNF.

![Figure 1. Effect of DSNF content on PP nanocomposites.](image_url)
The addition of MAPP improved the interfacial bonding between PP and DSNF which was confirmed by SEM (figure 2). The observation under SEM in figure 2(a) and 2(b) reveals the fracture surface of PP and PP nanocomposite without the added MAPP in which it was ductile and had a few spots of brittle fracture surface. The lack of wettabiliy adhesion in composites caused poor interlocking between the fibre and the matrix [14]. Meanwhile, figure 2(c) shows the tensile fracture surface for PP/DSNF-MAPP. The fracture surface mainly consisted of ductile fracture and proves that the addition of MAPP coupling agents aids to improve the tensile strength of the PP nanocomposites. This also suggests that the interfacial adhesion between polymer and fiber reinforcement improves with the addition of MAPP coupling agent [15].

![Figure 2. Tensile fracture surface for (a) neat PP, (b) PP/DSNF, (c) PP/DSNF-MAPP.](image)

The tensile modulus of PP/DSNF without MAPP and PP/DSNF with MAPP are shown in figure 3. The tensile modulus of PP/DSNF without MAPP decreased as the fiber loading increased. This result is similar to the tensile strength shown in figure 1. It also shows that at a higher fiber loading, the bonding between fiber and PP became poorer [13]. On the other hand, the addition of 2.5 wt% MAPP towards the PP/DSNF 1% nanocomposite resulted in a slight drop of tensile modulus by 4.4%. In contrast, the tensile modulus of PP/DSNF 3% and PP/DSNF 5% increased after the addition of maleic anhydride coupling agent. This proves that MAPP enhances the interfacial adhesion of filler-matrix. The tensile modulus of PP/MAPP-DSNF 5% was lower than that of PP/MAPP-DSNF 3%. This is because 2.5 wt% MAPP was not sufficient to fully improve the matrix-reinforcement bonding which caused some of the fiber to experience entanglement [15].

![Graph showing tensile modulus](image)
Figure 3. Effect of DSNF content on PP nanocomposites.

The TGA curve shown in figure 4 describes the weight loss of the PP, PP/DSNF, and PP/DSNF-MAPP nanocomposites with the respective temperatures. Table 1 shows the thermal properties of PP nanocomposite obtained from the TGA. The presence of MAPP in the PP/DSNF had a slight effect in terms of the thermal stability. This is because the sample underwent a weight loss of 15% where the weight of the sample reduced with the presence of DSNF and MAPP. Besides that, the degradation temperature increased with the addition of DSNF. This was due to the addition of DSNF that contained hydroxyl group (OH) bonds which allowed it to degrade faster [16]. However, the addition of MAPP coupling agent improved the degradation temperature because at 990 °C, the composite still had not degraded fully to 0% weight loss. The same trend was observed in the study by Zampaloni et al. [17], whereby the addition of MAPP improved the degradation temperature of kenaf polypropylene composites.

![Figure 4. TG curves for PP, PP/DSNF and PP/DSNF-MAPP biocomposites.](image)

Table 1: TG data of PP/DSNF biocomposites.

| Sample             | Temperature at 15% weight loss (°C) | Final temperature (°C) | Char residue at 600°C, (%) |
|--------------------|-------------------------------------|------------------------|----------------------------|
| PP                 | 521                                 | 650                    | 13.3                       |
| PP/DSNF            | 480                                 | 580                    | 0.6                        |
| PP/DSNF-MAPP       | 472                                 | 990                    | 1.25                       |

The melting behaviour of the PP composites was analysed using differential scanning calorimetry (DSC). The DSC data analysis shown in figure 5 is tabulated in Table 2. The table describes the onset melting, melting temperature T_m (°C), melting enthalpy (Δ H_f), and percentage of crystallinity (%X_c) of the composites. The melting temperature of all 2 samples had no significant change. The neat PP’s melting temperature was the highest compared to PP/DSNF and PP/DSNF-MAPP. The addition of reinforcement reduced the crystallinity of the composite. According to Lee et al. [18], the addition of
MAPP into polypropylene reinforced with wood flour fiber increases the crystallinity and tensile strength of the composites.

![Graph showing Differential Scanning Calorimetry (DSC) analysis of PP/DSNF biocomposites.](image)

**Figure 5.** Differential Scanning Calorimetry (DSC) analysis of PP/DSNF biocomposites.

| Sample          | $T_m$ (°C) | $\Delta H$ (J/g) | Crystallinity ($\%X_c$) |
|-----------------|------------|------------------|-------------------------|
| PP              | 160.1      | 9.86             | 4.7                     |
| PP/DSNF         | 162.4      | 8.23             | 3.9                     |
| PP/DSNF-MAPP    | 173.6      | 12.37            | 6.0                     |

The percentage of crystallinity shows that PP/DSNF-MAPP had the highest value compared to PP and PP/DSNF nanocomposite. The addition of MAPP increased the chain scission and reduced the number of crosslinking chain which gave better higher crystallinity and better mechanical strength [19].

4. Conclusion
From the analysis conducted, it can be suggested that the use of durian skin nanofiber (DSNF) as reinforcement improves the mechanical and thermal properties of PP nanocomposite with the addition of MAPP. The tensile strength and tensile modulus improve with the addition of a MAPP coupling agent. Thus, it can be defined concluded that the interfacial adhesion between the matrix and reinforcement improved due to the introduction of the MAPP coupling agent. The crystallinity of PP/DSNF nanocomposites also increased after the addition of the MAPP coupling agent based on the DSC analysis. Research on the suitability of DSNF as a reinforcement is worth exercising to produce polymer composites using waste material for a greener environment.

**Acknowledgement**
This work was financially supported by the Fundamental Research Grant Scheme (FRGS14-108-0349) from the Ministry of Education Malaysia. The authors would like to thank International Islamic University Malaysia for the research facilities in making this study a success.

**References**
[1] Cheung H Y, Ho M P, Lau K T, Francisco C, David Hui 2009 Composites: Part B 40 655–663
[2] Anuar H and Ahmad Z 2011 Composites: Part B 42 462-465
[3] Prasad P and Kochhar A 2014 Journal of Environmental Science, Toxicology and Food Technology 5 1-7
[4] Manshor M R, Anuar H, Nur Aimi M N, Ahmad Fitrie M I, Wan Nazri W B, Sapuan S M, El-Shekeil Y A, Wahit M U 2014 Material and Design 59 279-286
[5] Khedari J N, Nankongnab N, Hirunlabh J and Teekasap S 2004 Building and Environment 39 59–65
[6] Nur Aimi M N, Anuar H, Manshor M R, Wan Nazri W B and Sapuan S M 2014 Industrial Crops and Products 54 291-295
[7] Fuqua M A and Ulven C A 2008 The Canadian Society for Bioengineering 084364
[8] Charoenvai S 2014 Composite Science and Technology 20-28
[9] Deng H, Reynolds C T, Cabrera N O, Barkoula N M, Alcock B and Peijs T 2010 Journal Applied Polymer Science 118 30-41
[10] Bajwa D, Bajwa S and Holt G 2015 Polymer Degradation Stability 120 212-219
[11] Nur Aimi M N, Anuar H, Maizirwan M, Sapuan S M, Wahit M U and Zakaria S 2015 Sains Malaysiana 44 1551–1559
[12] Dessouky H M, Mahmoudi M R, Lawrence C A, Yassien K M, Sokkar T Z N and Hamza A A 2009 Polymer Engineering Science 49 2116–2124
[13] Smith E R, Howlin B J and Hamerton I 2013 Journal of Materials Chemistry A 12971-12980
[14] Joseph P V, Rabello M S, Mattoso L H S, Joseph K and Thomas S 2002 Composites Science Technology 62 1357-1372
[15] Chun KS, Husseinsyah S, Osman H 2013 Advanced Materials Research 747 645-648
[16] Patpen P, Abdul Rahman Rusly, A, Talib R and Abdan K 2015 International Journal on Advanced Science Engineering Information Technology 5 343-349
[17] Zampaloni M, Pourboghrat F, Yankovich S, Rodgers B, Moore J and Drzal L 2007 Composites Part A Applied Science and Manufacturing 38 1569-1580
[18] Lee K Y, Blaker J J and Bismarck A 2009 Composites Science and Technology 69 2724-2733
[19] Tugiman N, Mohamad Z and Wan Abdul Rahman W A 2010 Universiti Teknologi Malaysia 1-4