

THERMAL AND MECHANICAL PROPERTIES OF LACCASE ENZYME-TREATED KENAF FIBRE REINFORCED RECYCLED POLYPROPYLENE COMPOSITES

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ABSTRACT

Composites were prepared from lignocellulose based kenaf fibre with recycled polypropylene (RPP) and studied the thermal and mechanical properties. Biological treatment such as Laccase enzyme treatment was used to treat kenaf fibre for the enhancement of interfacial property between fibre and matrix by removal of lignin which holds and binds the cellulose fibre together. Both enzyme activity and soaking time duration were considered as treatment variables. Maleic anhydride grafted polypropylene (MAPP) was used with a ratio of 1:10 as coupling agent to fibre. A twin screw extruder was used to mix the blends and after that test specimens for mechanical testing were prepared by an injection molding machine. Fibre loading was considered as 10, 20, 30, 40 and 50% by weight. Various tests of the composites such as tensile, melt flow index (MFI) and thermogravimetric analysis (TGA) were done to evaluate the properties of the composites and compared with the untreated fibre reinforced composites. Experiment showed that, the best tensile strength (TS) achieved at 40% loading of fibre and enzymatic treatment of fibre enhanced the TS by 40%. Activation energies were calculated through Broide's equation and found using fibres, enhanced the activation energies of the composites by 5 kJ/mol at the first stage of degradation. It was also found that, RPP degrades at one stage whereas composites degrade at two stages. Incorporating fibres decrease the activation energies of the composites but treatment of fibre enhanced the activation energy. Scanning electron microscope (SEM) of the fractured surface showed that, treatment of fibre improves the interfacial bonding between fibres and matrix. Densities of the composites were also studied in this experiment.

Keywords: Composites, Kenaf Fibre, Laccase, Enzyme, Thermal and Mechanical Properties.

1. INTRODUCTION

A number of lignocelluloses based natural fibres has been used to produce bio-composites with various types of polymer matrices for last few decades. Still new fibres are being added for the reinforcement purpose and as filler materials. To produce light weight composites materials with higher specific properties is possible due to low density of the natural fibre compared to synthetic fibre such as glass fibre, carbon fibre etc. Not only that to reduce the demand of limited resources of petroleum product such as polymer, recycled plastic also has been drawn research attention to the researchers. Moreover, natural fibre based composites can be produced at low cost and low energy consumption with less CO₂ emission. Although, the advantages for using natural fibres in the polymer composites, few drawbacks are mentionable such as natural fibre composites absorb moisture and high percentages of fibre loading results poor interfacial bonding between fibre and matrix. Due to poor interfacial bonding between hydrophilic nature of natural fibre and hydrophobic nature of polymer and to improve mechanical and thermal properties of the composites a lots of compatibilizing agents [1-2] etc. are being used. Accept using compatibilizing agent, fibre surface modifications have been found fruitful in previous

researches.

Fibre surface modification can be done successfully and moisture absorption by the composites can be reduced through chemical treatments such as acetylation, mercerization, methylation, cyanoethylation, benzoylation, permanganate treatment, acrylation [3-8]. Yan li [9] has reported in his work for the case of hemp fibre treatment that, the higher chelator concentration treated hemp fibre composites had the highest tensile strength of 42 MPa, an increase of 19% compared to composites with untreated hemp fibre.

However, composites preparation along with various effects such as Laccase enzyme treatment of fibre on composites properties, coupling agent and fibre loading effect in terms of various mechanical and thermal properties are widely discussed in this work.

2. EXPERIMENTAL

2.1 Materials

Kenaf fibres were taken from Kampung Merchong agro-based company in Pahang- a state of Malaysia. Recycled polypropylene used mainly from car bumper and vehicle battery case which named commercially as PP black copo from a local recycling company.

Commercial Laccase enzyme, supplied by NOVOZYMES (Novozyme 51003) was used for the treatment of the fibre which has maximum enzyme activity of 80U/ml. Coupling agent used was Maleic Anhydride Grafted Polypropylene (MAPP), commercially named as Polybond 3200 was supplied by MTBE (M) Sdn Bhd, Gebeng, Kuantan, Pahang. The properties of MAPP as follow (Table 1):

Table 1: Physical properties of MAPP

Form	Pellets
Melt flow index	115 g/10min (ASTM D-1238)
Density at 23 °C	0.91 g/cc (ASTM D-792)
Melting point °C	157 °C
Maleic Anhydride Level	1.0 weight%

2.2 Methods

2.2.1 Fibre Treatment Through Laccase Enzyme

Enzyme activity 40, 60 and 80 U/ml were used to treat the fibre for 2hrs of soaking time duration. After that at 80 U/ml of enzyme activity was used to treat the fibre for 2, 4 and 6hrs of soaking time duration. Acetic acid was used to control the p^H of the solution at 5.5. Soaking was done at 25 °C with air flow for better treatment. After that fibre was washed for long time by tape water until p^H reached to 7. Then, fibre was air dried.

2.3 Preparation of Composites

Air dried kenaf fibre was shredded into small size (2 to 5 mm) by a plastic crusher. Shredded fibre was dried at 70 °C in an oven until reached the moisture content of below 5%. Both untreated and treated fibre were individually compounded into RPP with and without coupling agent by means of a Prism Eurolab 16 twin-screw compounder having barrel temperatures from 170 °C to 190 °C from the feeding zone to the die zone, respectively. The fibre to coupling agent ratio was 10:1. The incorporated fibre contents in composites were 10, 20, 30, 40 and 50% (by weight). The compounded samples were prepared into test specimens by injection moulder using NESSEI injection molding machine model- PNX60 machine. Tensile specimens were prepared according to ASTM D638 Type I.

2.4 Melt Flow Index (MFI)

Melt flow index of each sample was determined according to ASTM D1238 (230 °C per 2.16 Kg) using Dynisco melt flow indexer (LMI 4000 series). An average of 3 runs was taken for each sample.

2.5 Density Measurement

A gas pycnometer (Micromeritics, MODEL-Accupyc II 1340) was used to determine the density of the composites with raw and treated fibre using Helium gas at 25 °C.

2.6 Tensile Test

Tensile test for composites were carried out using a

Universal Tensile Machine (SHIMADZU, Capacity 20 KN) with a load cell of 5 KN. Tests were performed as specified in ASTM D 638 - Type I: Test method for tensile properties of plastic. The gauge length was 65 mm and the crosshead speed of testing was 10 mm/min. Five specimens were tested for each batch. Tensile strength and tensile modulus (TM) were taken for analysis.

2.7 Thermogravimetric Analysis

For thermogravimetric analysis TA instrument- TGA Q500 was used with nitrogen atmosphere. The maximum temperature was used 600 °C with heating rate 20 °C/min. Around 5 mg weight of sample was considered using platinum pan. Kinetic parameters for the thermal degradation were determined from the TGA graphs using the following equation, given by Broido [10]:

$$\ln\ln(1/y) = -E_a/RT + \ln\{(RZ/E_a\beta)T_{max}^2\}$$

Where,

y = Fraction of nonvolatilized material not yet decomposed,

T_{max} = Temperature of maximum reaction rate,

β = Heating rate,

Z = Frequency factor,

E_a = Activation energy.

R = Gas constant (8.314 J/mol.K)

In figure 8, a curve was drawn to find out the activation energy of the RPP. Here, from the TGA curve we took the values of y and calculated the values of $\ln\ln(1/y)$ and put in y axis whereas temperatures as 1/T in kelvin scale put in x axis. Finally from the slope of the trend line the activation energies of the composites have been calculated.

2.8 Characterization of Composites by SEM

A scanning electron microscope (ZEISS- EVO 50) was used to analyze the morphological images of the fractured composite materials. The samples were gold pattered before viewing under the microscope.

3. RESULTS AND DISCUSSION

3.1 Melt Flow Index of Composites

The melt flow index of supplied RPP is around 5 g/10 min but decreases with fibre loading for RPP/kenaf composites even with coupling agent (Table 2). The MFI of RPP/Kenaf at 40% fibre loading is 0.4 and 0.3 g/10 min with and without coupling agent respectively. Enzyme treated kenaf fibre reinforced RPP composites have a MFI of 0.22 g/10min. So, it reveals that, the more fibre in the composites, the more viscous the melt and more molecular weight. At the same time it can be summarized that laccase enzyme treatment makes the composites more viscous while it has gone through MFI testing which indicates more difficult process ability.

Table 2: MFI of RPP and composites

Formulation	Melt flow Index (g/10 min)
RPP	5.58
10%kenaf+RPP	2.54
20%kenaf+RPP	1.78
30%kenaf+RPP	0.46
40%kenaf+RPP	0.40

50%kenaf+RPP	0.22
40%kenaf+RPP+MAPP	0.33
80U40%K+RPP+MAPP	0.22

3.2 Density of the Composites

RPP itself has a density of 0.91 g/cc and fibre loading increases the density of the composites and at 50% fibre loading it reaches 1.16 g/cc. Laccase enzyme treated composites found 1.10 g/cc. With coupling agent and without treatment at 40% fibre loading found a density of 1.12 g/cc. At 40% fire loading without treatment and without coupling agent found a density of 1.04 g/cc.

Table 3: Density of the composites

Formulation	Density g/cc
RPP	0.91
10%	1.00
20%	1.02
30%	1.04
40%	1.07
50%	1.16
Raw40%MAPP	1.12
80U40%K+RPP+MAPP	1.10

3.3 Tensile Properties of Composites

Experiment showed that, TS increases with fibre loading up to 40% and after that it decreases. The maximum TS achieved at 40% is 18.29 MPa which is 18% higher than RPP (15.46 MPa). Thus, incorporating fibre as reinforcement showed an improvement regarding TS of the composites (Fig.1.); this is may be due to the formation of more hydrogen bonds between fibre to fibre and fibre to matrix at optimum fibre/matrix ratio. But at higher percentage, such as 50% it decreases because more fibre agglomerate together and an uneven distribution may be occurred. Using coupling agent showed an improvement of TS by 37% and composites with 40% fibre loading gives TS of value 25.17 MPa. Laccase enzyme treatment of fibre increases the TS of the composites. The best result obtained at 80 U/ml of enzyme activity with 4hrs of soaking time duration. At 2hr socking time duration, the best TS found at enzyme activity of 80 U/ml. After that, at 80 U/ml of enzyme activity, the best result obtained at 4hr of soaking duration. This may be the optimum condition of treatment regarding amount of fibre socked in the solution. Laccase enzyme treatment may lead to the fibre surface to expose more -OH group to make hydrogen bonds with the polymer matrix by degrading lignin the cementitious material of plant based fibre. The best TS 25.77 MPa at 80 U/ml of enzyme activity which is almost 40% greater than that of raw fibre based composites without coupling agent (Fig.2. & Fig.3). Regarding tensile modulus (Fig.2 & Fig.3.) same trend of results was observed for the composites based on raw fibre with and without coupling agent and treated fibre based composites with coupling agent. Tensile Modulus at 40% fibre loading, for the case of raw fibre based composites without coupling agent showed a value of 896 MPa whereas with coupling agent it was 1051 MPa (80 U/ml of enzyme activity and 2hr of socking time) and 1078 MPa (80 U/ml of enzyme activity and 4hr of socking

time).

At 50% fibre loading, agglomeration and poor dispersion of fibre probably the reason of showing lower TS and TM than loading at 40%.

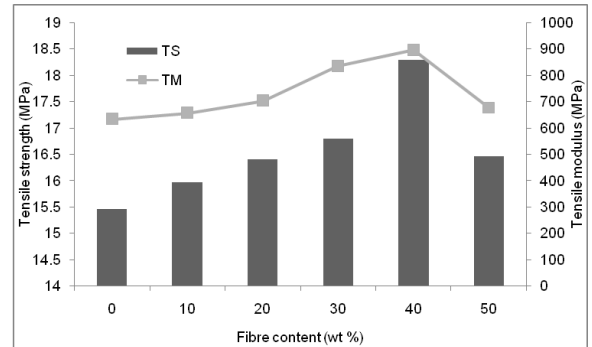


Fig 1. TS and TM of RPP and composites at various percentages of raw fibre loading (without coupling agent).

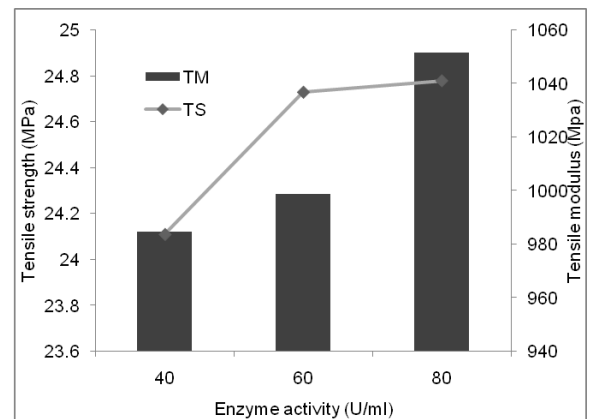


Fig 2. TS and TM of composites at 40% fibre loading at various enzyme activity with coupling agent (at 2hr of soaking time duration).

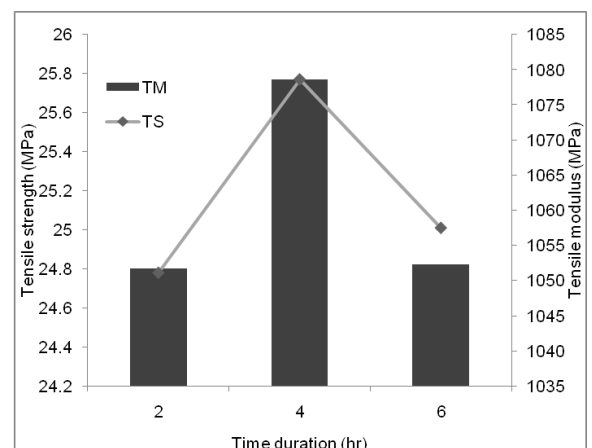


Fig 3. TS and TM of composites at 40% fibre loading at 80 U/ml of enzyme activity with various soaking time duration (with coupling agent).

3.4 Scanning Electron Microscope of Composites

SEM examination of fractured surfaces of the RPP based fibre composites without coupling agent revealed poor interfacial bonding. Micrographs indicated fibre pull-out, debonding, delamination and fibre breakage. At high fibre loading fibre-to-fibre contact is greater and dispersion problems are evident. In the Fig.4. fibre pull-out is apparent. The presence of voids (as shown in Fig.4.) may create stress concentration points which in turn reduce the strength of the samples.

Due to hydrogen bonds formed between fibres and the wide difference in polarity between lignocellulosic fibres and the matrix, the fibres tend to agglomerate into bundles and become unevenly distributed throughout the matrix.

It is obvious that fibre pull-out is one of the main modes of failure. Fibres are shown to be oriented in a random arrangement (Fig.4.) There is also almost same but less and short fibre seen the fractured surface of enzyme treated fibre (Fig. 5.) This is may be due to well treatment of fibre but not optimum regarding matrix to fibre weight ratio. The more fibre expose may sometime show less adhesion to the matrix. It can also be seen that the surface of composite materials with 40% filler percentage with coupling agent is relatively smooth compared to other composites without coupling agent.

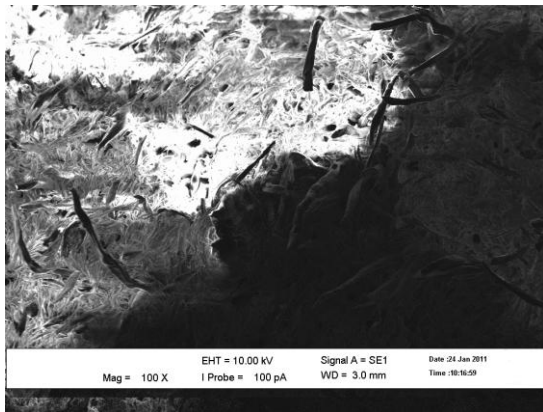


Fig 4. SEM of fractured surface of composites with raw fibre without coupling agent at 40% loading.

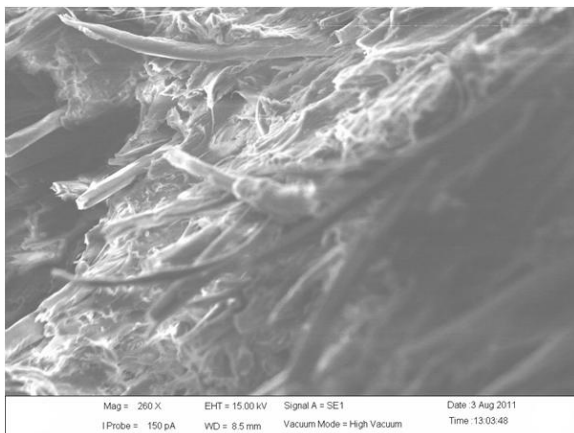


Fig 5. SEM of fractured surface of composites with laccase enzyme treated fibre with coupling agent at 40% loading.

Thermogravimetric analysis of composites

Using MAPP did not show any significant improvement regarding thermal stability. The trends of the curve were almost same except the residue increases with fibre loading (Fig.6. & Fig.7.) In table 4, the thermal properties of the RPP, composites with raw and treated fibre with coupling agent are shown. We can find that using fibre makes the composites degrade at two stages whereas RPP degrades at only one stage. The residues are also increasing with the fibre loading. The more significant part is for the first stage of degradation of the composites the activation energies of the composites are almost have around 42 KJ/mol but in the second stages it was decreasing with the fibre loading. This may be due to the reason of diffusion of fibres at higher loading of fibres percentage in the composites but coupling agent in that case improve the activation energies around 5 KJ/mol at same loading percentage of fibre. But treated fibre with coupling agent at first stage having activation energy of 46.28 KJ/mol whereas at the second stage the value was 78.71 KJ/mol.

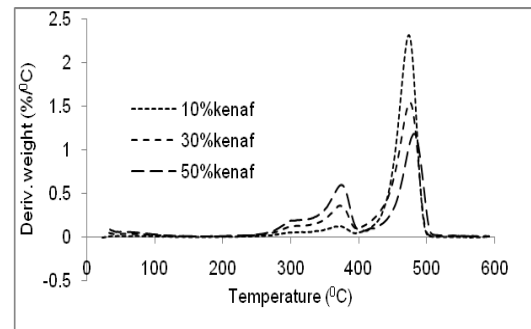


Fig 6. TGA analysis of composites with raw fibre

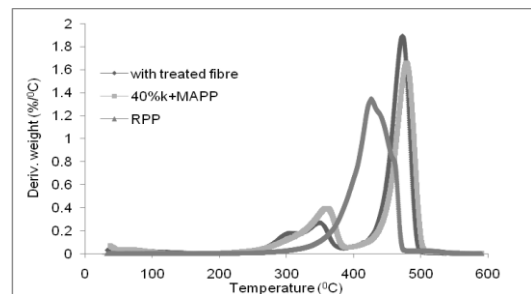


Fig 7. TGA analysis of composites with raw and treated fibre (with coupling agent)

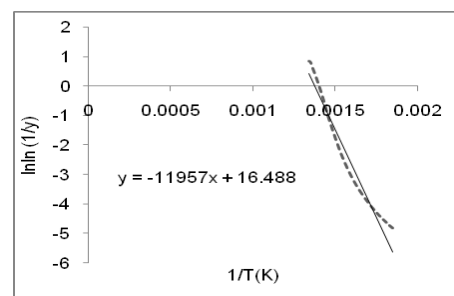


Fig 8. lnln(1/y) vs 1/T curve to calculate activation energy of RPP.

Table 4: Thermal properties of RPP and composites

Forml	Stage	Temp (°C)	T _{max}	Act. enrg
RPP	1 st	267-472	420	99.41
10%kenaf+	1 st	254-374	351	42.89
RPP	2 nd	380-497	469	120.7 3
20%kenaf+	1 st	237-382	352	42.00
RPP	2 nd	390-497	470	107.3 6
30%kenaf+	1 st	237-389	362	43.78
RPP	2 nd	389-497	470	83.86
40%kenaf+	1 st	221-391	365	44.37
RPP	2 nd	392-501	473	67.44
50%kenaf+	1 st	221-394	367	42.12
RPP	2 nd	402-504	477	61.75
40%kenaf+	1 st	247-381	351	50.90
RPP+MAPP	2 nd	406-502	477	72.05
40%k(enzy me treated)+RP	1 st	229-371	341	46.28
P+MAPP	2 nd	389-495	470	87.71

4. CONCLUSIONS

Significant improvement was found regarding TS and TM of composites based on treated fibre with coupling agent. In that case, at 80 U/ml enzyme activity with 4hr of soaking time duration is the best condition for fibre treatment. In this investigation, it was found that TS and TM increases with fibre loading up to 40%. The better adhesion as shown by scanning electron microscopy between filler and matrix was found in case of composites with treated fibre and coupling agent while the rest of the composite materials without coupling agent showed debonding and agglomeration of fibre, thereby decreasing their interfacial adhesion.

Removal of non-cellulosic compounds is also suspected to have increased the amount of OH groups exposed on the fibre surface, which could assist in bonding with the matrix in the presence of MAPP, as evidenced by the increase in composite tensile strength.

Melt flow index showed negative trend with the incorporation of fibre & adding MAPP. Fibre treatment in that case enhanced more to lower down the value. Thus, very low process ability at higher loading as well as for enzyme treatment can be concluded.

Using fibres enhanced the thermal stability of the composites and degrade at two steps while recycled polypropylene at one step.

5. ACKNOWLEDGEMENT

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