EFFECT OF FLEXURAL AND THERMAL PROPERTIES OF SUSTAINABLE KENAF FIBRE AND RICE HUSK WITH MINERAL FILLED PP HYBRID COMPOSITE

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Abstract— Hybrid composite is of value added composite for industrial demand, hybrid composite has optimised and balance properties to encounter some disadvantages exhibited by individual fillers. Sustainable fillers are much needed by industry, which are from waste agriculture or plant origin. They can be sourced fillers incorporated with mineral fillers to form thermoplastic hybrid composite. PP composite utilizing individual fillers such as $CaCO_3$, kenaf or rice husk have been investigated. Hybrid composite properties such as flexural and thermal properties are analysed in this study. Hybrid composite fabrication using both sustainable plant origin kenaf fiber and agricultural waste, rice husk particulate incorporated with calcium carbonate ($CaCO_3$) into polypropylene (PP) was extruded by utilizing twin screw compounder. Using fixed ratios of PP and $CaCO_3$, hybrid composite with various compositions of kenaf fiber and rice husk particulate were compounded with kenaf fibres in ranges between 5% up to 35% and rice husk 5% up to 30% by weight. In this study, the incorporation of kenaf/rice husk/$CaCO_3$/PP hybrid composite on mechanical and thermal properties were investigated. The thermal stability of the component was examined by thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC). The DSC results showed some changes in melting temperature (Tm), crystallization temperature (Tc) and the degree of crystallinity (X_C) with the incorporation of hybrid fillers. Thermal gravimetric analysis (TGA) indicated thermal stability of hybrid composite filled with both kenaf fiber and rice husk particulate.

Keywords— Kenaf Fibre, Rice Husk, Hybrid Composite, Flexural properties, Thermal properties.

I. INTRODUCTION

Nowadays, fibre reinforced plastis used natural fiber which act as the reinforcement for composites. This is mainly due to attribute such as lower density, recyclability, lower cost, renewability, wide availability compare to the carbon and glass fiber. These natural fiber reinforced polymer composites are able to minimize the environmental pollution [1]. Natural fiber are lignocellulosic material and being used to improve the properties of hybrid composite and can be tailored to specific properties for actual application.

Lignocellulosic fibre offers various attractive benefits and are more ecofriendly. Other than that, its exploitation can lower cost of production, present harmless contribution to health and is less abrasive. They also provide greater deformability and advantageous to the mechanical, physical and thermal properties of materials. The primary purpose of adding mineral filler into the hybrid composite is to reduce the cost of productions of the material compund. Moreover, the mineral filler mixed with lignocellulosic enhances the properties hybrid composite [2]. Hybrid composites are made by combining two or more kinds of different fibres in a common matrix. Hybridisation of two kinds of short fibre in different length and diameter offer beneficial advantages over the use of fibre alone in a single polymer matrix [3].

Hybrid composite can be able to play an important role to become the solution regarding future pollution issues. Due to the environmental awareness, concern of environmental friendly and sustainable managment, growing global waste problem has created interest to renewable resource such as kenaf fibre and rice husk particulate. They can act as reinforcement and thermoplastic polymer as the matrix to develop hybrid composite. In realization of green technology, hybrid composite may be able to revolutionise automotive, household and other related plastics composite industry.

In the present study, we used PP resin as matrix and sustainable kenaf fiber and rice husk particulate as reinforcing filler to prepare a hybrid composite. Hybrid fillers from three sustainable materials such as kenaf fibre, rice husk waste and calcium carbonate can be formulated for high filled hybrid composite. $CaCO_3$ are abundant and it can contribute to mineralisation of land. Due to ecological aspects of the fillers used, market acceptance and consumer perception can be achieved [4]. Use of $CaCO_3$ into polymer matrix is extensively exploited in composite to reduce the amount of resin matrix used, to improve performance and reduce cost [5]. Flexural and thermal properties are important to impart bending strength of composite and determining transition and operating temperature and thermal stability of composite. Hence, in this research the effect on flexural and thermal properties of kenaf fibers and rice husk particulate fillers in $CaCO_3$/PP hybrid composites were investigated.

II. METHOD

2.1. Materials and Sample preparation

The polypropylene (PP) used in this research was supplied by TITAN (M) Sdn. Bhd. Kenaf fiber and

rice husk particulate were 50 mesh respectively, which obtained by MARDI. While $CaCO_3$ was supplied by ZANTAT sdn Bhd with size 2000 mesh. Kenaf and rice husk were placed in an oven for drying in temperature 100 °C until the fiber kenaf, and rice husk particulate reached the minimum temperature 1 % - 2 % of moisture content. The kenaf fiber and rice husk particulate were incorporated with PP and $CaCO_3$. The incorporated compound was melted by twin screw extruder profile temperature range between 175°C and 185°C from the feed zone to die zone. Incorporated pallets were fabricated and compressed by hot press at the 185°C in sheet form. The components prepared are as given in Table 1.

Table1: Composition of the formulations

Samples	PP (%)	Kenaf (%)	Rice Husk (%)	$CaCo_3$ (%)
P0	40	-	-	20
P1	40	10	30	20
P2	40	15	25	20
P3	40	20	20	20
P4	40	25	15	20
P5	40	30	10	20
P6	40	35	5	20

2.2. Flexural Test

Flexural strength was measured according to ASTM D790 specification to determine the ability of a material to withstand bending force applied perpendicular to its longitudinal axis. The test was carried out using the three point loading system applied to supported beam. Sometimes it is referred as cross breaking strength where the maximum stress developed when a bar shapes test piece acting as a simple beam, is subjected to a bending force perpendicular to the bar.

2.3. Thermogravimetric Analysis (TGA)

Sample about 5-10 mg were used for each composition and were set heat at temperature 30 °C to 900 °C at 10 °C/ min under an air flow rate 50 mL/min. This analysis was carried out using a perkin Elmer Thermogravimetric Analyzer.

2.4. Differential Scanning Calorimetry

About 5-10 mg of sample at temperature 30-300 C under nitrogen atmosphere was performed with a Perkin Elmer Differential Scanning Calorimetry Analyzone. The heating and cooling rates were set at 30 C min^{-1} . To determine the degree crystallinity in accordance with the following equation:

$$Xc = \frac{\Delta H_m}{\Delta H^*} \times 100\%$$

Where ΔH_m and ΔH^* are the melting heat of fusion of the hybrid composite and 100 % crystalline PP.

III. RESULTS AND DISCUSSION

3.1. Flexural Strength Test

Fig. 1 shows the effect of both kenaf fibre and rice husk particulate on bending strength in $CaCO_3$/PP. Flexural strength is the ability of hybrid composite withstands bending forces applied perpendicular to its longitudinal axis. The interfacial strength depends on the surface of the natural fiber due to nature of fiber or particule interaction with the matrix.

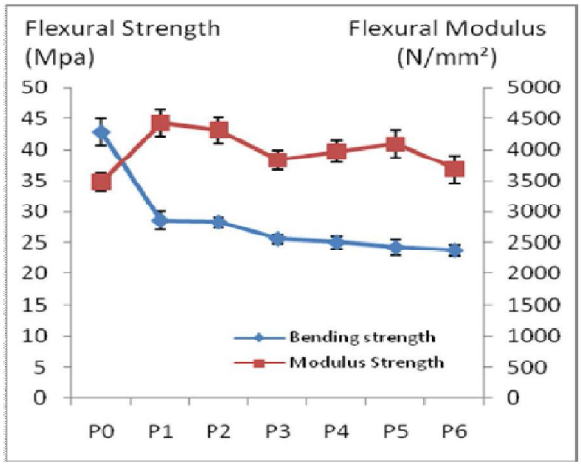


Fig 1. Flexural strength and flexural modulus of the hybrid composite

It was observed that P1 with 10 % kenaf fibre and 30 % of rice husk particulate having flexural strength values had the highest flexural strength ~ 28.6 MPa because of the high particulate-matrix compatibility, good particulate-matrix interaction and wetting. High Rice husk existence contributes to the bonding strength of hybrid composite due to silica compatibility and interaction with $CaCO_3$ and matrix PP. Interaction of rice husk with $CaCO_3$ and HDPE matrix had been investigated by NoorZuhaira et al [6] and high flexural strength was found to be highest using high rice husk composition in hybrid composite. Intrinsically, rice husk particulate has high stiffness due to its high rigidity of mainly silica content. This provides the high hybrid composite stiffness to better adhesion for kenaf and rice husk.

Bending strength is the highest stress at the moment of rupture: The flexural strength which ranges from 28 to 23MPa is higher than tensile strength which ranges from 13 to 8 MPa for the same composition [7].The higher flexural strength is due to failure of stress when bending force is applied, the neutral axis shifts toward the compression face, and thus tend to strengthen the sample.

The result shows that upon variation in kenaf composition, increase of kenaf composition slightly decreases the bending strength of about 3-4% only. The bending strength is still maintained at around 25-24 Mpa. This indicated that the interfacial adhesion between both kenaf fiber and rice husk particulate with polymer resin can withstand the bending stress

onto hybrid composite. P6 with 35 % kenaf fiber and 5 % rice husk showed the lowest value of bending strength at 23.7 MPa. Poor adhesion between fiber-particulate with matrix were more pronounced with the kenaf fibre. The adhesion and interaction of fiber matrix were found to be lesser for fibrous type kenaf compared to rice husk particulate. Homogeneity between matrix fiber is probably less effective due to the shape of fibrous which has high L/D ratio and incompatibility of more hydrophobic kenaf fiber with $CaCO_3$ compared to rice husk having high silica content. Because of that, the matrix is unable to fully interact with fiber-particulate upon applying bending stress when the transfer process of fiber – particulate took place . Without fibre or rice husk, the strength of hybrid composite is higher with values of 42.9 MPa PP/ 20% CaCO3. Drastic drop in strength was observed, which is ~ 33% to 40% upon kenaf fiber and rice husk incorporation with similar fixed amount of $CaCO_3$.

Fig. 1 shows the tensile modulus result reflecting the effect of change in the content percentages of kenaf fiber and rice husk particulate. Increase in the rigidity of incorporating kenaf, and rice husk was exhibited through higher modulus ~ 30 % with modulus value of 4432.907 N/mm^2 with composite P1. Upon incorporation of higher rice husk, rigidity or stiffness were found to decrease. However, upon an increase in kenaf composition, modulus was found to increase. However, composite P6 had reduced modulus as more than 30% kenaf content, the rigidity upon bending stress applied started to reduce. This is probably too high content of kenaf ~35%, kenaf fibers started to agglomerate and reduce the interaction between kenaf-matrix and kenaf-$CaCo_3$, whereby the flexural modulus is 3684.2 MPa. The amount of rice husk is too low ~5% do contribute to the lower rigidity. Hence, optimized interaction of composite to achieve high modulus is provided by at least 10% rice husk and above

The value maximum of flexural modulus was formulated with 10% of kenaf fiber and 30 % of rice husk particulate into $CaCO_3$/PP. While P6 which contain 30 % kenaf fiber and 5 % rice husk particulate incorporate with $CaCO_3$/PP showed the minimum value flexural modulus 3684.255 N/mm^2.

3.2. Thermogravimetric Analysis (TGA)

Thermal decomposition of hybrid composite determined from the TGA is as shown in fig. 2 and fig. 3 while for decomposition peak data are shown in table 2. The peak temperature was determined by DTG peak where the maximum decomposite rate was obtained. The degradation of lignocellulosic fiber at high temperature at time of processing may lead to undesirable composite properties. Hence, it is essential that the degradation of the fiber must be determined for fabricated hybrid composite applications. The TG thermogram showed the hybrid composite exhibited a slight mass decrease around 80-160 °C due to water loss for all hybrid composite analysed. It is because the residual water in natural fiber kenaf and rice husk particulate were released ; released water vapour were produced at lower temperature compared to other components [8]. Further thermal degradation of hybrid composite takes place as a three step process, meanwhile for $CaCO_3$/PP composite it showed only two step process. Those result were confirmed by two weight loss process of $CaCO_3$/PP composite in fig 2 and three weight loss process in hybrid composite in DTG thermogram. In the first stage at temperature about 486.3 °C it shows the decomposition of PP and at the second stage shows the decomposition of $CaCO_3$ at temperature 743.6 °C. Table 2 shows the decomposition peaks of kenaf/rice husk/$CaCO_3$/PP hybrid composite. For hybrid composite of kenaf/rice husk/$CaCO_3$/PP, the first degradation peak is from hemicelluloses, cellulose and lignin present in natural fiber filler. The depolymerization of hemicelluloses and lignin occur between 300°C and 400°C. According to Tserki et al, hemicellulose is easily hydrolysed and have greater amorphous structure. It is in contrast with the cellulose and lignin, upon which, cellulose is very long polymer of glucose units and can improve the thermal stability of lignicellulosic fibers with higher crystalline structure [9].

Table 2: DTG values maximum decomposition temperature hybrid composite

Samples	First peak temperature (°C)	Second peak temperature (°C)	Third peak temperature (°C)
P0	-	486.25	743.55
P1	343.87	519.14	766.35
P2	337.21	512.95	764.45
P3	334.42	513.62	763.99
P4	330.52	514.57	758.12
P5	327.63	421.82	737.76
P6	325.15	416.38	726.36

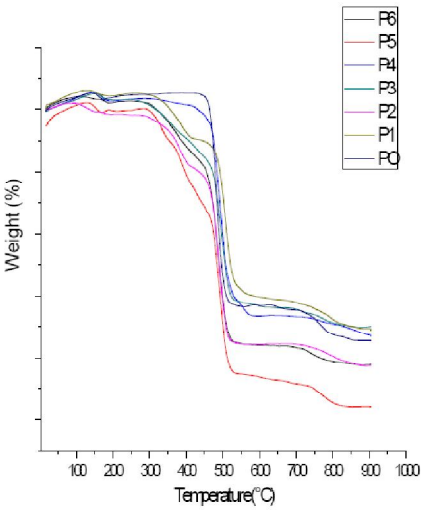


Fig.2 TGA curve of hybrid composite

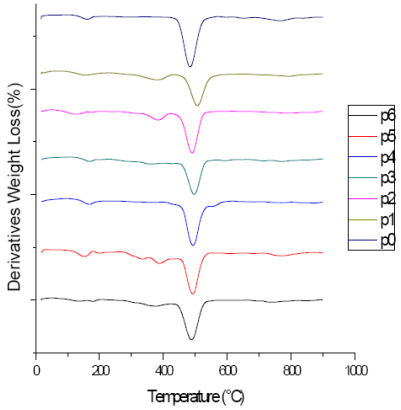


Fig. 3 DTG curve hybrid composite

Lignin have very high thermal stability, molecular weight and also difficult to decompose due to presence of phenolic groups [10].

The decomposition of the polymer structure in lignin starts at relatively low temperatures, of 200-275 °C, the main process occurring around 400 °C, with the formation of aromatic hydrocarbons, phenolics, hydroxyphenolics and guaiacyl- /syringyl-type compounds, most products having phenolic –OH groups [11]. The cleavage of the aromatic C−O bond in lignin leads to the formation of one-oxygen atom products, while cleavage of the methyl C−O bond forms two-oxygen atom products. The cleavage of the side chain C−C bond occurs between the aromatic ring and the α-C atom [12].Low heating rates favour the formation of oxygen-containing compounds, while more hydrocarbons and alkyl-phenol derivatives are formed at fast heating rates [13]. Therefore, one of the factors that can affect decomposition behavior is the heating rate. In our studies, heating rate is fixed at 50C/min .

The econd stage process are the decomposition peak, which took place between 410°C and 520°C. It is associated with the greatest weight loss due to the decomposition of PP backbone. The additional of kenaf increased the decomposition temperature of resin in hybrid composite due to the higher content of crystalline cellulose of kenaf fibre. The final decomposition peak occurred in hybrid composite due to $CaCO_3$ at temperature between 700°C and 800°C. The decomposition hybrid composite of $CaCO_3$ occurred at lower temperature with higher weight loss of kenaf depicting loss of lignin, hemicelluloses and finally cellulose between 200 °C-360 °C. With PP and $CaCo_3$ (PO) the DTG peak has negligible weight loss as kenaf and rice husk are not present as depicted in Figure 3.

When compared P2 and P4, it was found that the thermal stability of hybrid composite incorporated with high kenaf content is higher as compared to rice husk example for similar ratios of 25% kenaf and rice husk. For higher rusk husk content, the composition of rice husk at the first stage degradation may contain more crystalline cellulose of rice husk compared to kenaf fiber. According to MartiFerrer et al. (2004), the lignin and hemicellulose contents in rice husk fiber are lower than wood fiber while its cellulose content is much higher [14].

3.3 Differential Scannig Calolimetry (DSC)

The hybrid composite processing usually proceeds under non isothermal conditions and thermal transitions of hybrid composite were analysed as in Table 3 . its related thermogram is determined as in Figure 4. The crystallization and melting behavior of hybrid composite consist of kenaf/rice husk/CaCO3/PP were analysed by DSC.

Table 3 shows the T_m, T_c, ΔH, and X_c, values from the DSC analysis for the natural fiber kenaf and rice husk particulate in $CaCO_3$/PP hybrid composites.

Table 3: DSC result in hybrid composite

Samples	T_m (°C)	T_C (°C)	ΔH_m (J/g)	X_c (%)
P0	172.5	106.9	90.7	43.8
P1	176.0	112.4	74.5	36.0
P2	176.0	111.4	47.9	23.1
P3	171.5	112.9	61.2	29.6
P4	169.5	111.9	58.9	28.5
P5	173.0	112.4	72.07	34.8
P6	176.0	112.4	92.13	44.5

All of hybrid composites in T_m increase modesty in P1 and decline in P4, then increase again to P5 and P6 at temperature value 173.0 °C and 186.0°C respectively. From the DSC result the X_c shows the degree of crystallinity increase with each 5% of kenaf fiber loading higher. The thermogram of crystallization hybrid composite are presented in figures 2 and figure 3.

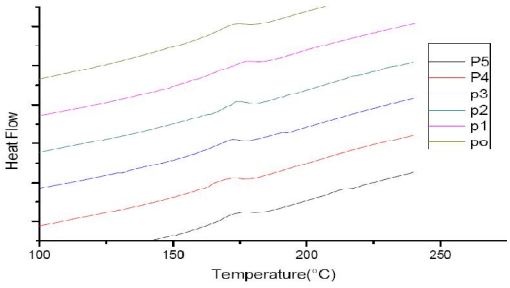


Fig. 4. Heating step for DSC curve hybrid composite

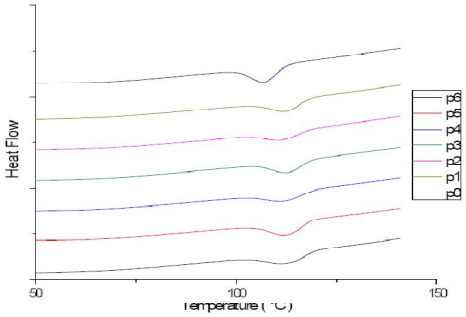


Fig 5 Cooling step for DSC curve hybrid composite

For $CaCO_3$/PP hybrid composite crystallization peak was observed at temperature value 106.9°C while for the hybrid composite these exothermic peak shifted to higher temperature in all cases. The T_c increased can be considered because of effect nucleation of natural fiber either kenaf fiber or rice husk particulate. It is because the natural fiber directly acts as sites for heterogeneous nucleating thus inducing the crytalization of the matrix. Supercooling process are enhanced with presence of fiber, where crystallization can occur at higher temperature ~ 112C. Calculation based on the extrapolated melting entalphy for 100% crystalline sample lead to the degree of crystallinity X_C reported in table 3. It can be noted that the crystallization peak temperatures slightly shift to higher values with the filler content. Furthermore, natural fibers act as nucleating agents due to the transcystallinity effect provided by strong interaction between the fiber and the matrix [15].

CONCLUSIONS

In conclusion, the addition of kenaf and rice husk into $CaCO_3$/PP hybrid composite has changed their flexural and thermal properties. About 10% kenaf fiber and 30% of rice husk particulate increase the flexural strength and flexural modulus.

The degree of crystallinity and the crystallization temperature of the matrix varies upon incorporation of the hybrid fillers . Without hybrid fillers, PP with CaCO3 has exhibited the non presence of the cellulose, hemicelluose and lignin from TGA and DTG thermogram. Transitiion peak from DSC thermogram showed increase in melting point Tm and Tc while degree of crystallinity reduced with kenaf composition sample P2 to P5 (15 to 25% pbw), with incorporation of the hybrid fillers.

When compared P2 and P4, it was found that the thermal stability of hybrid composite incorporated with high kenaf content is higher as compared to rice husk ie for similar ratios of 25% kenaf and rice husk.

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