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Effects of Coupling Agent on the Properties of Durian Skin Fibre Filled Polypropylene Composite

Hazleen Anuar, Nur Aimi Mohd Nasir, Yousuf El-Shekeil

Abstract**—**Durian skin is a newly explores natural fibre potentially reinforced polyolefin for diverse applications. In this work, investigation on the effect of coupling agent, maleic anhydride polypropylene (MAPP) on the mechanical, morphological, and thermal properties of polypropylene (PP) reinforced with durian skin fibre (DSF) was conducted. The presence of 30 wt% DSF significantly reduced the tensile strength of PP-DSF composite. Interestingly, even though the same trend goes to PP-DSF with the presence of MAPP, the reduction is only about 4% relative to unreinforced PP and 18% higher than PP-DSF without MAPP (untreated composite or UTC). The used of MAPP in treated composite (TC) also increased the tensile modulus, flexural properties and degradation temperature. The enhanced mechanical properties are consistent with good interfacial interaction as evidenced under scanning electron microscopy.

Keywords**—**Durian skin fiber, coupling agent, mechanical properties, thermogravimetry analysis.

I. Introduction

THE evolution of engineering materials with time demanded materials for the next few years to fulfill the concept of renewable, recyclable, eco-friendly, sustainable, and commercially viable. In light with this concept, it is a responsibility for material scientists to investigate and help the community to be less dependence on the commodities petro-chemical plastics-based. As plastic wastes are undesired pollutant in soil, rivers and marine, effort in research towards bio-composite and green materials [1] are actively undertaken. Among the different types of bio-composites those which contain natural fibres and natural polymers have a key role owing to its low density, low cost, biodegradability, acceptable specific properties and low energy consumption during processing [2]-[4].

Malaysia located at the horizontal line of the globe is blessed with various types of plants and natural fibres. One of the promising and new emerging fibre is durian. *Durio zibethinus* Murray, commonly known as durian, is one of the most important seasonal fruit in tropical Asia. It is a climacteric fruit belonging to the family *Bombacaceae*. It grows in the warm, wet conditions of the equatorial tropics and is cultivated in Southeast Asia, particularly Malaysia, Indonesia, Thailand and Philippines [5]. The processed durian skin is known as durian skin fibre (DSF) is a type of lignocellulosic fibre origin from plant.

To ensure green composite produce will satisfy the conditions for long-term applications, it is therefore necessary to understand and to compatibilize the fibre-matrix interface. Graft polymerization method which provides a simplest and versatile approach to property enhancement of natural fibres was adopted in the current research. Graft copolymers of polypropylene and maleic anhydride (MAPP) have shown to be very effective additives for natural fibre reinforced and filled polypropylene composites [6]-[9]. Maleic anhydride offers polar interactions and covalently link to the hydroxyl groups located at the surface of the lignocellulosic fibre [10]. Due to esterification reaction, the lignocellulosic became more hydrophobic and thus improved the compatibility at the interphase [10].

Realizing the importance of green materials with superior properties, thus the aim of this research is to prepare polypropylene composites reinforced with durian skin fibre via extrusion and injection moulding processes. As DSF is hydrophilic and PP is hydrophobic, compatibility of the elements in the presence and without MAPP was investigated and compared in terms of mechanical, morphological and thermal properties.

II. Experimental

A. Materials

Durian skin waste was obtained from local market. Durian skins were washed thoroughly with tap water to remove any adhering particles and dust. The skins were then chopped, ground, and dried in an oven at 80ºC for 12 h. DSF was sieved for 100-250 µm fibre size. Polypropylene (PP) grade 6331 was supplied by Titan Pro Polymers (M) Sdn. Bhd. Maleic anhydride polypropylene (MAPP) was supplied by Sigma Aldrich.

B. Composite Preparation

PP-DSF composite was extruded using Haake 600P twin screw extruder at 190 °C with screw speed of 250 rpm. The ratio of PP:DSF is 70:30 by wt%. About 5 wt% maleic anhydride polypropylene (MAPP) was added in the treated PP-DSF composite. Details of specimens prepared are tabulated in Table I. After completing the extrusion process and palletizing, PP-DSF composites were injection moulded for tensile and flexural specimens as per ASTM standard using BATTENFIELD HM 600/850 injection moulding machine at

Hazleen Anuar is with the International Islamic University Malaysia, Jalan Gombak, 53100 Kuala Lumpur, Malaysia (phone: 603-6196-5752; fax: 603-6196-4477; e-mail: hazleen@iium.edu.my).

Nur Aimi Mohd Nasir is with International Islamic University Malaysia, Jalan Gombak, 53100 Kuala Lumpur, Malaysia (e-mail: aimi_nasir@ymail.com).

Yousuf El-Shekeil is with Mechanical Engineering Department, College of Engineering, Yanbu Taibah University, Saudi Arabia (e-mail: y_shekeil@yahoo.com).

800 bars pressure, 20 s cooling time at 170 mm/s^{1} speed. Note that UTC is referring to untreated PP-DSF and TC is referring to treated PP-DSF composites.

TABLE I
COMPOSITIONS OF PREPARED PP-DSF COMPOSITES

	Polypropylene (wt%)	Durian Skin Fibre (WT%)	Maleic Anhydride Polypropylene (wt%)
PP	100	0	-
UTC	70	30	-
TC	70	30	5

C. Characterizations

The chemical compositions for hollocellulose and α-cellulose for DSF were determined using TAPPI 249-75 and 203 om-99, respectively. Composition of lignin was assessed using TAPPI 222 om-88. The content of hemicelluloses was calculated from the deduced compositions of hollocellulose with cellulose.

Tensile test was carried out according to ASTM D638 using Lloyd (Ametec) universal testing machine. The strain rate was 50 mm/min. A mean of 5 samples were taken for stress and strain calculations. Flexural test was also performed on the same universal testing machine according to ASTM D790. The load cell was 10 kN, the span length was 100 mm and the speed was 5 mm/min.

Scanning electron microscope (SEM) (JEOL, JSM-5600) was used to observe the fracture surface after the tensile test for both treated and untreated PP-DSF composites. The fracture ends of the samples were mounted on an aluminium stub and coated with a thin layer of gold to avoid electrostatic charging during examination. Fourier transform infrared (FTIR) analysis was carried out using a Perkin Elmer, Spectrum-100 machine to find the formation of bond.

Melt flow index of the composites samples were tested using Dynisco Polymer Test Melt Flow Indexer at the temperature of 190^{o}C to prevent fibre degradation, and at 2.16 kg load. The samples were set for 60 seconds for melt and cutting time. A total of three cuts were taken and the average was calculated. Thermogravimetry analysis (TGA) was carried out using a Mettler Toledo TGA/SDTA851e analyzer. The analysis was performed in the temperature range between room temperature and 600 ^{o}C at a heating rate of 10 ^{o}C/min in nitrogen atmosphere. A sample of 5–20 mg of the materials was heated in the sample pan.

III. RESULTS AND DISCUSSION

A. Durian Skin Fibre (DSF) Characteristics

Durian skin is a waste from durian fruit. About 45-50% durian skin is thrown as a waste from each durian fruit. At the moment, there are no specific or technical applications reported for this durian skin apart from being wasted. The durian fruits are large and heavy fruits with sharp hexagonal spines. Fig. 1 (a) shows waste of durian skin. Fig. 1 (b) is durian skin fibre after washing, chopping, grinding, drying and sieving.

SEM analyses of durian skin fibres in various forms were carried out to observe their surface morphology at micron level. Fig. 1 (c) shows fibrils of DSF in the bundles form and Fig. 1 (d) shows the smooth surface of DSF. The complex structure of durian skin fibre is composed of cellulose, hemicellulose and lignin and shown in Table II. High cellulose and hollocellulose contents reduce the brittleness of the lignocellulosic material [11].

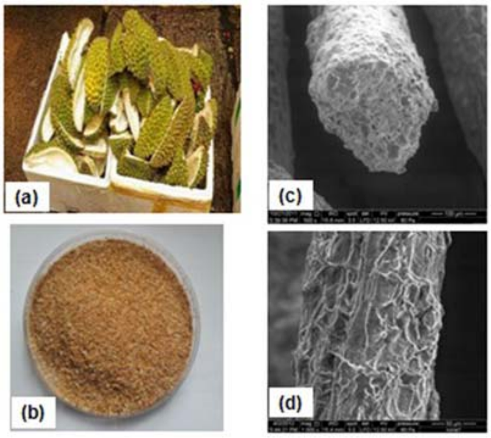


Fig. 1 Photos and micrographs of durian skin (a) and durian skin fibre (b)-(d)

TABLE II
THE COMPONENTS OF DSF

	Components (%)
Cellulose	60.7 ± 0.5
Hemicellulose	22.1 ± 0.5
Lignin	17.2 ± 0.5

TABLE III
MELT FLOW INDEX FOR MATRIX AND REINFORCED PP COMPOSITES

Composition	MFI (g/10 min)
PP	17.80
UTC	13.73
TC	14.40

B. Melt Flow Index (MFI) of PP-DSF Composites

MFI is a common method used in the industry to determine the quality of a polymer and to relate its flow to its application. MFI measures the viscosity or ability of a polymer in the molten state to flow under pressure through orifice of fixed-sized.

MFI for polypropylene composites in the presence of DSF and coupling agent are presented in Table III. Melt flow index for unreinforced PP is the highest at 17.80 g/10 min. The presence of DSF however reduced the MFI for PP composites. This shows that molecular movement of PP was restricted by the presence of DSF accordingly reduced the MFI by almost 23% and 19% for UTC and TC as compared to PP matrix. The flow properties of polymer can be influenced by average molecular weight or length of the polymer chain, the presence of additives that include fillers, inorganic impurities, stabilizers, colourants and flame retardants [12]. As MAPP promotes uniform distribution of fibre in the matrix, thus higher MFI value is expected relative to PP-DSF without MAPP.

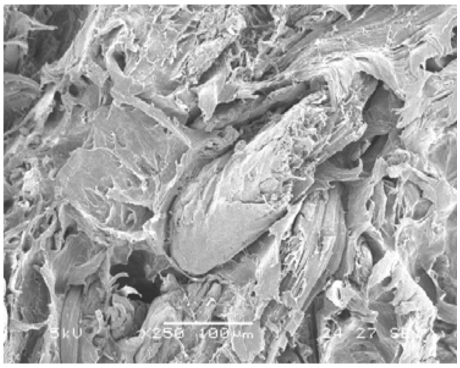
C. Mechanical Properties of PP-DSF Composites

The effect of DSF and coupling agent on tensile and flexural properties of PP composites are presented in Table IV. The presence of 30 wt% DSF shows slight reduction in tensile strength for both UTC and TC. The used of coupling agent, maleic anhydride polypropylene (MAPP) however improved the tensile strength for TC by about 18% compared to UTC. From Table IV also, tensile modulus for both composites recorded an enhancement approximately 37% than unreinforced PP. Tensile strain significantly dropped with DSF and coupling agent down to 85-86% for both systems. Interesting trends can be seen in Table IV for flexural properties. Flexural strength for UTC and TC improved by about 2% and 23%, respectively, compared to matrix. Flexural modulus for both composites was enhanced by about 21% and 28% relative to PP matrix.

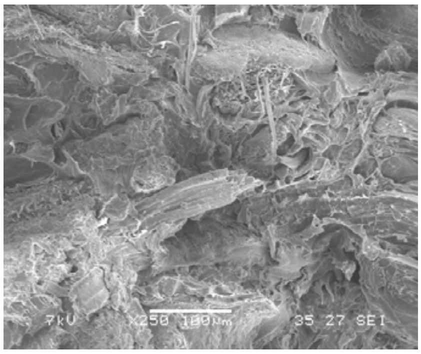
From Table IV, the presence of DSF and coupling agent significantly influenced the mechanical properties of polypropylene and its composites. Mechanical properties of composites are known to be affected by the characteristics of reinforcement fibre and matrix, interfacial adhesion between fibre and matrix, ratio of fibre-to-matrix and processing method used to fabricate the composites. In the fabrication of thermoplastic composites, optimum processing parameters which include time, temperature and processing speed are necessary to produce high performance composites [13].

DSF is a type of natural fibre which contains more than 80% cellulose and hemicelluloses. Due to nature of DSF, the incorporation of hydrophilic DSF into hydrophobic PP induced different polarity condition. Being hygroscopic, fibres tend to cling together in the bundles form and resist dispersion during extrusion [14]. Incompatibility between DSF and PP matrix will reduce the efficiency of stress transfer from matrix-to-fibre and vice versa as observed under SEM micrograph in Fig. 2 (a). Consequently, a minor decrement in tensile strength for UTC is noted as in Table IV compared to unreinforced PP. Thus coupling agent is needed to bridge the natural fibre and PP. The presence of voids is also clearly seen between PP and DSF in Fig. 2 (a). Voids will cause more weakening points, which in sequence will reduce the strength. These morphological observations evidenced the reduction in tensile strength of untreated PP composites.

However, an addition of coupling agent, the MAPP in PP-DSF composites improved the tensile and flexural properties than composites without MAPP. Improvements in mechanical properties of natural fibre-reinforced PP composites due to MAPP were also reported by other researchers [7], [9]. Studies on various treatments on flax/PP have shown that MAPP produces the best surface energy values resulted in highest tensile and flexural strength [15]. This indicates that coupling agent has improved the interfacial adhesion and yielding a higher strength and stiffness. This is qualitatively evidenced from the SEM micrograph in Figs. 2 (b) and (c). The probable mechanism occurred is illustrated in Fig. 3. Since MAPP is derived from PP, thus it is compatible and reduced wetting with PP [16]. The reinforcing effect is amplified through the chemical bonding that facilitates the efficient stress transfer between PP and DSF. FTIR in Fig. 4 confirmed that MAPP interacts with DSF forming covalent linkage and ester bonding between maleic anhydride (MA) and hydroxyl groups in DSF [10]. Peak at 1732 provides evidence of the esterification of the hydroxyl groups and increased stretching vibration of the carbonyl (C=O).



(a)



(b)

Fig. 2 Scanning electron micrographs of PP-DSF composites (a) without MAPP and (b) with MAPP at 250x magnification

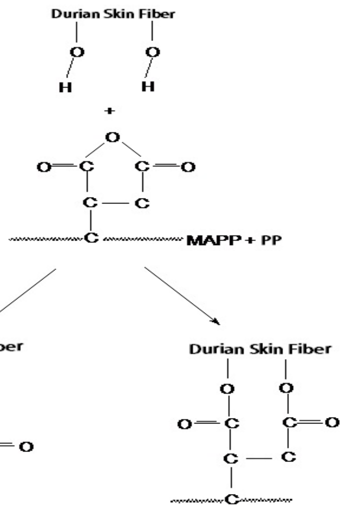


Fig. 3 Model of chemical bonding between PP-DSF with grafted MAPP

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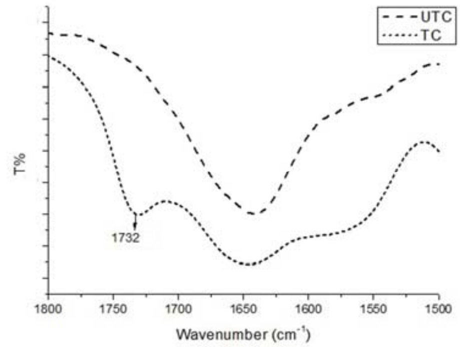


Fig. 4 FTIR spectra for PP-DSF with and without MAPP

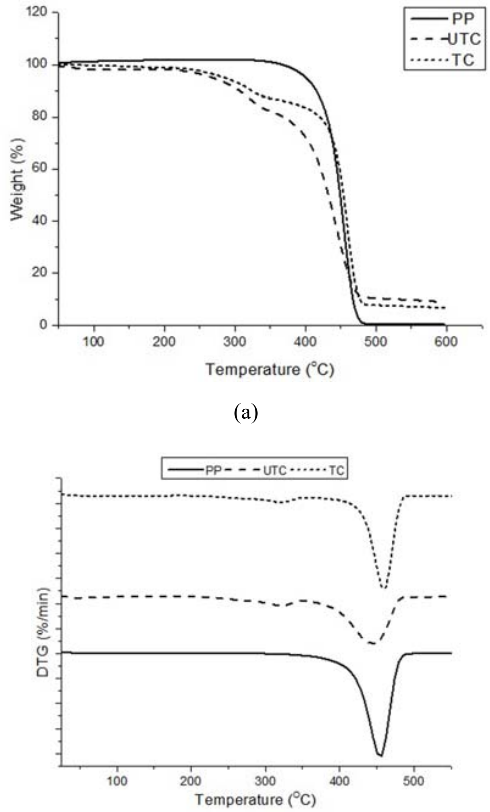
TABLE IV
MECHANICAL PROPERTIES OF UNREINFORCED POLYPROPYLENE (PP), TREATED AND UNTREATED COMPOSITES

	PP	UTC	TC
Tensile Strength (MPa)	36.3 ± 1.2	29.6 ± 1.3	34.9 ± 0.1
Tensile Modulus (MPa)	806.8 ± 60.4	1104.8 ± 50.0	1106.9 ± 70.8
Tensile Strain (%)	71.1 ± 1.4	10.7 ± 0.6	9.9 ± 70.8
Flexural Strength (MPa)	41.5 ± 0.2	42.3 ± 0.3	50.5 ± 0.3
Flexural Modulus (MPa)	1155.9 ± 95.4	1426.8 ± 159.4	1475.0 ± 94.6

D. Thermogravimetry Analysis (TGA) of PP-DSF Composites

Thermogravimetry (TG) curves for PP and reinforced PP composites are shown in Fig. 5 (a). The weight loss of unreinforced PP is occurred in one-step degradation from 420 to 480°C. This is confirmed with the existence of only one peak in derivative thermogravimetric (DTG) curve in Fig. 5 (b). The main chain of PP is carbon-carbon (C-C) bonds, thus it allowed increment in temperature for random scission to occur due to thermal degradation and thermal depolymerization at weak sites of polypropylene main chains [10], [17].

Thermal degradation for UTC and TC occurred in two-steps degradation process as seen in Fig. 5 (a) and Table V. The presence of two peaks is confirmed by the DTG curves in Fig. 5 (b). A shoulder can be seen at around 320 °C in Fig. 5 (b) for both UTC and TC. This could be assigned to decomposition of hemicelluloses [17]. For UTC, the maximum degradation occurred at 319.8 and 446.9 °C. Table V shows that there was more or less no change in term of degradation in the first peak for TC compared to UTC. However, the second degradation occurred at the expensed of +13.9 °C and +5.0 °C relative to UTC and PP matrix. Thermal stability improvements in natural fibre reinforced PP composites due to surface modification were also reported by previous researchers [10], [18], [19]. MAPP enhanced the interaction between PP and DSF and promotes esterification reaction between hydroxyl groups of DSF and anhydride functional groups in MAPP as seen in Fig. 3.



(a)

(b)

Fig. 5 Curves for (a) TG and (b) DTG for PP composites

TABLE V
THERMAL PROPERTIES OF PP COMPOSITES OBTAINED FROM THERMOGRAVIMETRY ANALYSIS

	First Peak (°C)	Second Peak (°C)	Char Residue at 600 °C
Matrix	-	455.8	0.46
UTC	319.8	446.9	9.57
TC	319.6	460.8	7.64

IV. CONCLUSION

Durian skin is a potential waste to reinforce polypropylene just like other natural fibres. Tensile modulus, flexural properties and thermal stability of PP were enhanced in the presence of durian skin fibre. The presence of maleic anhydride polypropylene significantly improved the properties of PP-DSF due to the existence of esterification linkage. The interaction of PP and DSF was observed under scanning electron micrograph.

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