

Effect of Potassium Permanganate on Tensile Properties of Sugar Palm Fibre Reinforced Thermoplastic Polyurethane

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Abstract

Background: The high-performance engineering products derived from natural resources are in great demand worldwide, based on renewability and environmental problems. **Method:** The outcome of Potassium Permanganate (KMnO_4) treatment on the tensile behaviours of treated Sugar Palm Fibre (SPF) with 6% NaOH reinforced thermoplastic polyurethane composites was investigated. The sugar palm fibres were treated by 6% NaOH solution, followed by KMnO_4 surface treatment of the alkali treated sugar palm fibres. Three different concentrations of KMnO_4 (i.e. 0.033, 0.066, and 0.125 %) were applied in the treatment. The extruder and hot press machines were used to mix the sugar palm fibres and polyurethane resin, to get the desired polyurethane composites. Tensile behaviours including (tensile strength and modulus, and the elongation at break) were investigated by following the ASTM D-638 standard. **Findings:** The highest tensile strength recorded was 8.986 MPa with KMnO_4 concentration of 0.125 %, with 6 % alkali pre-treatment. Therefore, the KMnO_4 concentration ~0.125 % exhibited best results for tensile test. **Improvements:** This study aids an improvement in the alkaline activation method for the TPU/SPF composite fabrication.

Keywords: KMnO_4 Treatment, NaOH Treatment, Sugar Palm Fibre, Tensile Properties, Thermoplastic Polyurethane

Introduction

Currently, a dispute to reduce environmental pollution has amplified the human conscientization, in relation with the exact removal of waste materials. Specifically, there is a determination to employ natural waste materials as renewable means for number of applications. Therefore, in current years there has been an evolution in the progress of materials meeting international implications including economic viability, usage, cost and environmental impression. Several experimental findings have been presented with emphasis on the application of natural fibres as strengthening filler in the composites with polymer patterns¹ of thermoplastic or thermoset, in nature.

The investigation of natural fibres composites, considers the following parameters; the attribute of natural

fibre engaged, the surface activation of the fibre, and the composites treating in the last possessions of the material. These are very imperative factors, the material could be employed in extensive range of applications, which includes packaging industry, aerospace, sports, construction, and particularly in the automotive industry². The fibre intended to improve the adhesion, after chemical treatment, do not only change the surface but also support in improving the strength for better adhesion of the fibre with the polymer matrix. This may reduce the water absorption of composites with improvement in their mechanical properties.

In³ presented mechanical properties the jute fibres composites while studying the influence of stearic acid, potassium permanganate KMnO_4 , toluene diisocyanate, and polypropylene when improved with maleic anhy-

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drude actions. It was mentioned that by adding jute (55.89 wt%), in the matrix resulted in a significant improvement in the mechanical behaviours (tensile, flexural and impact tests). Out of these, KMnO_4 treatment was observed to be, the most operative to enhance the tensile by (53.06 MPa to 68.26 MPa) and modulus by (2557 MPa to 3278 MPa) strength behaviours, when compared with composites treated with other treatments, respectively.

In⁴ studied a compatibility between the hydrophilic cellulose fibre and hydrophobic polypropylene PP by sodium hydroxide treatment of cellulose fibres, isocyanates, maleic anhydride modified polypropylene MAPP benzyl chloride and permanganate stated that tensile properties improved by different treatments considerably, but with different changing gradations. The KMnO_4 concentration were between 0.055- 0.2 %, it was proved from the results that after 0.055 % KMnO_4 the tensile strength dropped. In⁵ established 60 DT Light Posts, by applying five diverse chemical surface activations with two respective composites, respectively to get a support. The surface treatments containing engraving with Potassium permanganate; 10% hydrogen peroxide; 21% sodium ethoxide, then with potassium permanganate and 10 vol. % HCl; were executed on the post's surface. The backlog was achieved by means of (A) Core Paste XP (Dent Mat) and (B) Unifil Flow (GC), respectively. Potassium permanganate results exhibited a noteworthy influence on micro-tensile interfacial bond with both the tested materials. Later the post-superficial actions improved the bond durability predominantly of the Core Paste XP.

In⁶ found a good interfacial adhesion of natural fibre as reinforcement for polymeric composites with epoxy matrix, by alkali KMnO_4 treatments on the mechanical properties.

Thermoplastic polyurethane (TPU) displayed good mechanical properties and it has elastic nature like the natural rubber. TPU is polar in nature, which reduces the fibre-polymer incompatibility. Moreover, it is environmental friendly (for recycle)⁷.

The sugar palm fibre (SPF) presents higher resistance and durability to the sea water and the bad weather⁸. The availability of SPF in the nature make its cost very low. However, SPF, like all natural fibre, faces some difficulties that prevent its widespread use, such as hydrophilicity. In⁹ used different concentrations of NaOH solution to treat the SPF reinforced TPU matrix. The 6 % NaOH solution

showed improved tensile modulus and strain. However, the highest tensile strength calculated in SPF treated fibre, at 6% of NaOH solution was recorded to be ~5.49 MPa⁹.

The present study is focused on the effect of different potassium permanganate concentrations (0.033-0.066 %), on the tensile properties of the fibre treated with 6% of NaOH; matrix adhesion of TPU and SPF composites (to enhance the NaOH treatment method). All the specimens were treated by NaOH and surface activated by KMnO_4 , lately, to optimize the best used concentration of KMnO_4 for a higher tensile strength. ASTM standard D638¹⁰ standard, of the composites was employed to measure the tensile properties.

2. Materials and Methods

The materials employed in this study are Estane[®] 58311 is an 85A Polyether- Type Thermoplastic Polyurethane (TPU), was used as supplied by manufacturers (Bayer Co. Malaysia). Sugar palm fibre SPF was collected locally in raw form, in the city of Raub, Pahang, Malaysia. Sodium hydroxide pellets NaOH used of Grade AR, Potassium Permanganate KMnO_4 Elixir brand High/Lab/AR Grade Fine Crystals and Acetone Dimethyl Ketone; 2-Propanone $\text{C}_3\text{H}_6\text{O}$, respectively were attained from Bayer Co. Malaysia.

2.1 Preparation of Fibre

The fibres were splashed thoroughly with tap water to get rid of dust and additional particulates, withered for two weeks in the atmospheric pressure at room temperature. Afterward grinded (machine Retsch ZM 200) and sieved by means of an auto shaker type FRITTSCH, in order to achieve the fibre size of 250 μm , as studied in previous research work¹¹.

2.2 Treatment of Fibre

The hydrophilic nature of the SPF makes the adhesion between the fibre and the hydrophobic TPU poor, which results in a weak composites structure¹¹. For a good adhesion purpose, the clean, dried, and grinded fibres were washed many times with distilled water, after being soaked into 6 %sodium hydroxide solution, for a time period of 90 minutes^{11,12}. Afterwards, the fibre was left to complete dry for almost two weeks at atmospheric pressure and lab temperature¹¹. Finally, the treated fibres were soaked

in three different KMnO_4 (0.033, 0.066, to 0.125 %) concentrations, prepared in acetone.

2.3 Composite Preparation

TPU/SPF composite specimens, were fused by employing a Thermo SCIENTIFIC EUROLAB 16 extruder machine, with optimum rotating speed (40 rpm) at a temperature set of and 180-190-200 °C¹¹, respectively. Temperature and speed were set on the basis of previously reported studies, for the mechanical properties study of TPU/SPF composites. In the study, fibre loading of 30%, has been kept fixed, throughout the study with a 250µm fibre size. The treated fibre (with 6% NaOH) was treated with three different concentrations of KMnO_4 from 0.033, 0.066, and 0.125 %. A 30% fibre weight mixed into 70% TPU, extruded in extruder machine under optimum conditions of temperature of 180-190-200°C and at of 40 rpm¹¹. The extruded composite bits were later constrained by using square mould, and afterward by using the hot press LOTUS SCIENTIFIC 25-ton compression moulding with the press pressure maintained at 10 MPa and temperature of 190°C, for a time of 10 min¹³. For the moulding, the samples were pre-heated, up to 190°C. Finally, the prepared sheet was cooled down to a temperature of 50°C.

2.4 Tensile Testing

Tensile behaviours were calculated by employing an Instron 3369Q3720 machine, following the ASTM D638¹⁰. The specimens were arranged in to by dumbbell shapes by a manual saw cutter. Five specimens were studied, at a crosshead speed of 5 mm/min, respectively.

2.5 Scanning Electron Microscope

The scanning electron microscopy (SEM) (Carl Zeiss model EVO, Germany) was employed to study the morphology of the composites (specimens), after the tensile test.

3. Results and Discussion

Figure 1 displays the tensile strength of samples with altered concentrations of potassium permanganate solutions. It is evident that the tensile strength amplified steadily with the increase in the KMnO_4

concentrations. The strength calculated was 6 MPa with a KMnO_4 concentration of 0.033 %, which was later improved to around 9 MPa at higher (0.125 %) KMnO_4 concentration, respectively. The KMnO_4 surface activation has improved the surface properties of natural fibre in a polymer matrix^{14,15}. That correlates with many researchers using different chemical treatment for the natural fibre polymer activation¹⁶. Tensile property enhancement, is a clear evidence of good impact of KMnO_4 treatment, on the tensile strength on the fibre which was treated with NaOH at 6% concentration.

Figure 2 displays the tensile modulus behaviour of the matrices with different KMnO_4 activations, respectively. It is clear that the modulus amplified rapidly with the growing KMnO_4 concentrations. There was a dramatic rise in the modulus values for all the KMnO_4 activated samples, in comparison with treated composites when activated by 6 % NaOH, individually. The modulus was 300 MPa for 0.033 %, and improved largely to 900 MPa for 0.125 % KMnO_4 . This results were in agreement with many authors that use KMnO_4 previously to make the surface more rough and active, and to remove lignin and wax^{16,17}.

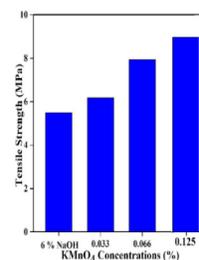


Figure 1. Effect of Potassium Permanganate Treatment on the Tensile Strength of TPU/SPF Composites.

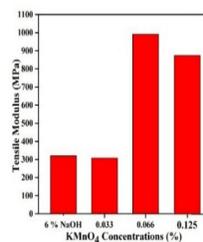


Figure 2. Effect of Potassium Permanganate Treatment on the Tensile Modulus of TPU/SPF Composites.

Figure 3 shows depicts the tensile strain values with diverse KMnO_4 concentrations, respectively. It is clear that the strain decreased down with the increase in KMnO_4 concentration. The strain calculated at 0.033 % concentration was 6 %, which reduced to almost 1% for KMnO_4 concentration of 0.125 %, respectively^{16,18}. KMnO_4 is used chemically for cleaning the surface of plant fibre, where a natural fibre action as strong aqueous solution with concentrated base to yield greater inflammation with subsequent alterations in the fine assembly, dimensions and morphology, effecting the mechanical behaviours as well.

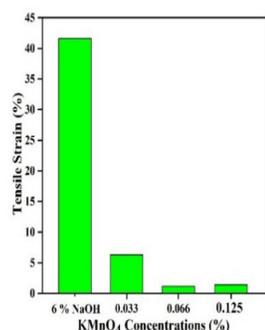


Figure 3. Effect of Potassium Permanganate Treatment on the Tensile strain of TPU/SPF Composites.

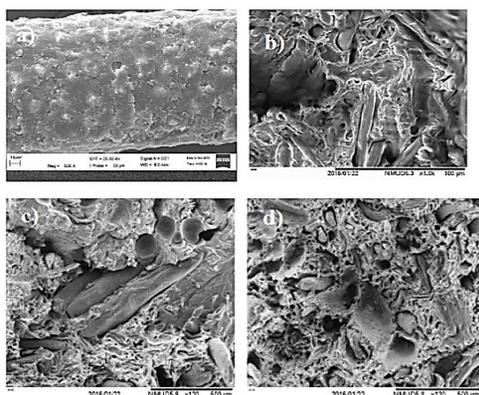


Figure 4. The Surface Illustration of (a) Untreated, (b) Treated by 0.033, (c) 0.066, and (d) 0.125 wt.% with KMnO_4 by SEM Analysis of SPF Reinforced TPU.

The surface assembly of the untreated SPF fibres, is presented in Figure 4a. It is visible that the raw fibres surfaces were dense and smooth with different impurities, revealed with white dots in the Figure. The holes are

produced due to fibres, pulled out from the matrix, while the surface look like as clean, intact and free from any following polymer. After employing the KMnO_4 activation on the surface shown in Figure 4b, the fibres get fragmented nearby the surface and do not permit holes on the ruptured surface. When higher KMnO_4 solution concentration (0.066 and 0.125 wt. %) was used, an irregular and tarnished surface was observed, which is an indication for the elimination of impurities shown in Figure 4c and 4d, respectively. These analyses are in reputable agreement with the preceding studies reported by⁴.

4. Conclusion

The study of consequence of alkali activation on the tensile behaviors of sugar palm fibre strengthened thermoplastic polyurethane composites, has been found improved by KMnO_4 method. From the above outcomes, it is concluded that the chemical treatments by Sodium hydroxide solutions and KMnO_4 respectively, have improved all the tensile properties of ultimate composite systems except the tensile strain. The top concentration of chemical solutions KMnO_4 is 0.066% by weight that gives the best tensile modulus. However, the 0.125 % of KMnO_4 recorded the highest tensile strength. Nevertheless, the behavior of tensile strain for all diverse KMnO_4 treatment is still poor than treated value of (6% NaOH). Consequently, the KMnO_4 method successfully improved the tensile properties of the new TPU/SPF composites.

5. Acknowledgement

This work was supported financially by Ministry of Higher Education Malaysia and the University Malaysia Pahang through the Fundamental Research Grant Scheme RDU130138 and Graduate Research Scheme GRS1503124, respectively RDU 130138.

6. References

- Li WY, Jin AX, Liu CF, Sun RC, Zhang AP, Kennedy JF. Homogeneous Modification of Cellulose with Succinic Anhydride in Ionic Liquid Using 4-Dimethylaminopyridine as a Catalyst. *Carbohydrate Polymers*. 2009; 78(3): 389–95. Crossref
- Ku H, Wang H, Pattarachaiyakop N, Trada M. A Review on the Tensile Properties of Natural Fibre Reinforced

- Polymer Composites. *Composites Part B: Engineering*. 2011; (42):856–73.
3. George G, Jose TE, Jayanarayanan K, Nagarajan E, Skrifvars M, Joseph K. Novel Bio-Commingled Composites Based on Jute/Polypropylene Yarns: Effect of Chemical Treatments on the Mechanical Properties. *Composites Part A: Applied Science and Manufacturing*. 2012; 43:219–30. Crossref
 4. Joseph P, Joseph K, Thomas S. Short Sisal Fibre Reinforced Polypropylene Composites: The Role of Interface Modification on Ultimate Properties. *Composite Interfaces*. 2002; 1(9):171–205. Crossref
 5. Monticelli F, Toledano M, Franklin R Tay, Cury A H, Goracci C, Ferrari M. Post-Surface Conditioning Improves Interfacial Adhesion in Post/Core Restorations. *Dental Materials*. 2006; 22(7):602–09. Crossref PMID:16289722
 6. Alsaeed T, Yousif B, Ku H. The Potential of Using Date Palm Fibres as Reinforcement for Polymeric Composites. *Materials and Design*. 2013; 43:177–84. Crossref
 7. Liu D, Song J, Anderson DP, Chang PR, Hua Y. Bamboo Fibre and its Reinforced Composites: Structure and Properties. *Cellulose*. 2012; (19):1449–80. Crossref
 8. Ishak M, Sapuan S, Leman Z, Rahman M, Anwar U, Siregar J. Sugar Palm (Arengapinnata): Its Fibres, Polymers and Composites. *Carbohydrate Polymers*. 2013; 91 (2): 699–710. Crossref PMID:23121967
 9. Mohammed AA, Bachtiar D, Siregar J, Rejab M. Effect of Sodium Hydroxide on the Tensile Properties of Sugar Palm Fibre Reinforced Thermoplastic Polyurethane Composites. *Journal of Mechanical Engineering and Sciences (JMES)*. 2016; 10(1):1765–77. Crossref
 10. Standard, A.S.T.M. Standard test method for tensile properties of plastics. ASTM International. Designation: D, 638. 2003.p.1–13.
 11. Mohammed AA, Bachtiar D, Siregar J, Rejab MR, Hasany SF. Physicochemical Study of Eco-Friendly Sugar Palm Fibre Thermoplastic Polyurethane Composites. *BioResources*. 2016; 11(4): 9438–54. Crossref
 12. Bachtiar D, Sapuan S, Hamdan MM. The Effect of Alkaline Treatment on Tensile Properties of Sugar Palm Fibre Reinforced Epoxy Composites. *Materials and Design*. 2008;29(7): 1285–90. Crossref
 13. El-Shekeil Y, Sapuan S, Zainudin E, Khalina A. Optimizing Processing Parameters and Fibre Size for Kenaf Fibre Reinforced Thermoplastic Polyurethane Composite. *Key Engineering Materials*. 2011; 471-472:297–302. Crossref, Crossref
 14. Mohanty A, Misra M, Drzal L. Surface Modifications of Natural Fibres and Performance of the Resulting Biocomposites: An Overview. *Composite Interfaces*. 2001; 8(5): 313–43. Crossref
 15. Joseph K, Thomas S, Pavithran C. Effect of Chemical Treatment on the Tensile Properties of Short Sisal Fibre-Reinforced Polyethylene Composites. *Polymer*. 1996; 37(23): 5139–49. Crossref
 16. Xue L, Lope TG, Satyanarayan. Chemical Treatment of Natural Fibre for Use in Natural Fibre-Reinforced Composites: A Review. *Polymer Environment*. 2007; 15(1):25–33. Crossref
 17. Zheng Y, Liu Y, Wang A. Kapok Fibre Oriented Polyaniline for Removal of Sulfonated Dyes. *Industrial and Engineering Chemistry Research*. 2012; 51(30):10079–87. Crossref
 18. John MJ, Anandjiwala RD. Recent Developments in Chemical Modification and Characterization of Natural Fibre-Reinforced Composites. *Polymer Composites*. 2008 Jan; 29(2): 187–207. Crossref
 19. FluidChe 2017 Available from: <http://fluidsche.ump.edu.my/index.php/en/>
 20. The Center of Excellence for Advanced Research in Fluid Flow (CARIFF) Available from: <http://cariff.ump.edu.my/>
 21. Natural resources products prospects - International Conference on Fluids and Chemical Engineering FluidsChE 2017 Malaysia,). *Indian Journal of science and technology*. 2017; S2(1).
 22. University Malaysia Pahang. Available from: www.ump.edu.my