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BIOCOMPOSITE OF EPOXIDIZED NATURAL RUBBER/ POLY(LATIC ACID) / CATAPPA LEAVES AS SHOE INSOLE

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ABSTRACT

Epoxidized natural rubber/ polylactic acid blends with catappa fibre filler were prepared by melt blending followed by compression molding to fabricate test samples. The effect of fibre loading which is catappa fibre on physical and mechanical properties of biocomposite ENR/PLA/KTP were investigated. This research was to study the optimum percentage of catappa fibre besides to prove that catappa fibres exhibit antibacterial property. The characterization carried out throughout the study was to investigate the capability of biocomposite to be used as insole application. The tensile strength was optimum at 15% fibre loading while the modulus strength increased with increasing fibre loading. Impact strength decreased with high fibre content. Morphology examination showed good fibre dispersion in the matrix at 15% KTP fibre. Percentage of water absorption was observed to increase when fibre loading was increased. The antibacterial test showed positive results whereby biocomposite ENR/PLA/KTP showed inhibition activity towards Gram positive bacteria (*Staphylococcus aureus*) which is the common bacteria can be found in shoe insoles.

Keywords: Biocomposite; epoxidized natural rubber; poly(lactic acid); melt blending; catappa fibre

INTRODUCTION

Insole is a part of material located inside of shoe i.e. a layer between shoe and feet. Insole usually bring comfort to the individual that is wearing shoe. The materials used for insole include rubber and thermoplastic. Rubber is one of the materials mostly used in insole manufacturing. Nowadays, the use of plastics from non-renewable crude oil brings environmental concerns due to plastic slow degradation. In polymer industries plastic disposal issues become the main problem. In this modern technology, industry of insole has brought the professional way in making insole using renewable material without polluting the environment. Poly(lactic acid) (PLA) which is known as biodegradable polymer brings bio based material and good mechanical properties [1]. However, PLA is blended with other polymer to give flexibility and toughness. Polymers have been widely applied especially in insole manufacturing. Insole mostly made of different kind of polymers such as blending of rubber and thermoplastic to give flexibility, impact absorption capability and support to the individual that is wearing shoes. This can be proved when impact energy is higher, energy absorption on the insole will be lower due to properties of insole which is thin [2].

Biocomposite is a composite material that is made up of natural fibre as the filler or reinforcement while the polymer material as the matrix. Natural fibres which act as the

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reinforcement in composite give mechanical strength and toughness in composite system. In recent years, the use of natural material brings a great attention to researchers. There are a lot of studies being done in biocomposite using natural fibres as reinforced filler such as jute, sisal, hemp and many others as natural fibre composites [3]. Biocomposites have a lot of advantages since they are low cost, recyclable, do not pollute the environment and easy processing.

Blending of thermoplastic and elastomer is able to give main characteristics of rubber and plastic. In modern technology, blending of thermoplastic and elastomer are added with filler to produce composite with high mechanical strength. Natural fibre is well known for its low density, high tensile strength and high modulus [4]. Natural fibre which acts as reinforcing matrix increases the composite performance [5]. Thermoplastic elastomer can be easily processed without using vulcanizing agent [6].

In this study, blending of thermoplastic and elastomer reinforced with catappa leaves (KTP) fibre was investigated. Epoxidized natural rubber (ENR) and poly(lactic acid) act as matrix while catappa leaves fibre act as reinforcing filler. The physical and mechanical properties of biocomposite ENR/PLA/KTP are investigated. The physical and mechanical properties of biocomposite were then compared with synthetic shoe insole. Antibacterial properties of catappa leaves were studied to prove that catappa leaves are antibacterial.

MATERIALS AND METHODS

Epoxidized natural rubber (ENR-50) was obtained from Malaysian Rubber Board. Poly(lactic acid) was obtained from Sigma Aldrich. Catappa leaves were obtained from Serdang, Selangor and were processed in the National University of Malaysia.

Preparation of KTP fibres

Catappa leaves were cut into small pieces. Leaves that have been cut were dried in an oven at the temperature of 60˚C to ensure the leaves are dried thoroughly. Then, KTP fibres were grond using a grinder. KTP fibres were then washed, rinsed and sieved. Next, the sieved KTP fibres were dried in an oven at the temperature of 70˚C. The fibres was then sieved at size between 125-250µm.

Preparation of Biocomposite

Matrix and filler composition is tabulated in Table 1. Composition 60/40 of ENR/PLA with various KTP fibres were prepared. Processing parameter used were temperature of (170˚C), rotor speed of (60 rpm) and blending time (15 minutes). Poly(lactic acid) was first added into the internal mixer for 5 minutes. After 7 minutes, ENR was added followed by KTP fibre. Biocomposite ENR/PLA/KTP produced was hot pressed at temperature of 170˚C with pressure of 70 N/m^2 for 5 minutes. Then, the composite was cooled for 10 minutes to retain its mold shape. Composites with thickness of 1mm and 3mm were prepared to investigate physical and mechanical properties.

Tensile test

Tensile strength was tested using Universal Testing Machine model Instron 5566. Composites with thickness of 1mm were cut according to ASTM D412 using dumbbell cutter. Dimension of sample was 70mm x 12.5mm. Load cell used was 10kN while crosshead speed was 10mm/ min.

Table 1 Composition ENR/PLA and KTP fibre

Sample	Material composition	
	ENR/PLA (%)	KTP fibre (%)
A	60/40	0
B	60/40	5
C	60/40	10
D	60/40	15
E	60/40	20
F	60/40	25

Impact Test

Impact strength was tested using Fructoscope Pendulum Machine model Ceast 6545. Composites with thickness of 3mm were cut according to ASTM D638 using dumbbell cutter. Composite dimension was 65mm x 12mm. Pendulum force used was 2J.

Water Absorption Test

Water absorption test was carried out to determine the water uptake of samples. Samples were dried in an oven at temperature of 40˚C for 24 hours before being immersed in distilled water. Sample dimension was 50mm x 50mm x 30mm. Weight and dimension of sample were recorded every day for 14 days. Percentage of water was calculated using the following equation:

Percentage of water absorption (%),

$$\frac{W_t - W_o}{W_o} \times 100\ \%$$

W_t = Final weight of composite after being immersed in water
W_o= Initial weight of composite before immersed in water

Morphology Examination

Morphological examination was conducted using Field Electron Scanning Electron Microscopy (FESEM) model Supra 55V. Morphological examination was tested on fractured surface of samples after tensile test.

Antibacterial Test

Disc agar diffusion method was used for the antibacterial assay. Disc size with diameter of 6mm were punched using a paper puncher. Discs of every percentage of ENR/PLA/KTP were autoclaved at 121˚C for 15 minutes. Sterile swab sticks were used to swab the standardized inocula of the *Escherichia coli* and *Staphylococcus aureus* onto the surface of prepared Mueller-Hinton agar plates. The plates were inverted and incubated at 37˚C for 24 hours then the zones of growth inhibition were observed.

RESULTS AND DISCUSSION

Tensile Properties

Fig. 1(a) showed values of tensile strength against percentage of KTP fibre. The figure showed that an increase occured on tensile strength when percentage of KTP fibre was increased and began to decrease its tensile strength when percentage of KTP fibre exceeded 15 %. Hence, the optimum KTP fibre was at 15% with the highest tensile strength which was 4.64 MPa. Increase in tensile strength of composite as fibre was added due to existence of strong interphase interaction between matrix and fibre. Strong interphase interaction resulted in better stress transfer ability of matrix-fibre. However, the

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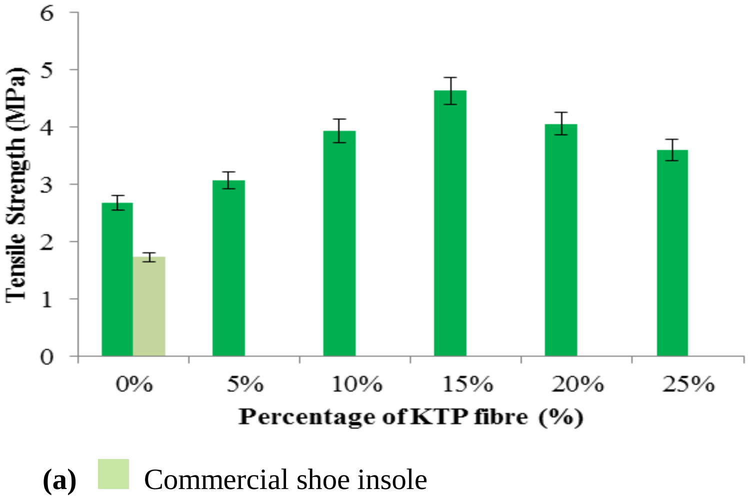
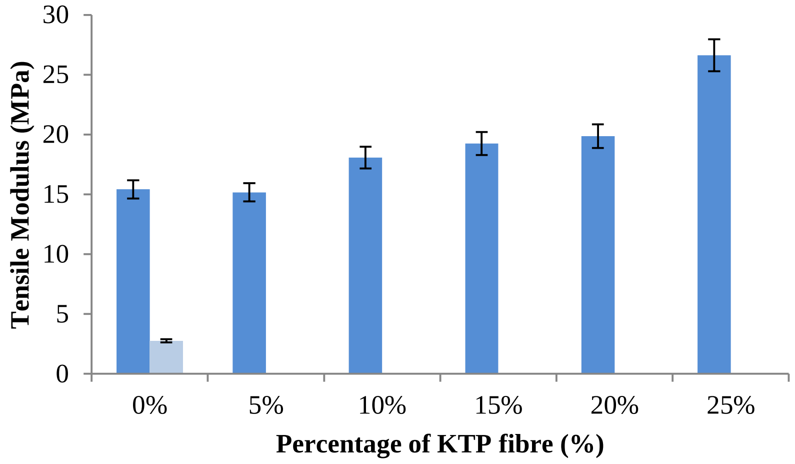
reduction in tensile strength at high fibre loading caused by the interaction between fibres increased thus contributed to agglomeration. In this research, the tensile strength of biocomposite ENR/PLA/KTP was compared with the tensile strength of commercial shoe insole. Tthe results obtained showed that the tensile strength of commercial insole was lower than that of the the biocomposite with natural fibre filler. This meant that bicomposite ENR/PLA/KTP is potentially useful in shoe insole application.

Fig. 1(b) showed values of tensile modulus against percentage of KTP fibre. Tensile modulus of composite increased as the percentage of KTP fibre was increased in ENR/PLA blend. At high fibre loading, the biocomposite exhibited high stiffness. This proved that incorporation of KTP fibre brought stiff effect in biocomposite ENR/PLA/KTP. High stiffness of biocomposite ENR/PLA/KTP was influenced by restriction of chain mobility of matrix [7]. High stiffness brought rigidity to the biocomposite. Tensile modulus showed decreasing value with low fibre loading because of low interaction of fibre-matrix. Based on the results of tensile modulus of commercial shoe insole, it showed that tensile modulus was lower compared to biocomposite ENR/PLA reinforced KTP fibre. Low tensile modulus indicated that the commercial shoe insole were less stiffer compared to biocomposite ENR/PLA/KTP.

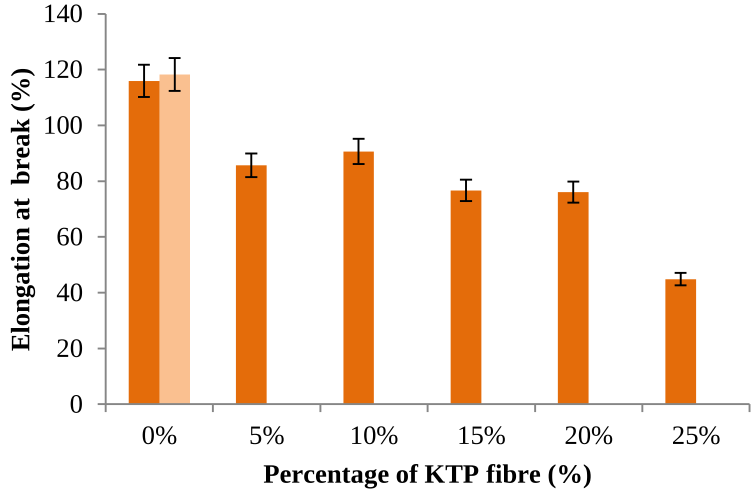
Fig. 1(c) showed the elongation at break decreased as the fibre loading was increased. This may be due to high fibre loading consequently led to low ductility of biocomposite ENR/PLA/KTP [8]. Elongation at break decreased with high fibre loading due to formation of agglomerate as the distribution of fibre in the polymer matrix ENR/PLA was poor [9]. Agglomeration of fibre resulted in low dispersion of fibre in polymer matrix. The result of elongation at break for commercial shoe insole showed that elasticity increased compared to biocomposite ENR/PLA/KTP thus proved that shoe insole without natural fibre filler was very elastic. Excessive elasticity promoted to low tensile strength.



(a)



(b) Commercial shoe insole



(c) Commercial shoe insole

Fig. 1 (a) Tensile strength, (b) Tensile modulus, (c) Elongation at break of ENR/PLA/KTP biocomposite

Impact Strength

Fig. 2 showed the impact strength of ENR/PLA/KTP biocomposite against percentage of KTP fibre. Impact strength showed decreasing value with increasing fibre loading. Increase in fibre loading led to low energy absorbance [10]. Low energy absorbance may be attributed to cracks propagating mechanism to occur quickly when the interface interaction between fibre and matrix was less efficient [11]. Thus, the fibres were pulled out. Besides, the impact energy showed an increase when the percentage of KTP fibre was decreased. This is because of there was good dispersion of fibres in the polymer blending.

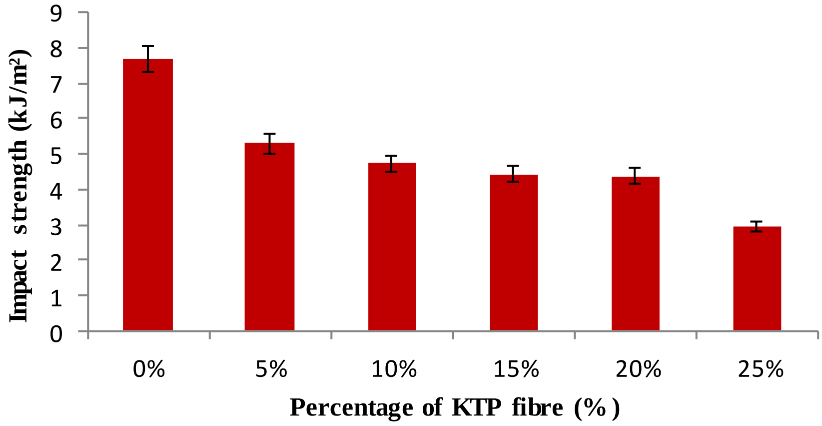


Fig. 2 Graph of impact strength (kJ/ m^2) against percentage of KTP fibre

Water Absorption

Fig. 3 showed that the percentage of water absorption increased when percentage of KTP fibre was increased from 5% to 25%. Percentage of water uptake increased with high fibre loading due to the presence of cellulose in natural fibre. Formation of hydrogen bond between hydroxyl group from water and cellulose took place. This may be also due to the hydrophilic nature of ester group in PLA and the oxirane group in ENR. ENR which is known as polar polymer caused the formation of hydrogen bond with water molecules [12]. This eventually caused the increase in water absorption. Water absorption for 25% KTP fibre had the highest reading which is 8.65%. This highest reading may be due to very poor adhesion between matrix and fibre.

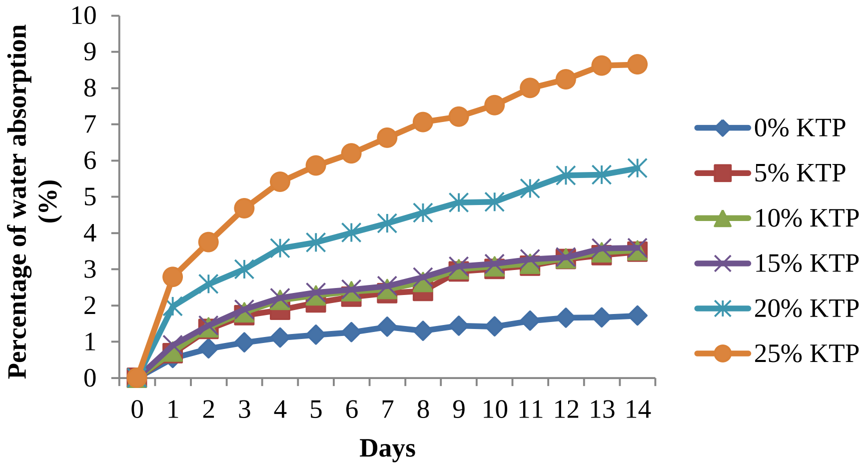


Fig. 3 Graph of water absorption against percentage of KTP fibre

Morphology Examination

The morphology surface of biocomposite are observed under same magnification at 500x. Fig. 4 (a) showed homogeinity of ENR-PLA matrix. Figure 4 (b) showed that the KTP fibre was not well bonded by the matrix ENR/PLA. The formation of fibre pulled out may be due to weak adhesion between matrix and fibre. Fig. 4 (c) showed that the matrix ENR/PLA was bonded well compared to 5% KTP. This was due to interaction of KTP fibre with ENR/PLA matrix was better and low agglomeration of fibre in matrix.

Fig. 4 (d) showed that the matrix and fibre had good phase interaction and adhesion. Fig. 4 (e) showed that there were empty voids formation due to poor interaction between ENR/PLA matrix and KTP fibre [8]. KTP fibre was easily pulled out thus mechanical strength of composite become lowered. Fig. 4 (f) showed more voids formation when the fibre loading increased because agglomeration of fibre increased and poor adhesion of matrix-fibre.

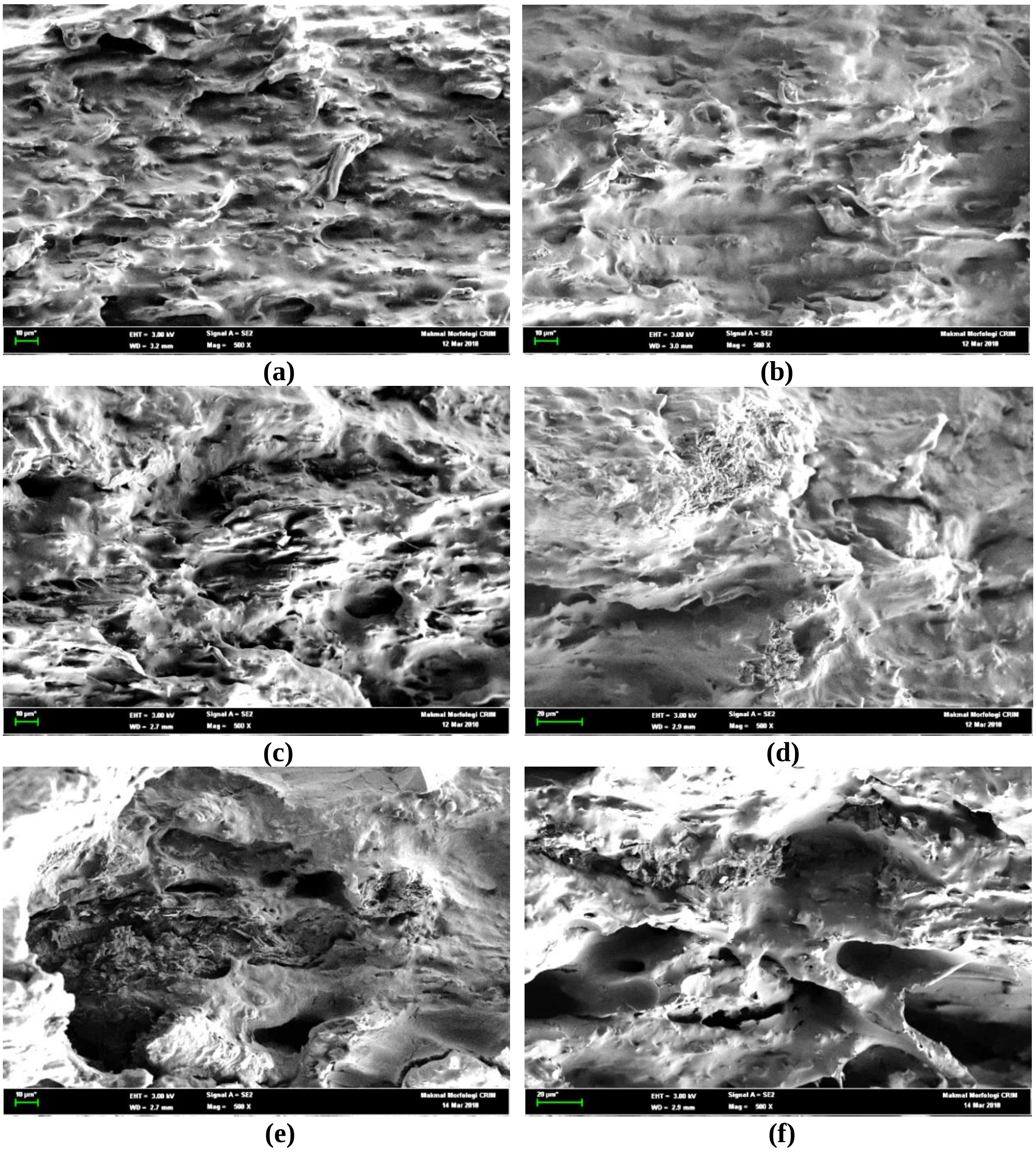


Fig. 4 SEM micrograph of biocomposite ENR/PLA/KTP with (a) 0% KTP, (b) 5% KTP, (c) 10% KTP (d) 15% KTP (e) 20% KTP (f) 25% KTP

Growth Inhibition of Antibacteria

Fig. 5 (a) and (b) showed the antibacterial activity of biocomposite ENR/PLA/KTP against Gram Negative bacteria *Escherichia coli* and Gram Positive bacteria *Staphylococcus aureus.* The biocomposite ENR/PLA/KTP showed more susceptible towards *Staphylococcus aureus* isolate compared to *Escherichia coli* isolate [13]. Study of antibacterial activity of catappa leaves reported that there are active components which was phenolic compound present in catappa leaves that allows them to have antibacterial potential properties [14].

Percentage of KTP fibre (%)	Antibacterial activities on *Staphylococcus aureus*	Antibacterial activities on *Escherichia coli*
0	X	X
5	X	X
10	X	X
15	/	X
20	/	X
25	/	X

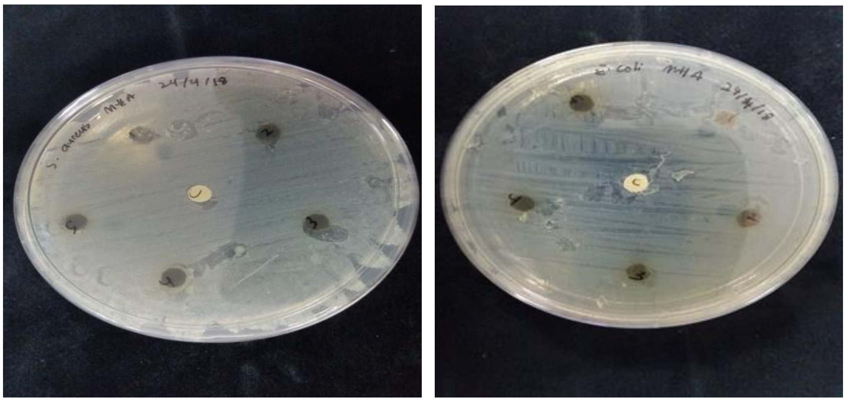

(a) **(b)**

Fig. 5 (a) Inhibition antibacterial activity of *Staphylococcus aureus* (b) Inhibition antibacterial activity of *Escherichia Coli*

CONCLUSION

Tensile strength and elongation at break of biocomposite ENR/PLA/KTP decreased as the fibre loading was increased. The tensile modulus of biocomposite increased with high fibre loading. Water absorption increased with high fibre loading. Inhibition of antibacterial activity showed that biocomposite ENR/PLA/KTP was susceptible to Gram positive bacteria *Staphylococcus aureus*.

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