Thermoplastic Elastomer composite using Benzyl Chloride Treatment on Kenaf Core Powder Mixing with Polypropylene and Virgin Acrylonitrile Butadiene Rubber

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Abstract. The thermoplastic elastomer composite based tensile properties and morphology of kenaf core powder (KCP) treated with benzoyl chloride filled polypropylene (PP)/ virgin acrylonitrile butadiene rubber (vNBR) composites were aim and investigated. The composites with different KCP loading from 0 wt % to 30 wt % with constant PP and vNBR (70 wt% and 30 wt%) were prepared using heated two-roll mill by melt mixing at temperature of 180 °C . Tensile properties of composites which is tensile strength, Young’s Modulus and elongation at break were investigated. The morphology of filler and composites were investigated using scanning electron microscope (SEM). The result shown, the tensile strength, elongation at break and Young’s modulus of treated composites have higher by 4 - 14 %, 4 - 13 % and 0.5 - 3 % respectively compare untreated composite. These findings were supported by micrograph diagram from the morphological study. KCP filler treated with benzoyl chloride has improved the adhesion and gave strong interfacial bonding between KCP filler and PP/vNBRr matrices which results in good tensile strength of composites.

1. Introduction
Kenaf is relatively commercially available and economically reasonably-priced among different natural fibre reinforcing material. Kenaf is usually denoted as industrial kenaf because of its first rate in interest for the manufacturing of industrial raw materials. Kenaf is a hardy, strong and tough plant with a fibrous stalk, proof to insect harm and calls for tremendously fewer amount of or no pesticides. There are three kinds of fibre which are bast, core and pith constitutes the kenaf plant [1]. On the other hand, kenaf is characterized by two distinct fibres bast and core which are 35% and 65% respectively [2]. The bark and core fibre are taken into consideration as two distinct sorts of raw material that can be distinguished by the way of their chemical composition anatomical appearances. The pith is comprising totally of parenchymatous cells, which are in form of polygonal not typically prismatic [3]. The kenaf bast fibres
possess putting mechanical properties that lead them as a replacements to glass fibres in polymer composites as reinforcing elements by according to researchers [4].

There are various chemical treatments and modifications being studied to improve the compatibility of matrix and fibre [5-8]. Pre-treatment the filler using alkali (sodium hydroxide) is a traditional way. This Alkali pre-treatment is still relevant to clean filler surface to prepare the filler with a better site for interaction until now. Then, this alkali pre-treatment will be followed by another type of chemical treatment, usually a coupling agent, using organic and inorganic chemical to enhance the tensile, water absorption and thermal properties of the composites [9,10]. Apart from the alkali pre-treatment, there are few more treatments have been applied to the fibre in order to improve the interfacial adhesion between fibre and matrix such as silane, isocyanate, and peroxide chemical treatment. Each of the chemical treatments has their own advantages depending on the type of filler and the matrix being used [11,12].

In this research, the kenaf core have been treated with benzoyl chloride as coupling agent for PP/vNBR composite. The surface modification of kenaf core have been analysed using Scanning Electron Microscopy (SEM). The untreated and treated kenaf core are mixed with PP and vNBR in order to develop the composite. The effects of benzoyl chloride treatment on tensile and morphological properties of PP/vNBR/KCP composites have been studies.

2. Material and Methods

Polypropylene (PP) Grade 6331 was obtained from Titan Pro Polymers (M) Sdn Bhd Johor with a melt flow index of 14 g/10 min at 230 °C and a density of 0.9 g/cm$^3$. The vNBR was obtained from Juara One Resources Sdn Bhd, Penang. Coupling agent benzyl chloride was supplied by A.R Alatan Sdn Bhd. Kenaf core is collected from Malaysia National Tobacco Board. The KC were grinded into powder. The KC powder was then sieved at a particle size of 150 μm. The KC powder was dried at 80 °C for 24 hour in the oven to remove the water content. Meanwhile the vNBR was cut into small piece with size 0.5 – 1 mm.

2.1. Chemical Modification of Kenaf Core powder.

35 g of Kenaf core powder merges in 6 % NaOH solution for 30 min at room temperature. Then KCP raised with distilled water. The treated KCP soaked in 10 % NaOH solution with added with 50 ml benzoyl chloride and agitated vigorously. After 15 min, the mixture filtering and washing with water. Then the treated powder was drying at room temperature. The KCP were then merges in ethanol for 1 hour to remove the unreacted benzoyl chloride. Finally, the KCP washed with water and dried in an oven at 80 °C for about 24 hour.

2.2. Sample Preparation PP/vNBR/KCP

Formulation of PP/NBR/KC composites is given in table 1. The mixing process was carried out by using heated two roll mill machine at 180 °C. PP was allowed to melt for 4 min, followed by vNBR and adding of KC filler after 6 min with total mixing time of 9 min. The PP/NBR/KC composites are prepared in 1 mm sheets by using compression-moulding. The hot-press machine was preheated for 6 min at 180 °C, 3 min of compressing and 2 min of cooling down the sample composite. The total preparation time is 11 min. After the compression process, the composite moulded into square shape with the thickness of 1 mm thin. The moulded composite was cut into dumbbell shape according to ASTM 412 using a Wallace die cutter S6/1/6A.

| Material | Composition (wt %) |
|----------|--------------------|
| PP       | 70                 |
| vNBR     | 30                 |
| KC       | 5,10,15,20,25, 30  |

(wt%)-weight percent.
*Similar composition of material for treated KCP

2.3. Tensile Properties
The tensile tests were conducted on 5 samples for each formulation according to ASTM D638 standard by using a Universal testing (intron 3366) machine. The testing was carried out at a crosshead speed of 5 mm/min of dumbbell specimens and was performed at room temperature. Tensile strength, young’s modulus, and elongation at break will be measured.

2.4. Scanning Electron Microscopy (SEM)
SEM is used to study the surface morphology sample. SEM is a scientific instrument which utilizes a focused beam of electrons to inspect objects with much higher magnification and resolution. Scanning electron microscopy (SEM) model JOEL JSM-6460LA was used in this research. All samples were coated with platinum by using an auto fine coater model JFC-1600 from Japan to avoid electrostatic charging and poor image resolution during the testing. The morphological studied, analysed tensile fracture surface of composites for untreated and benzoyl chloride treatment. The observed samples were taken from the 1 mm dumbbell fracture surface samples from the tensile test. In this analysis, the magnification used was 300x magnifications.

3. Result and discussion

3.1. Tensile Properties
Figure 1-3 shown the tensile strength, elongation at break, $E_b$ and Young’s modulus of PP/vNBR/KCP composite. The tensile strength of composites decreasing with the increasing of KCP loading. The tensile strength of the composites decreased due to the inability of the filler to support stress transferred from the PP matrix [13,14]. Poor interfacial adhesion between KCP and the matrices raise the stress concentration area and decrease the tensile strength of composite [15,16]. Meanwhile, the tensile strength of treated PP/vNBR/KCP composites shows higher tensile strength when compared with the untreated composites. Results indicated that the PP/vNBR/KCP composite with 5 wt% kenaf loading exhibits tensile strength increase 1.7 MPa more compare untreated composite. The improvement in tensile strength after treatment indicate that the treatment enhancement the KCP-PP/vNBR interaction.

![Figure 1: Tensile strength of PP/vNBR/KCP composites.](image_url)

Figure 2 shows the elongation at break, $E_b$ of PP/vNBR/KCP composites. The $E_b$ drop with the increasing of KCP loading. This due to the raise in stiffness of the compound with the adding of KCP filler. The PP/vNBR/KCP composites with benzoyl chloride treatment, shows an improvement of $E_b$. The improved are due to a good filler distribution and better adhesion between KCP and PP/vNBR [17].
Figure 2: Elongation at break, $E_b$ of PP/vNBR/KCP composites

Figure 3 shows Young’s modulus of PP/vNBR/KCP composites. The Young’s modulus shows a slight increased with the increase of KCP loading. This make the soft matrix become rigid with additional of KCP filler. KCP was able to minimise the movement of segmental PP/vNBR matrices. PP/vNR/KCP composites with the benzoic chloride treatment show higher Young’s modulus values than the untreated composites [18]. The improvement on Young’s modulus was due to a good interfacial adhesion between treated KCP with PP/vNBR matrices [15].

3.2. Morphological Properties

Figure 4 (a-b) shows the tensile fractured surface morphology of PP/vNBR/KCP composites with KCP loading of 30% untreated and treated composites. Based on figure 4 (a), it can be clearly seen that the filler is pulled out from the matrix which is primarily caused by weak interfacial adhesion. This happens because the matrix-cellulose interface does not present homogeneity due to opposite nature of the components (hydrophobic PP/vNBR versus hydrophilic cellulose) [8,19]. Thus, the stress transferred across the interface is very poor. However, Figure 4 (b), adding coupling agent to composite enhances the dispersion in the matrix and enables direct contact between cellulose fibre and PP/vNBR matrices [20]. The PP/vNBR/KCP composite with benzoic chloride treatment showed an enhancement in interfacial adhesion. The less filler pulled out was observed. The particles are seem to be embedded strongly in the matrix. This is as result of an agreement with the increase of tensile strength of PP/vNBR/KCP with benzoic chloride treatment [15].
4. Conclusion

In this research, the effect surface modification using benzoyl chloride as coupling agent on KCP filler mixing with PP/βNBR based on tensile and morphology properties are investigated. Based tensile properties, the tensile strength and elongation at break of untreated PP/βNBR/KCP composites decreases by 4-23% and 7-36% respectively with increasing of KCP filler loading. Meanwhile, the tensile modulus increases by 2-13% with increasing filler loading. However, the treated PP/NBR/KCP composite have higher tensile strength, elongation at break and Young’s modulus. The increasing by 4-14% of tensile strength, 4-13% of elongation at break and 0.5-3% of Young’s modulus of treated composites compare with untreated composite. The chemical treatments improved the interfacial bonding between the KCP filler and the thermoplastic polypropylene matrix in the fabricated composites and thereby resulted in greater tensile strength, elongation at break and Young’s modulus values. The benzoyl chloride which act as coupling agent causes changes in the linkages between fibre and matrix part of the compound. The pre-treatment of sodium hydroxide ionizes the hydroxyl group to the alkoxide, thus increases the surface roughness in addition to mechanical interlocking. This have been supported by SEM of surface morphology of KCP filler. The SEM of fractured surface of treated composites, show enhancement in interfacial adhesion between KCP filler and PP/VNBR matrices and have less pull out compare to untreated composite.

Reference

[1] Karimi S, Tahir P, Karimi A, Dufresne A and Abdulkhani A 2014 Kenaf bast cellulosic fibers hierarchy: A comprehensive approach from micro to nano *Carbohydr. Polym.* **101** 878–85

[2] Abdul Khalil H P S, Yusra A F I, Bhat A H and Jawaid M 2010 Cell wall ultrastructure, anatomy, lignin distribution, and chemical composition of Malaysian cultivated kenaf fiber *Ind. Crops Prod.* **31** 113–21

[3] Md. Tahir P, Ahmed A B, SaifulAzry S O A and Ahmed Z 2011 Retting process of some bast plant fibres and its effect on fibre quality: A review *BioResources* **6** 5260–81

[4] Faruk O, Bledzki A K, Fink H P and Sain M 2012 Biocomposites reinforced with natural fibers: 2000-2010 *Prog. Polym. Sci.* **37** 1552–96

[5] Mustafa W A, Saidi S A, Zainal M and Santiagoo R 2018 A Proposed Compatibilizer Material on Banana Skin Powder (SP) Composites Using Different Temperature *J. Adv. Res. Fluid Mech. Therm. Sci.* **43** 121-7
[6] Huda M S, Drzal L T, Mohanty A K and Misra M 2008 Effect of fiber surface-treatments on the properties of laminated biocomposites from poly(lactic acid) (PLA) and kenaf fibers Compos. Sci. Technol. 68 424–32

[6] Sreekala M S, Kumaran M G, Joseph S, Jacob M and Thomas S 2000 Oil palm fibre reinforced phenol formaldehyde composites: influence of fibre surface modifications on the mechanical performance Appl. Compos. Mater. 7 295–329

[7] Mohanty A K, Misra M and Drzal L T 2002 Sustainable Bio-Composites from renewable resources: Opportunities and challenges in the green materials world J. Polym. Environ. 10 19–26

[8] George J, Sreekala M S and Thomas S 2001 A review on interface modification and characterization of natural fiber reinforced plastic composites Polym. Eng. Sci. 41 1471–85

[9] Akil H M, Omar M F, Mazuki A A M, Safiee S, Ishak Z A M and Abu Bakar A 2011 Kenaf fiber reinforced composites: A review Mater. Des. 32 4107–21

[10] Lai S and Li P 2017 Effect of Thermoplastic Polyurethane-Modified Silica on Melt- Blended Poly ( Lactic Acid ) ( PLA ) Nanocomposites Polym. Polym. Compos. 25 583–92

[11] Ragunathan S, Mustaffa Z, Kamarudin H, Sam S T and Ismail H 2017 The effect of polypropylene maleic anhydride on polypropylene/(recycled acrylonitrile butadiene rubber)/(sugarcane bagasse) composite J. Vinyl Addit. Technol. 23 228–233

[12] Zainal M, Santiagoo R, Ayob A and Mustaffa W A 2017 Mechanical properties and chemical reaction of 3-aminopropyltriethoxysilane of polypropylene, recycle acrylonitrile butadiene rubber and sugarcane bagasse composites Int. J. Microstruct. Mater. Prop. 12 55

[13] Majid R A, Ismail H and Taib R M 2016 Benzoyl Chloride Treatment of Kenaf Core Powder: The Effects on Mechanical and Morphological Properties of PVC/ENR/kenaf Core Powder Composites Procedia Chem. 19 803–9

[14] Ragunathan S, Ismail H and Hussin K 2014 Comparison of processing and mechanical properties of polypropylene/recycled acrylonitrile butadiene rubber/rice husk powder composites modified with silane and acetic anhydride compound J. Thermoplas. Compos. Mater. 27 1651–66

[15] Nor N A M and Othman N 2016 Effect of Filler Loading on Curing Characteristic and Tensile Properties of Palygorskite Natural Rubber Nanocomposites Procedia Chem. 19 351–8

[16] Blackley D C 1983 Synthetic Rubbers: Their Chemistry and Technology (London: Applied Science Publishers)

[17] Ismail H, Ragunathan S and Hussin K 2011 Tensile properties, swelling, and water absorption behavior of rice-husk-powder-filled polypropylene/(recycled acrylonitrile-butadiene rubber) composites J. Vinyl Addit. Technol. 17 190–7

[18] Zainal M, Aihsan M Z, Mustafa W A and Santiagoo R 2018 Experimental Study on Thermal and Tensile Properties on Polypropylene Maleic Anhydride as a Compatibilizer in Polypropylene / Sugarcane Bagasse Composite J. Adv. Res. Fluid Mech. Therm. Sci. 43 141–8

[19] Santiagoo R, Ismail H and Hussin K 2012 Effects of Acetic Anhydride on the Properties of Polypropylene(PP)/Recycled Acrylonitrile Butadiene(NBRr)/Rice Husk Powder(RHP) Composites Polym. - Plast. Technol. Eng. 51 1505–12