CALCIUM CARBONATE COMPOSITION EFFECT UPON MORPHOLOGY, WATER ABSORPTION AND FLEXURAL PROPERTIES OF HYBRID FILLED KENAF AND RICE HUSK

[1]NOOR ZUHAIRA ABD AZIZ, [2]RAHMAH MOHAMED

[1,2]Faculty of Applied Sciences (FSG),
Universiti Teknologi Mara (UiTM) Shah Alam, Malaysia
E-mail: [1]noorzuhaira@gmail.com, [2]greenkayangan@gmail.com

Abstract— The effectof calcium carbonate ($CaCO_3$) on flexural, water absorption and morphology of kenaf/$CaCO_3$/HDPE and rice husk/$CaCO_3$/HDPE hybrid composites was examined. In this study the hybrid composites with varying weight of up to 70%, HDPE, up to 30% $CaCO_3$and fixed 30% of natural fiber was compounded separately using twin-screw extruder at 50rpm. Water absorption of the hybrid composite increased with the addition of $CaCO_3$ mineral filler. Hybrid composite consist kenaf have higher ability to absorb water due to the high cellulose compared to rice husk hybrid composite. The flexural test showed that in general, addition of up to 20% $CaCO_3$ into both hybrids composite had increased the flexural strength and flexural modulus.

Keywords— Hybrid Composite, Natural Fiber, Mineral Filler, Flexural Properties, Water Absorption Behaviour.

I. INTRODUCTION

The development of new material from polymer composites is important to produce material that has specific properties and low manufacturing costs. The interest in the utilization of natural fibers in thermoplastic has increased recently mainly due to the need in overcoming the environmental problem caused by agricultural by-product [1]. Utilization of lignocellulosic fiber offer the low cost of production, renewability, biodegradability, less abrasiveness and greater deformability thus provides advantages to the mechanical, physical and thermal properties of the material. Furthermore filler from natural fiber such as kenaf and rice husk are lighter, cheaper, and provide much higher strength[2].

However after many investigations have been made on the potential of the natural fibers as reinforcement for composites, N. Venkateshwaran et al. had agreed that in several cases the result shown that the natural fiber composites have good stiffness but still not provide optimum strength for composite [3]. Therefore hybrid composite will be the alternative to enhance the strength properties of the composite reinforcement by lignocellulosic fibre. Hybrid composites are material made from two or more types of different fibres. The advantages of one fibre can complement some disadvantages imparted by another fibre. By hybridization, if proper material are design it is possible to achieve a balance between performance and cost of processing hybrid composite which would not be obtained with a single kind of reinforcement [4-6].

The commonly used of mineral filler such as silica, talc, $CaCO_3$, mica, kaolin, wollastonite, feldspar and barytes. The use of each mineral filler is depends on the physical attributes of the mineral to a specific application. The superior properties of inorganic mineral filler can lead to better compound performance other than saving material cost factor. They can extend the resin, increase stiffness and strength and improve impact performance. Besides that, mineral fillers prevent hang-up in dies and neutralize the products of degradation. From above advantageous offered by mineral filler, it is shown that mineral filler can complement some properties of natural fibre composites which might lack in terms of mechanical properties. B. Kord also had stated that hybridization of natural fiber with mineral filler was used to improve the physical and mechanical properties of wood plastic composites (WPC) [5].

In this work, rice husk/$CaCO_3$composition and kenaf/$CaCO_3$composition will be compounded in the thermoplastic HDPE and their properties will be compared on flexural and water absorption properties.The different amount of $CaCO_3$ mineral filler and polymer matrix HDPE used to determine the effect of $CaCO_3$ in the hybrid composites.

II. DETAILS EXPERIMENTAL

2.1. Materials

HDPE used in this study was supplied by TITAN (M) Sdn. Bhd. The 50 mesh kenaf fibers and rice husk particulate were obtained from MARDI. The 2000 mesh of $CaCO_3$ was obtained from ZANTAT Sdn. Bhd.

2.2. Procedures

The rice husk flour was mixed with HDPE and $CaCO_3$. The compound mixture was melted by extruded using twin screw extruder at temperature profile range between 160^{o}C and 190^{o}C from feed to die zone. Compounded pallets were fabricated and compressed by hot press at the temperature of 190^{o}C. The same process was repeated and rice husk was substituted with kenaf. The compositions prepared are as given in Table I.

Table 1: Composition of the Studied Formulations

Samples	HDPE (%)	Kenaf (%)	Rice Husk (%)	$CaCO_3$ (%)
K1	70	30	-	-
K2	60	30	-	10
K3	50	30	-	20
K4	40	30	-	30
RH1	60	-	30	10
RH2	50	-	30	20
RH3	40	-	30	30
RH4				

2.3 Composite Characterization

Water absorption properties were measured according to ASTM D570-98. This test method determine the amount of water absorb into sample. The samples were undergoing the long term immersion. The weighing process was repeated every 24 hours for first two weeks and every once a weeks until the increase in weight per week shows constant result.
The water absorption was determined as:

$$\% \text{ Water Absorption} = \frac{w_1 - w_0}{w_o} \; x \; 100 \qquad (1)$$

where w_1 is the mass of the sample after immersion, and w_0 is the mass of the samples before immersion.
Flexural test was measured according to ASTM D790 specification. The test was carried out using the three-point bending test Instron Machine. The cross-head speed applied was 5mm/min.
Morphological studies of the hybrid composites were carried out using a Field Emission Scanning Microscope (FESEM) SUPRA-40 VP with software INCA Suite versions 4.12 with the magnification, 5000x. The impact fracture surfaces of the specimen were observed by microscope. The fracture surfaces were gold-sputtered to prevent electrostatic charge build-up during evaluation.

III. RESULTS AND DISCUSSION

3.1. Water Absorption

The water absorption of both kenaf/HDPE and rice husk HDPE composites with addition of $CaCO_3$ are shown in Fig. 1. From the graph we can observed that increasing in immersion time had increase the amount of water uptake by composite. In the early stage both unfilled and filled composites had significantly increase in water absorption and after a certain time all composites start to reduce the water uptakes from the surrounding till it reach saturation point. Saturation point is where composite absorb no more water and the water content in composite remained constant [7].
The addition of $CaCO_3$ in both unfilled composites had increase the water absorption rate. This might be due to the properties of the $CaCO_3$ that have high tendency to agglomerate. The size of $CaCO_3$ used in this study was small ~1500 mesh as comparedto kenaf and rice husk. It is well known that the more smaller in size of particle the more easily the particle to agglomerate. This agglomeration would weaken the interfacial adhesion between the filler and matrix which thus lead to variation in the formation of gap in interfacial region. Increasing the gap in interfacial region could increase the amount of water molecules to penetrate into composite and the being trapped inside the gap.

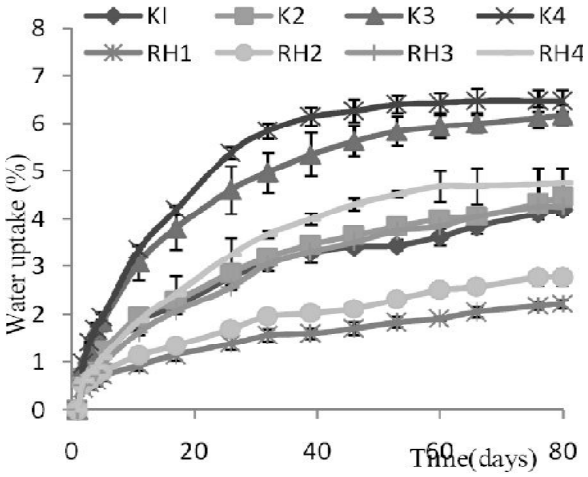


Fig. 1 Water absorption behaviors for hybrid composite

It well exhibit that particulate form of filler had higher tendency to produce agglomerate compared to fibrous form. Rice husk and $CaCO_3$ were the particulate form whereas kenaf was the fibrous form. From the result, it obvious shown that the water absorption of kenaf/HDPE composite was higher than rice husk/HDPE composite with addition of $CaCO_3$ filler loadings. This was due to the higher cellulose in kenaf fiber form. When $CaCO_3$incorporated in the rice husk/HDPE composite, the existence of high amount of agglomeration had increased the gap in interfacial between the filler and matrix thus increasing the water absorption of the composite. However, the amount of cellulose in kenaf given more impact in water absorption properties compared to the gap appears between the filler and matrix in all filled composites. Kenaf had the ability to absorb water due to the high cellulose content which formed high hydrogen bonding from its hydroxyl group and water molecules. The ability of rice husk to allow water molecules penetrate had lowered. Its absorption ability isless efficient than kenaf even though its origin from similar cellulose, hemicellulose and lignin.
Although calcium carbonate, which is polar and have hydrophilic sites [8], it may not be as good as the cellulosic fibers of the kenaf do attract moisture or water molecules. In this project, the stearic acid acts as surfactant which lowers the surface energy of the calcium carbonate which has high energetic hydrophilic surface. The stearic acid enhances the wetting of the calcium carbonate and matrix HDPE ; this reduces the particles tendency to agglomerate and thus decreasing the void in composites which may

cause the moisture or water absorption increase[9]. Furthermore, the natural fiber used in this study was untreated. Thus, the tendency to absorb water molecule are highly expected to be brought about by natural fiber compare to $CaCO_3$ filler loading in the hybrid composite.

3.2. Flexural Strength

From the Fig. 2, it could be observed that bending strength increased with addition of $CaCO_3$ filler. Kenaf/$CaCO_3$/HDPE composite produced higher bending strength compare to other unfilled and filled composites. The highest bending strength was K3 composite follow by K2 which contain 60%HDPE 30%kenaf 10%$CaCO_3$ and 50%HDPE 30%kenaf 20%$CaCO_3$ respectively. While RH3 and RH4 showed the lowest bending strength, 16.7MPa and 15MParespectively. Kenaf/HDPE composite experience a significant changing pattern with addition of $CaCO_3$ filler compared to rice husk/HDPE composite.

Although HDPE polymer matrix loading decrease, all filled composites increased in flexural strength with addition of $CaCO_3$ filler. Thus, it is indicated there were good interactions remaining between CaCO3 filler with both unfilled composites. This could be possible due to the better adhesion between the $CaCO_3$ and kenaf/HDPE and rice husk/HDPE composites.

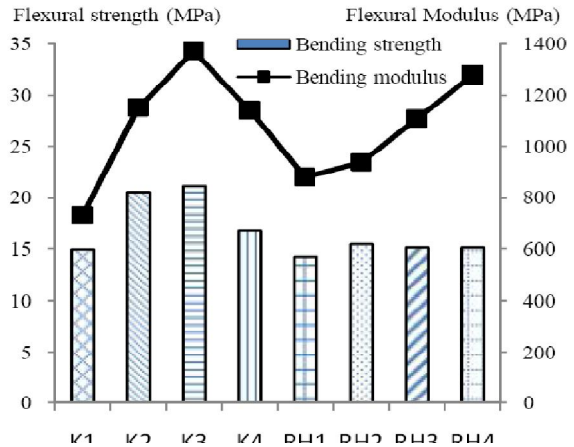


Fig. 2 Flexural strength and flexural modulus of the hybrid composites

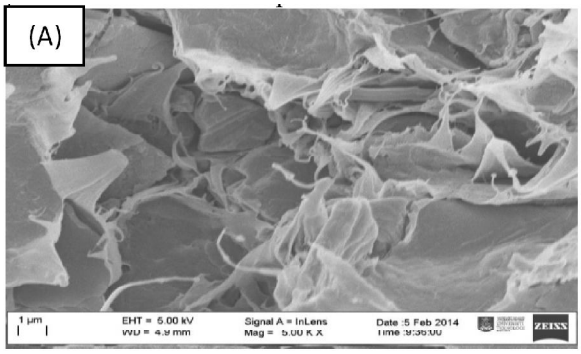
Exceeding $CaCO_3$ filler loading (>20%) in unfilled composite had decreased the bending strength as could be significantly observed in K4 and RH4 composites. The higher filler used in hybrid composite the higher probability of agglomerate to occur. Higher amount of agglomeration in composite could form an aggregation that caused poor interfacial adhesion and weak bonding between filler-matrix. The optimum $CaCO_3$ filler loading in kenaf/HDPE and rice husk/HDPE composites were 20% wt.

It is interesting to observe that the effect of similaraddition filler of $CaCO_3$ in kenaf/HDPE composite was more significantlycompared to rice husk/HDPE composite. Kenaf/HDPE composite experiences rapidly increase in bending strength while rice husk/HDPE gradually increases with addition of $CaCO_3$ filler loading. This might be due to the shape of the filler in the composite. Kenaf fibrous form was different with $CaCO_3$ particulate form. This difference in shapes of filler could improve the bonding between filler-matrix by filling in the void appeared in the composite. The voids occur due to weak compatibility between two different hydrophobic HDPE and hydrophilic fillers in the hybrid composites. The different shape of kenaf fibrous and $CaCO_3$ particulate fillers could integrate by creatingfullfiller network which reduces voids as much as possible. As well know the void could decrease the interfacial adhesion between the filler-matrix bonding which decreased the strength of the composite. Therefore, different shape of kenaf fibrous and $CaCO_3$ particulate filler could help to improve the interfacial adhesion of composite by filling in voids thus helping to reduce the amount of void that exist in composite. Meanwhile, similar shape of rice husk and $CaCO_3$ filler would form a strong bonding between filler-filler interactions rather than filler-matrix bonding. It produced high tendency to bondbetween and produced high amount of agglomerate.Thus, weakens the interfacial adhesion of the hybrid composites.

The higher flexural modulus was K3 follow by RH4, 1369 MPa and 1276 MPa respectively. The increasing flexural modulus with addition on $CaCO_3$ filler might be due to smaller size and higher surface area of $CaCO_3$ particle. Intrinsic modulus of $CaCO_3$is higher than other fillers. According to Hongwei He et al. [10]and Hattotuwa G.B. et al.[11], higher surface area could cause decreasing in mobility of the macromolecules thus improve filler-matrix adhesion.

3.3 Morphology

Fig. 3 is the FeSEM of impact fracture of kenaf/$CaCO_3$/HDPE and rice husk/$CaCO_3$/HDPE hybrid composite.Fig. 3(A) show better dispersion between the kenaf fiber and HDPE which presentas few agglomerate and void. The FeSEM micrographs in Fig. 3(C) of the unfilled composite show clearly phase of delamination and non-adherence which predominates of rice husk particulate in HDPE.



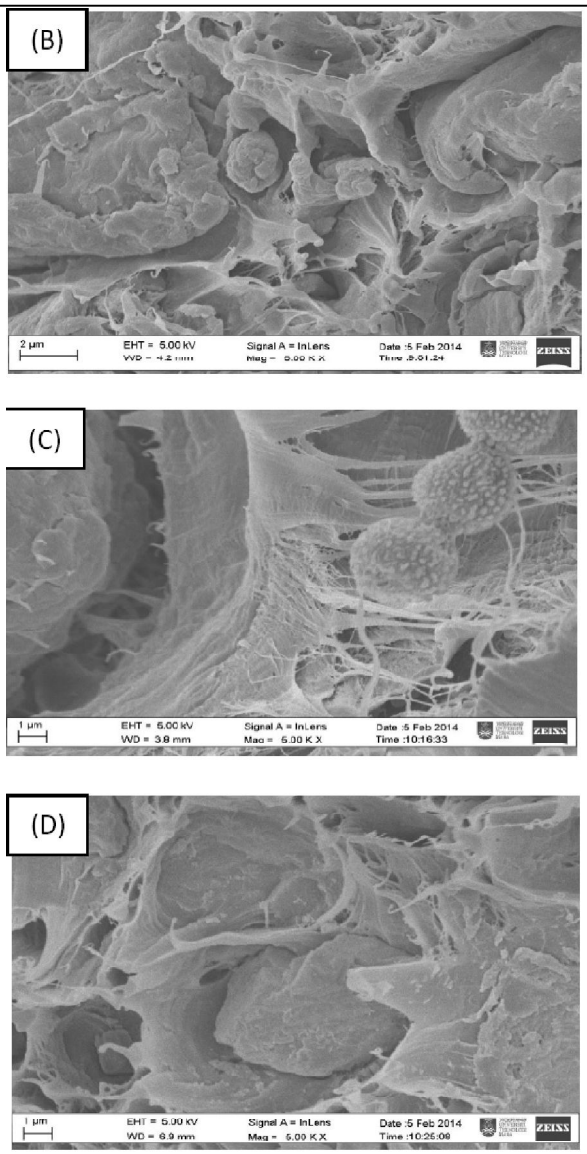


Fig. 3 FeSEM micrograph of impact fracture surface of hybrid composite at magnification x5000: (A) K2, (B) K3, (C) R2, (D) RH3

The delamination that occur at the interphase between rice husk and HDPE was indicate the wet-out of fibers by polymer matrix thus weaken the fiber-matrix bonding [10].

As the $CaCO_3$ used in kenaf/HDPE and rice husk/HDPE composites, the distribution and interaction between filler and polymer matrix was improved. From Fig. 3(B), it was found that the kenaf fibers and mineral fillers were embedded into the HDPE polymer matrix. This proved that there are strong interfacial adhesion between the fillers and polymer matrix. Besides that, the existence of $CaCO_3$ in the kenaf/HDPE composite also help to reduce the amount and size of void due to the different shape of particulate $CaCO_3$ with fibrous form of kenaf fiber. The larger size of agglomerate can be seen in Fig. 3(D) was due to the similar particulate filler shape of rice husk and $CaCO_3$ in HDPE composite. The affinity shape between both particulate filler had formed strong interaction between fiber-fiber bonding and also increases the amount of cavities and void in hybrid composites.

CONCLUSIONS

From this study, the following conclusion could be drawn:

1. All filled hybrid composite experience increasingwater absorption with addition of $CaCO_3$ fillers due to the incompatibility between the filler and matrix that caused agglomeration and void.
2. Increasing in water absorption of kenaf/$CaCO_3$/HDPE hybrid composite is more significant compare to rice husk/$CaCO_3$/HDPE hybrid composite with addition of $CaCO_3$ mineral filler. This was due to the high cellulose content in kenaf compare to rice husk.
3. Flexural strength of both hybrid composites was increased with addition of $CaCO_3$ filler. However higher loading of $CaCO_3$ (>20%) decrease the flexural strength due to poor interfacial adhesion and agglomeration.
4. Similar shapes of fiber form could increase the agglomeration since fiber-fiber tends to strongly interact with each other. Deterioration of flexural properties of hybrid compositewas observed.
5. The presence of agglomeration and void in high loading calcium carbonate exhibited in FeSEM micrograph explained that poorer interfacial adhesion between filler and matrix in hybrid composite exists.

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