Journal of Polymer Science and Technology 3(2) 2018:29-34
ISSN: 2550-1917

EFFECTS OF EGGSHELL POWDER ON MECHANICAL PROPERTIES AND MORPHOLOGY OF NR/HDPE-MENGKUANG FIBER HYBRID COMPOSITES

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ABSTRACT

This study investigated the physical and mechanical properties of hybrid composites from natural rubber (NR)/high density polyethylene (HDPE)/*Mengkuang* fiber (MK)/eggshell powder (KT). Preparation of hybrid composites, NR/HDPE/(MK/KT) was produced using composition 40/60/(20) with filler material, MK/KT was varied at 0/20, 5/15, 10/10, 15/5 and 20/0. Preparation of hybrid composites is produced using melt blending method in internal mixer at 135°C and mixing rate at 50 rpm for 18 minutes. The resulting samples were tested in terms of strain testing, impact test and water absorption test, while the structure and morphology were characterized using Fourier Infrared Transformer (FTIR) spectroscopy and scanning electron microscopy (SEM). In this study, the hybrid composite with MK/KT 5/15 filler provides optimum yield with maximum stress strength of 7.84 MPa and maximum impact strength of 6.60 kJ/m^2. In addition, the treatment of MK fibers covers pre-treatment with sodium hydroxide (NaOH) solution, and immersion with hexadecyltrimethoxysilane (HDS) solution has been performed to enhance the physical and mechanical properties. The composition of the filler with the highest percentage of mengkuang fiber with 20% showed an increase in water absorption rate. Overall, the addition of egg shells has been shown to enhance the physical and mechanical properties of resulting composite.

Keywords: *Hybrid composites, Mengkuang fiber, Eggshell, Melt blending*

INTRODUCTION

Natural fibers are the best alternative to replace the existing synthetic fibers for its advantages that can be recycled, environmentally friendly, easily accessible and cost-effective. There are various types of natural fibers such as cotton/cotton yarn, flax, hemp, jute and sisal which also contain high amounts of cellulose [1]. Over the last few decades, studies on thermoplastic and natural fibers have grown significantly due to the mechanical and physical properties of composite materials that can be modified according to the market requirements [2]. Coconut husk, paddy husk, palm oil debris and other agricultural industrial wastes are widely used as natural filler in composite production [3]. Hybrid composites made from waste materials are also a great option to develop new materials with low costs and specific properties. Researcher prepared hybrid composites made with newspaper fibers and poplar wood flour. They observed that the addition of both fibers enhanced the tensile and flexural modulus as compared to neat polypropylene, but increasing wood flour reduced flexural and tensile moduli [4]. Hybrid composite production, which requires low cost, is advantageous because high cost fillers can be combined with cheaper materials to produce good composites. In addition to cost savings, hybrid composite production can help in terms of improvement in mechanical properties as well as helping to maintain ecosystem balance [5].

The mengkuang fiber (Pandanus Atrocarpus) is an example of natural fiber that is still less developed in the production of composite materials. Mengkuang leaves have the main uses such as the manufacture of handicraft items including mats and baskets and usually grow on the edges of paddy fields, water strings, swamps and rivers. Eggshell is one of good GCC (ground calcium carbonate) filler replacement due to its availability and high content in calcium carbonate. Most importantly, it is generated from bio-source. It has been reported that ground eggshell was used as filler for non-polar polymers such as HDPE, LDPE and PP in which eggshell calcium carbonate helped improve Young's modulus of the filled polymers [6].

The suitability of mengkuang fiber and eggshells in the NR/HDPE mixture was studied in terms of physical and mechanical properties while morphological examination was carried out to see the dispersion of the filler across the matrix surface. Next, alkaline pre-treatment and immersion using HDS were performed on the surface of the MK fiber to enhance the interaction between the fibers. Most studies showed that NaOH treatment increases the mechanical properties of the composites [7,8]

EXPERIMENTAL

Materials used in this study were SMR-L grade natural rubber from Felda Malaysian Rubber Sdn. Bhd whereas, high density polyethylene from Etilinas Polyethylene Sdn. Bhd. Mengkuang fiber was obtained near Beserah, Kuantan while eggshell was from unused waste through Kolej Ibrahim Yaakub cafe. Both materials were processed at laboratory in Universiti Kebangsaan Malaysia.

Preparation of filler MK/KT

MK fiber and KT powder were used as filler in this study. Mengkuang leaves were cut small into 2 cm long and dried in oven for three days. The dried leaves were ground using fiber cutting machine (Model AZM). The MK powder was washed thoroughly for 72 hours until the dark green solution become clear. After that, MK fiber was dried in oven at 60°C for 24 hours. The fiber was sieved to size of 125-250 µm using sieve shaker (Retsch Test Sieve, model AS200). Next, eggshells were washed and dried under sunlight overnight. The dried eggshells were ground using blender and sieved to size of less than 125 µm with sieve shaker.

Hybrid Composites Preparation

Hybrid **c**omposites of TPNR were prepared in an internal mixer (Haake Rheomix 600) at 135°C, 50 rpm for 18 minutes. The composition of matrix NR/HDPE were 40/60 with the variation of filler MK/KT between 0% to 20% filler loading. MK fiber and KT powder were added first in the internal mixer followed by NR at minutes of three. In the fifth minutes, HDPE was added and left in the internal mixer for 13 minutes to make sure the composites were well blended. Next, resulting composites will be hot pressed for 15 minutes at 145°C with pressure of 70kg/cm^2. Composites with 1 mm and 3 mm thickness were prepared for the physical and mechanical analysis. Table 1 shows the formulation of hybrid composites used throughout in this study.

Table 1 Composition of studied materials

Composites	Ratio of matrix (NR/HDPE)	Mengkuang Fiber (%)	Eggshell (%)
A	40/60	20	0
B	40/60	15	5
C	40/60	10	10
D	40/60	5	15
E	40/60	0	20

Characterization and Mechanical Testing

Tensile properties were measured using universal testing machine according to ASTM D412 standard. Load cell was kept at 1kN with crosshead speed of 500 mm/min. 1 mm thick dumbbell shaped specimens were cut using Hollow Die Punch cutter. The data reported are tensile strength and Young's Modulus. The average stress and tensile modulus were calculated from at least 5 samples. Meanwhile, impact strength was measured by an Izod impact tester in accordance to ASTM D256 for an average 5 samples. The test was performed on specimens with dimensions of 65 mm x 12 mm x 3 mm. Each sample was notched with 1 mm depth and immersed in liquid nitrogen for 30 s. Scanning Electron Microscope (LEO 1450 VP model) was used to study the morphology of the materials at different magnifications. The investigation was performed on the fractured surface of the tensile test samples.

Water absorption Test

The specimens for this test used the same standard and dimensions with impact strength test. Sample was dried in an oven at 80^{o}C for 24 hours. Specimen weight, length and thickness were measured. Weight of samples before immersed in water was recorded first. Within 2 weeks, the differences in the weight of samples were recorded using the following equation:

$$\text{Water uptake}(\%) = \frac{w_2 - w_1}{w_1}\ x\ 100$$

where, w_2 is the specimen weight after immersed in water and w_1 is specimen weight before immersed in water.

Infrared Spectroscopy Analysis

The surface structure of the treated and untreated MK fiber was characterized by Fourier Transform Infrared (FTIR) to differentiate the functional group that presence on the surface fiber. The sample was analyzed in the absorption mode in the wavenumber range of 4000-640 cm^{-1}.

RESULTS AND DISCUSSION

Tensile Strength

The effect of filler loading MK/KT on the tensile strength of hybrid composites is shown in Fig. 1. The tensile strength of NR/HDPE blend increases with increasing eggshell powder loading up to 20%. Therefore, the most optimum hybrid composites filler loading is at MK/KT 5/15 with the highest tensile strength of 7.83 MPa.

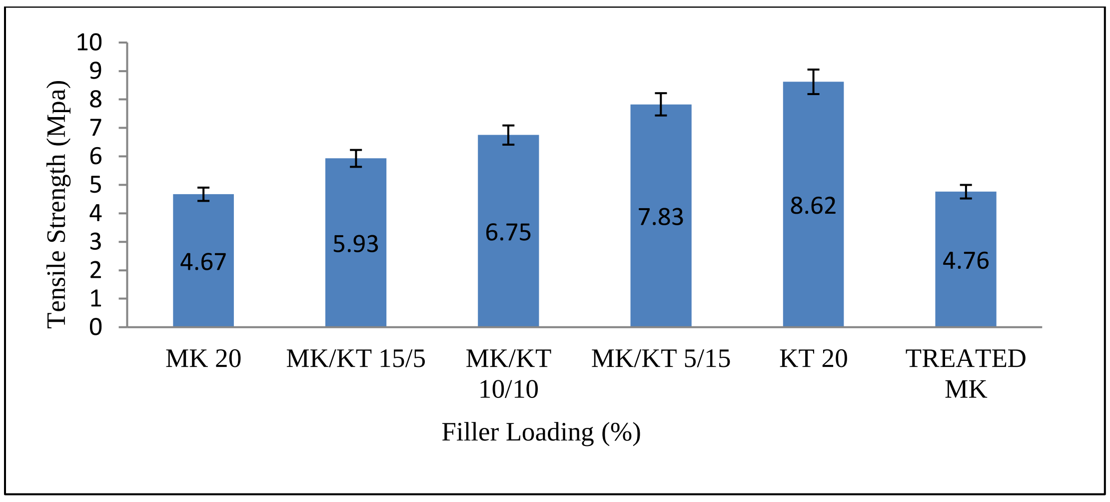

Fig. 1 Effects of filler loading on tensile strength

Additional of eggshell powder increased the tensile strength. The higher eggshell powder loading makes the sample produced become strong and hard to break. The increase in tensile strength is due to the formation of nearly uniform distribution of eggshell particles in NR/HDPE matrix. The enhancement of the tensile strength indicated that the eggshell powder has filled the microspores between mengkuang fiber and the matrix and gives a well dispersion of the filler in the matrix [9]. It is also clearly seen, that the composites with eggshell powder only have a higher tensile strength than the composites with unfilled eggshell, which attributed to the great fineness of the eggshell particles which resulted in more uniform distribution.

Tensile Modulus

Fig. 2 shows the effect of filler loading on tensile modulus. The observation indicates that the incorporation of fiber will improve the stiffness of the composites. However, the tensile modulus of composites is decreased with an increasing replacement of eggshell powder. This could be due to the restricted movement caused by the filler when eggshell powder is added. Addition of eggshell powder has reduced the rigidity of the hybrid composites. Formation of agglomeration will lead to insufficient homogeneity and also the rigidity of the composites [9].

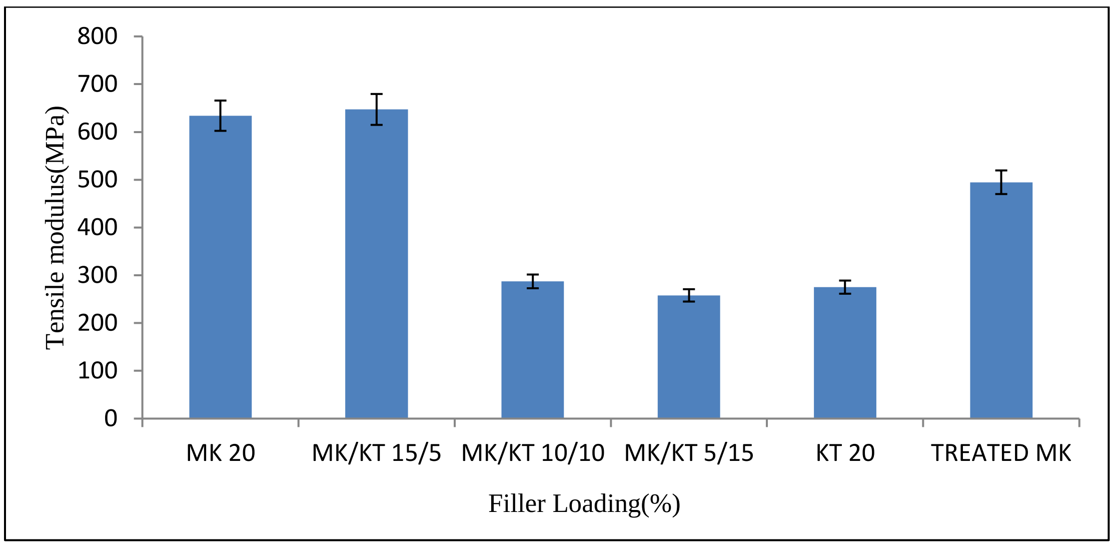

Fig. 2 Effects of filler loading on tensile modulus.

Impact test

Fig. 3 shows effect of filler loadings on impact strength. It is clear that additional of eggshell powder filler has a noticeable positive influence in increasing impact properties of hybrid composites. Eggshell powder has been known to impart toughness to the PE matrix because of formation of interparticle ligaments, which promote plastic deformation and the transition of the composite from a brittle state to a ductile state [10]. Furthermore, treatment on the fibers at 5% improves the toughness to 8.04 kJ/m^2. The increase in the value of this impact strength has proven that the treatment on the surface of the mengkuang fiber has improved the adhesion between the fibers and the matrix, thus prevent the fault from occurring quickly during the impact test. Good treatment will result in strong adhesion and subsequently causing the fracture to occur only on high strength.

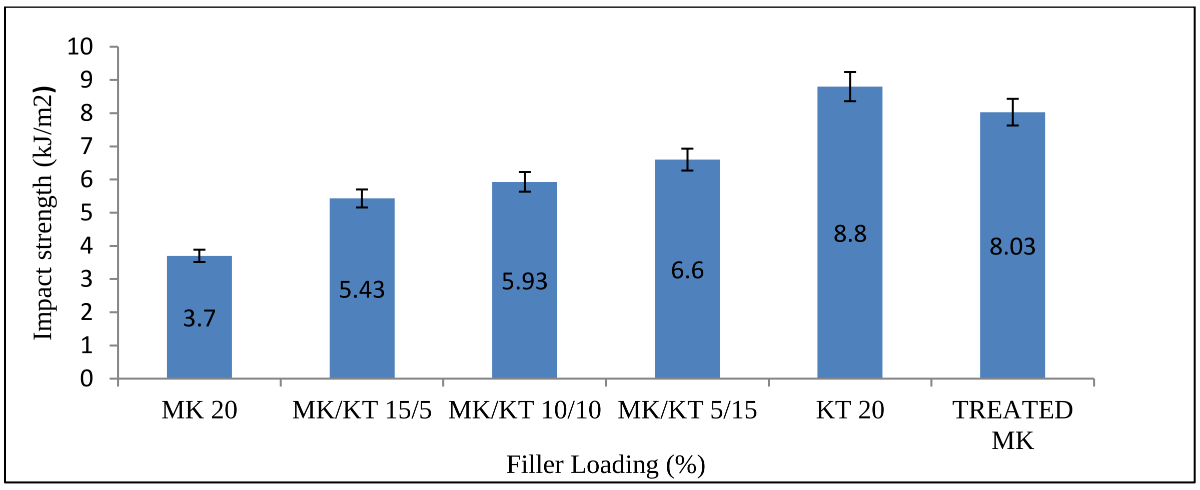

Fig. 3 Effects of filler loadings on impact strength

SEM Micrograph

Fig. 4, 5, 6, 7 and 8 shows the typical SEM micrographs of NR/HDPE/MK fiber reinforced composites with incorporation of the eggshell powder. For each composite, two different scales of observation are used to analyze the fiber-matrix interface with the additional of eggshell powder.

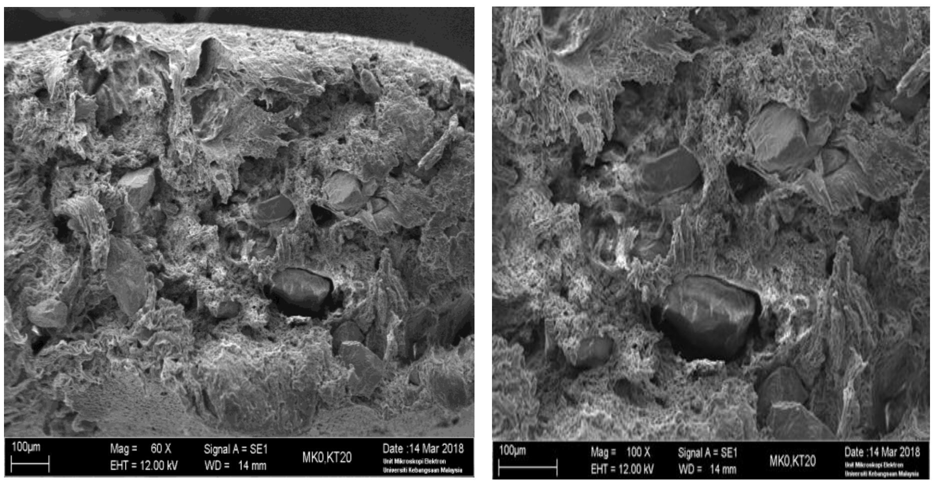

Fig. 4 Hybrid composite SEM micrographs for the percentage of filler MK/KT 0/20 on magnification 60x and 100x

Fig. 4 shows the SEM micrograph for samples with filler MK/KT 0/20 at 60x and 100x magnification. Based on the diagram above, it can be seen that some dark dark spots represent a strong adhesion between the filler KT and the NR/HDPE matrix. The strong adhesion between the matrix and the filler has been proven by an increase in the properties of composite mechanics. The small size of the KT filler allows KT filler to be scattered more evenly in the NR/HDPE matrix.

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ISSN: 2550-1917

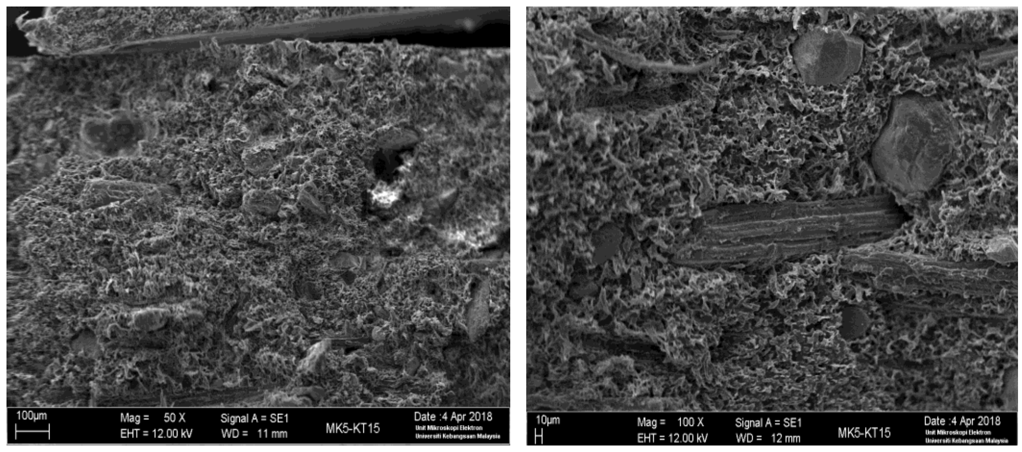

Fig. 5 Hybrid composite SEM micrographs for the percentage of filler MK/KT 5/15 on magnification 50x and 100x

Next, in Fig. 5 showing the SEM micrograph for filler MK/KT 5/15 in magnification 50x and 100x. Based on the diagram above, with the addition of 5% of the MK, the composite dispersion distribution is better and uniform as the filler is more scattered into the matrix. The attachment between the matrix and the filler is also strong, where it can be seen with the lack of visible cavity on this composite. A strong interaction between matrix and filler will indirectly enhance the mechanical properties of composites [11]. At 50x magnification, there are several small holes indicating that KT is pulled out during the stretching test. There is also a bit of clear space in the interface between the fibers and the matrix. This is the case with the presence of hemicellulose, lignin and glossy materials that are still attached to the surface of the fibers so that the fibers can not stick with the matrix together.

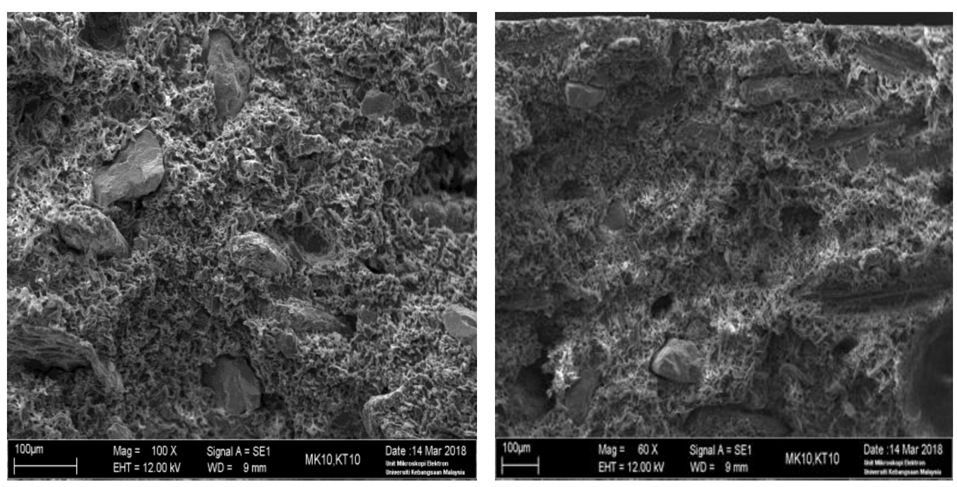

Fig. 6 Hybrid composite SEM micrographs for the percentage of filler MK/KT 10/10 on magnification 100x and 60x

Whereas, for the micrograph in Fig. 6 above, it can be noted that the composite surface is more dense and produces more empty holes between the filler and the matrix. These holes represent the cavity which indicates that there is no strong adhesion between the filler and the polymer matrix. This is due to the MK and KT fibers that have been pulled out during the stretching test.

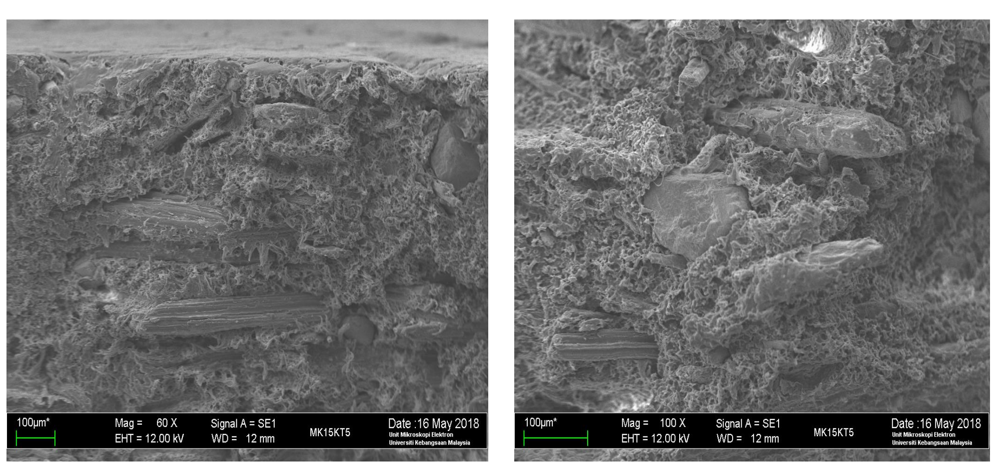

Fig. 7 Hybrid composite SEM micrographs for the percentage of filler MK/KT 15 /5 on magnification 100x and 60x

Fig. 7 showed the SEM micrographs for filler MK/KT 15/5 in magnification of 100x and 60x. The addition of mengkuang fiber as much as 15% clearly indicates that the mengkuang fiber is strongly bonded to the matrix. The blending between the matrix and the filler are well blended, thereby causing a good interfacial interaction between the filler and the matrix. The well-dispersed stresses between coagulating fibers and matrix polymers resulting in an increase in the stretching modulus as a results of stress.

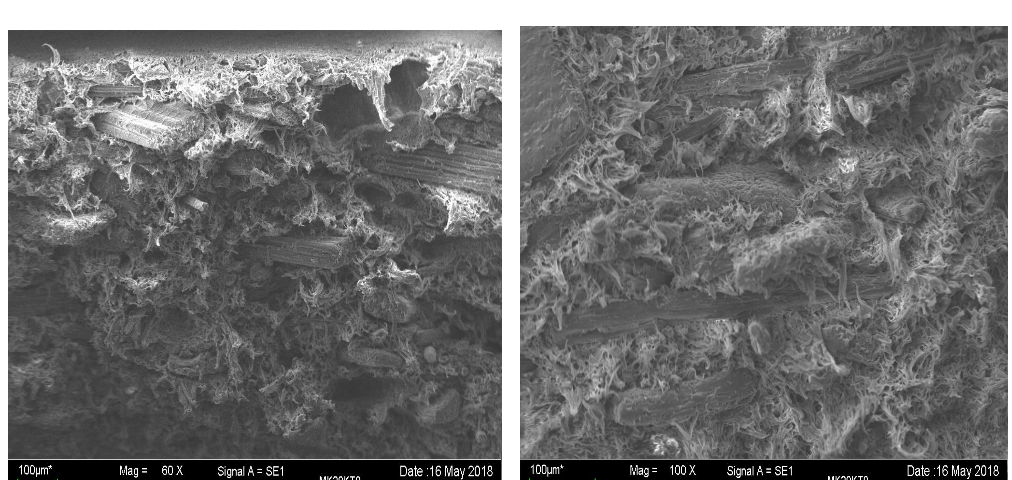

Fig. 8 Hybrid composite SEM micrographs for the percentage of filler MK/KT 20/0 on magnification 60x and 100x

In Fig. 8 showing the SEM micrograph for filler MK/KT 20/0 at magnification of 60x and 100x. From the observation, it is clearly seen that the mengkuang fiber are pulled out of the matrix. The withdrawal of fiber has resulted in a decrease in the composite mechanical properties. Mengkuang fiber used has led to the formation of agglomeration, where weak interactions between fillers and

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matrices were occurred [9]. Therefore, in this composition, the composite polymer properties are lower compared to composite polymers in other compositions.

Water Absorption Test

The water uptake results of all samples are presented in Fig. 9, showing that the percentage of water absorption of NR/HDPE/KT composites show less water uptake as it has filled the microspores between the matrix and filler. But for higher fiber loading composites, water uptake is the highest due to hydrophilic nature, making the mengkuang fiber easy to absorb water. After treatment is done, the fiber has been modified by forming a better bonding interface and absorption of water. The treated fiber makes the adhesion level better, thereby preventing the spread of water molecules. A strong adhesion between the interfaces makes the fiber become more hydrophobic and less absorbing water.

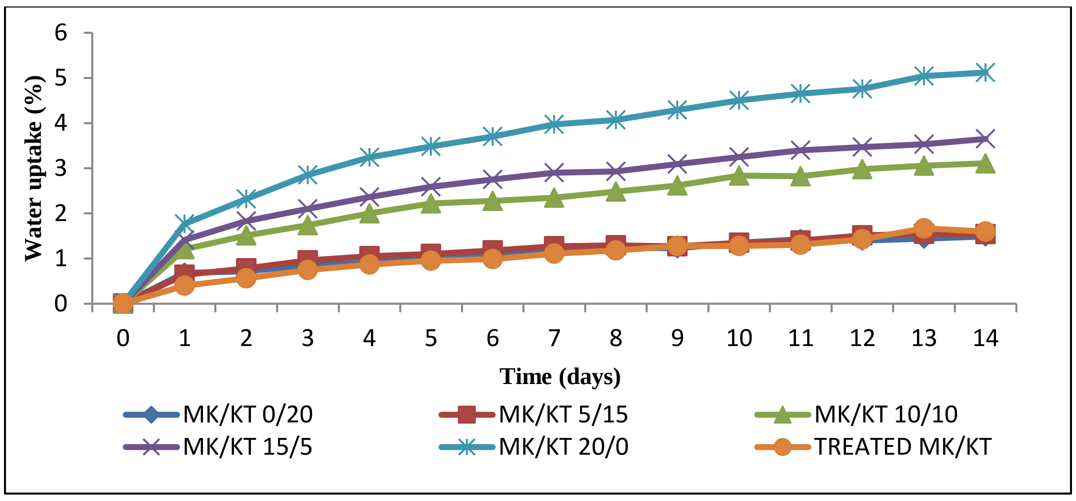

Fig. 9 Percentage of water uptake versus time with different filler loading

Infrared Spectroscopy Analysis

Fig. 10 shows the peak of FTIR spectra of treated and untreated mengkuang fiber with NaOH and silane from wavenumber of 600cm^{-1} to 4000cm^{-1}. Generally the spectrum of FTIR for natural fibers is due to absorption by functional groups found in cellulose, hemicellulose and lignin molecules. The absorption peak for each spectrum, representing certain functional groups are shown in Table 2.

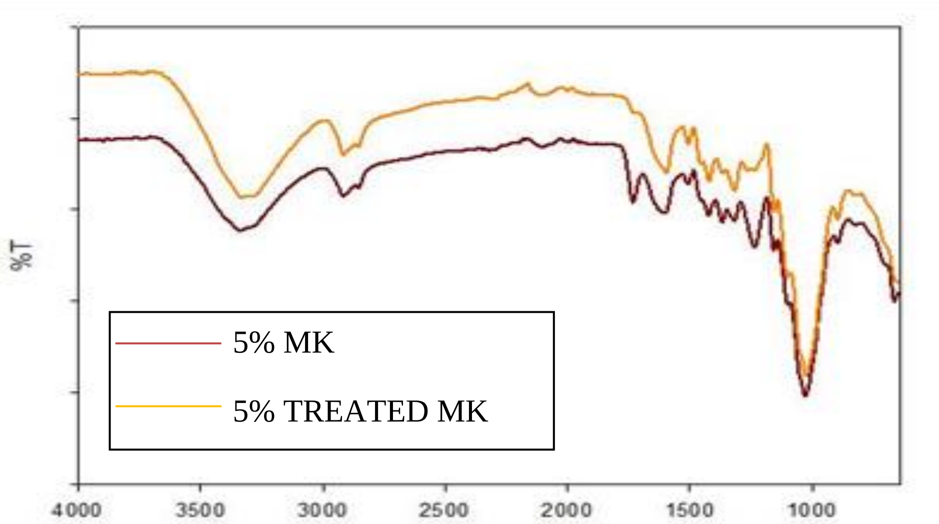

Fig. 10 FTIR spectrum of mengkuang fibre treated and untreaed with NaOH and silane

Table 2. FTIR assignments of treated and untreated mengkuang fiber with NaOH and silane

Peak	Wavenumber, cm^{-1}	
	Untreated	Treated with NaOH and silane
O-H stretching	3403	3333
C-H stretching	2916	2915
C-O stretching	1028	1026
C=O stretching	1732	-
Si-O-Cellulose	-	1233
Si-O stretching		1100

The broad peak at 3333-3403 cm^{-1} of hydroxyl group is due to O-H functional groups that present in the mengkuang fiber which contributing to their hydrophilic nature. The lignocellulosic fibers was mainly composed of cellulose, hemicellulose and lignin [12]. The peak around 1026-1028 cm^{-1} corresponding to stretching of C-O from methoxyl and hydroxyl groups in lignocellulose fiber. Furthermore, after treating with 4% NaOH, carbonyl group is not present at peak around 1732 cm^{-1} because of some hemicellulose on the surface of mengkuang fiber is removed. With silane treatment, Si-O-Cellulose bond clearly be seen at peak of 1233 cm^{-1} due to the pre-hydrolysis reaction process with a hydroxyl group on the surface of the fiber [13]. The peak at 1100 cm^{-1} is attributed to the stretching of Si-O silane used in the fibre.

CONCLUSION

The addition of eggshell powder as a filler by certain percentage has improved the mechanical properties and better surface morphology of the hybrid composites especially with the 15% KT. Water absorption test showed that the hybrid composites has low water uptake after addition of eggshell powder. Therefore, this study proved the suitability of eggshell powder as a filler in making hybrid composites.

ACKNOWLEDGEMENT

Authors would like to acknowledge Universiti Kebangsaan Malaysia for the grant (GUP-2017-123), facilities, equipment, and funding support for making this study successful.

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