Effect of Absorbed Radiation Dose on the Mechanical Properties of Kenaf Fibers

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This paper focuses on the effect of absorbed radiation dose by electron beam on the mechanical properties of untreated and pre-treated kenaf fibers with sodium chlorite ($NaClO_2$), which were subsequently grafted with glycidyl methacrylate (GMA). Changes to properties of the fibers after graft polymerization process were analysed via Fourier transform infra-red spectroscopy (FTIR) analysis. The morphological changes were observed by field emission scanning electron microscopy (FESEM). The results indicated that untreated kenaf fibers showed superior mechanical properties compared to treated kenaf fibers. This was mainly due to deterioration in lignin content as the concentration of $NaClO_2$ increased. Lignin is responsible for keeping microfibrils intact. Thus, the reduction in lignin content leads to alteration in the mechanical strength of fibers, as it causes bond cleavage between lignin and polysaccharide molecules. On the other hand, non-radiated kenaf fibers showed higher tensile strength and tensile modulus compared to radiated kenaf fibers for all doses. The tensile strength of non-radiated kenaf fibers was around 245.8 MPa, which reduced up to 224.3 MPa when subjected to irradiation of 10 kGy. However, the tensile strength of kenaf fibers irradiated at 100 kGy was recorded at 125.6 MPa. Grafted kenaf fibers exhibited moderate mechanical properties and significant changes were observed as the absorbed radiation dose increased. This research would provide the technical basis for preparation of radiation-induced grafted kenaf adsorbents with an overview on emphasizing a significant factor which affects the mechanical properties of kenaf fibers.

Key words: Kenaf fiber; radiation; electron beam; graft polymerization; mechanical properties

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One of the new trends which had spread in the modern civilized world is, to design and create new materials in order to meet the growing necessities of new technologies such as cleaner energy resources, better health care, and green separation processes. Hence, it is essential to modify the properties of polymers in order to align them to designed tailor-made specifications for target applications. Cellulose is one of the most abundant natural bio-polymers found in nature. Cellulose is easily renewable, biodegradable, and possesses excellent chemical and physical properties, which make it appropriate to be used as an anchor in various applications such as composites, adsorbents, coating materials, and so on. However, the nature of cellulose with inactive surface and compact crystal structure requires prior modifications to improve some of its properties in order to serve the target purposes. The modifications of cellulose-based materials can be done through several methods, such as carboxymethylization as reported by Yan *et al.* [1], grafting as reported by O'Connel *et al.* [2], and cross-linking as reported by Rimdusit *et al.* [3]. Lately, radiation-induced grafting technique was executed precisely in the preparation of a cellulose-based adsorbent material for the removal of heavy metals from water [4].

Among the cellulose-based materials, kenaf fibers have shown a lot of potential as an adsorbent [5]. Kenaf fibers can be used as an adsorbent for heavy metal adsorption from various aqueous systems either through its natural characteristics or grafting with other functional monomers [6]. However, kenaf fibers still need to undergo a series of processes in order to serve the targeted applications as an adsorbent. Although kenaf fibers has been proven to be an environment-friendly and cost-effective adsorbent, yet it still suffers several major drawbacks, especially after being exposed to several processes. The most concerning drawback is interrelated to the mechanical properties of kenaf fibers. Mechanical properties of kenaf mainly rely on chemical compositions of the fibers. Kenaf fibers are composed of microfibrils of cellulose in the matrix of hemicellulose and lignin [7]. Lignin is one of the important constituents of lignocellulosic fibers, which are made of phenol. Phenol will change into quinone with exposure to ionizing radiation, which protects the fibers from graft polymerization. Thus, pre-treatment on removal of lignin in lignocellulosic fibers is essential before the fibers are subjected to a radiation grafting process [8]. However, the fibers

should be pre-treated partially using ionizing radiation, in order to obtain a grafting yield.

Removal of phenol and subsequent radiation and grafting process leave an inevitable impact on mechanical properties of the fibers, which will eventually lead to degradation of the cellulose backbone of kenaf fibers. Therefore, an understanding of the effects of pre-treatment, radiation, and grafting process conditions on the mechanical properties of kenaf fibers is important before undertaking radiation graft polymerization process onto cellulosic materials. A few previous studies had reported on radiation-induced grafting on cellulose fibers for metal adsorption. Namely, the effect on emulsion graft polymerization process conditions on kenaf by pre-irradaition technique using different monomers, glycidyl methacrylate (GMA) [6] and 4-chloromethylstyrene (CMS) [9]. Apart from that, emulsion graft polymerization of GMA by pre-irradiation technique onto non-woven cotton fabrics [10] and hyacinth fibers [11] were performed, as well for the removal of heavy metals from water. However, none of these studies had focused on the effect of every single process involved, on the mechanical properties of the cellulose fibers. In this present study, the effects of the acid treatment, absorbed radiation dose, and graft polymerization on tensile properties of kenaf fibers were investigated. Moreover, this research would provide the technical basis for preparation of radiation-induced grafted kenaf adsorbents with better performance in terms of durability.

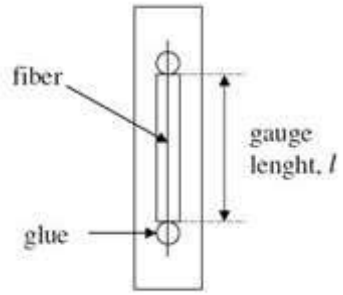
MATERIALS AND METHODS

The treated kenaf fibers were prepared according to our previous research and used as the trunk material for grafting [6]. The acid treatment was tested according to TAPPI T222 om-02 Standard Method for determination of acid-insoluble lignin in wood and pulp using sodium chlorite ($NaClO_2$) from Merck Sdn. Bhd. (Bandar Sunway, Malaysia) as the bleaching agent. The water-retted kenaf bast fibers were supplied by National Kenaf and Tobacco Board (NKTB), Malaysia. Concentrated nitric acid, HNO_3, 65% (Merck) was used to adjust pH. The monomer: GMA, with analytical grade and chemicals such as surfactants: polyoxyethylene (20) sorbitan monolaurate (Tween-20) and isopropanol (IPA), were obtained from Sigma-Aldrich (M) Sdn. Bhd. (Subang Jaya, Malaysia). All the chemicals were used as received.

The morphological changes of the kenaf fibers were analyzed with field emission scanning electron microscope (FESEM) Hitachi SU8000 (Japan). The samples were coated with 30 sec of platinum coating. For the cross-section, the fibers were placed in a mould with their transverse surface facing the cutting face of the mould. The mould was filled with epoxy resin and placed in an oven set at 60°C for 24 hours to polymerize. The embedded fibers were cut with a microtome to get a smooth cross-section surface.

Fourier Transform Infra-red (FTIR) spectra were recorded in the frequency range of 4000 – 400 cm^{-1} using Bruker Tensor II (Germany) in Attenuated Total Reflectance (ATR) mode.

The strength of the kenaf fibers was obtained using the universal testing machine, INSTRON at the Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia. The tests were done in accordance to ASTM D3379-75 Standard Test Method for Tensile Strength and Young's Modulus for High Modulus Single-Filament Materials. The specimens were set as shown in Figure 1. The cross head rate in this study was 3 mm/min and the gauge length was fixed at 30 mm, with load cell capacity of 10 N.



Correct spelling: length

Figure 1. Tensile specimen setting for kenaf fibers

1. Acid Treatment

Sodium chlorite ($NaClO_2$) is a medium-strength acid and generally used as a bleaching agent. $NaClO_2$ was prepared in water at varying concentrations, varying from 0.1% to 1.0% (w/v). $NaClO_2$ solutions were heated to 70°C using a hot plate. Prior to that, the pH of the $NaClO_2$ solutions was adjusted to 4 by using 5 M nitric acid (HNO_3). 2.5 g of kenaf fibers was added to the solutions and the mixtures were stirred for 6 hours. Upon completion, kenaf fibers were removed from the solutions, washed repeatedly with distilled water, and left to dry overnight in an oven at 60°C.

2. Radiation-induced Graft Polymerization

The experimental procedures and parameter values for radiation-induced graft polymerization process was based on our previous research [6]. About 0.2 ± 0.01 g of kenaf fibers was weighed accurately; as the fibers are very light, and sealed in a polyethylene zipper bag. ***[are the authors sure they used only 1 zipper bag for all the samples – Aznan]*** The fibers were purged with nitrogen (N_2) for 2 minutes to remove dissolved oxygen. The zipper bag which contained the samples was placed on a tray and transported into the radiation chamber via a conveyor system. The sample was radiated with an electron beam at different doses. The selected irradiation doses for this study were 10, 30, 50, 70, and 100 kGy. After irradiation, the fibers were immersed in 100 ml of 3% GMA emulsified with 1% Tween-20. The grafting reaction was then allowed to react up to 3 hours at 40°C in a water bath. After the reaction, the grafted kenaf was washed repeatedly with IPA to remove excessive monomer and homopolymer of poly-GMA. The weight of the GMA-grafted kenaf was determined after drying the fibers in a vacuum oven set at 40°C for 24 hours. The percentage of grafting (PG) was calculated using the equation as stated below;

$$PG\ (\%) = ((W_1 - W_0)/W_0) \times 100 \qquad \text{(Eq. 1)}$$

Where, W_0 is the initial weight of kenaf and W_1 is the weight of kenaf after grafting. The overall methodology process for this work is depicted in Figure 2.

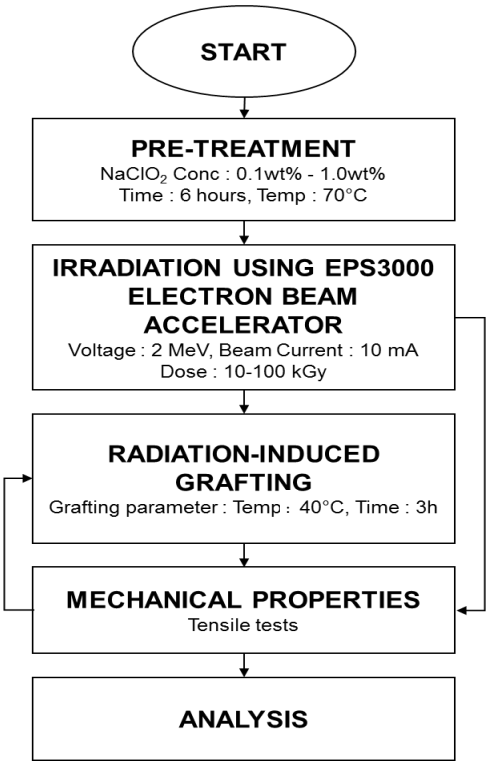


Figure 2. Methodology process

RESULTS AND DISCUSSION

1. Tensile Tests

Figure 3 shows the tensile strength and tensile modulus of pre-treated kenaf fibers at different concentrations of $NaClO_2$. The concentration of $NaClO_2$ varied between 0.1% to 1.0%. The tensile strength decreased prominently at the concentrations of 0.1% and 0.5%. Thereafter, significant changes in tensile strength were not observed as the concentration of $NaClO_2$ increased further. On the other hand**,** the tensile modulus remained almost consistent with the increase in $NaClO_2$ concentration. Kenaf fibers are hallowed centered cellulosic fibers which consist of cellulose, hemicellulose, lignin, and pectin. Lignin is incorporated with hemicellulose through radical crosslinks and this network holds the cell walls together stiffly [7]. On the contrary, sodium chlorite is a well-recognized strong oxidizing agent and it is capable of isolating impurities such as lignin from cellulose during the course of pre-treatment process [6]. As the $NaClO_2$ concentration increases, the removal of lignin is expected to be massive, leading, eventually, to a reduction in the strength of the fibers by imparting bond cleavage between lignin and polysaccharide molecules [8]. This explains well the reduction in tensile strength as the concentration of $NaClO_2$ increased. Removal of lignin merely stayed consistent as the concentration of $NaClO_2$ reached 0.5%, which resulted in the constant tensile strength, thereafter. Incorporation of cell walls is made into lignin via crosslinks of arabinoxylanes to lignin. This crosslinks impart the structure of lignocellulosic fibers which are responsible for good mechanical properties [9]. However, pre-treatment of lignocellulosic fibers with $NaClO_2$ mainly targets on degradation of lignin, therefore other components such as cellulose and hemicellulose are safe from any severe effects. Thus, tensile modulus promply stays consistent throughout pre-treatment process at different concentrations of $NaClO_2$.

The kenaf fibers subjected to pre-treatment at the concentration of 0.5% $NaClO_2$ were further used for irradiation and grafting processes, thereafter. Figure 4 shows the tensile strength and tensile modulus of non-radiated (0 kGy) and radiated kenaf fibers. The absorbed radiation dose given was between 0 to 100 kGy. Only kenaf fibers pre-treated at the concentration of 0.5% $NaClO_2$ were used in this part of the experiment. The highest tensile strength (224.3 MPa) and tensile modulus (26.1 GPa) were measured when the fibers were radiated at 10 kGy, while fibers radiated at 100 kGy had the lowest tensile strength and tensile modulus. Both tensile strength and tensile modulus decreased with the increase of radiation dose. It can be evidenced that the tensile strength significantly decreased at high dose (100 kGy). Tensile strength for non-radiated kenaf fibers was found to be 245.8 MPa, which was higher than the radiated samples. It is believed that the high energy from the electron beam radiation might have damaged the fibers, resulting in a decrease in tensile strength and tensile modulus, which in turn led to much more inferior mechanical properties, as compared to non-radiated fibers. This may be due to the rupture of the kenaf fibers' microstructures, which is a direct effect of electron beam irradiation [10]. Previously, a few studies had reported similar outcomes, whereby the mechanical performance of cellulosic materials was certainly impacted by ionizing radiation [12] [13] [14].

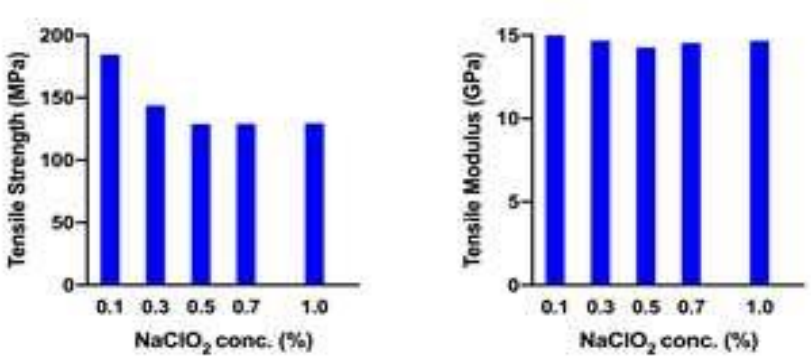


Figure 3. Tensile strength and tensile modulus of pre-treated kenaf at different concentrations of $NaClO_2$

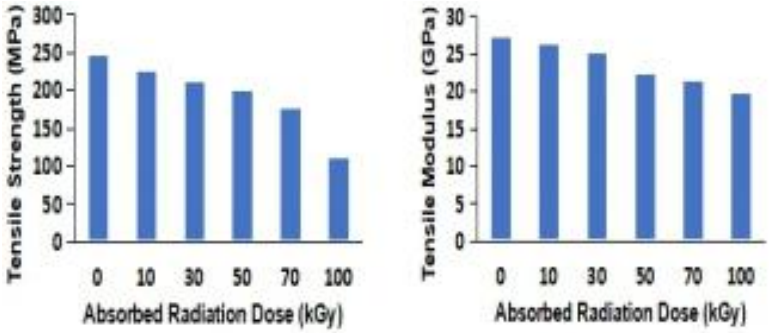


Figure 4. Tensile strength and tensile modulus of radiated kenaf at different doses

The pre-treated kenaf fibers irradiated at different irradiation doses were subsequently subjected to grafting process. The percentage of grafting, PG (%) for each sample is exhibited in Table 1. As shown in Table 1, PG increased with increasing dose. However, there was a large increment in PG at 100 kGy. This was because the final weight of the kenaf fibers after grafting was used to calculate PG (%) gravimetrically. As such, any remaining PGMA homopolymer in the samples could cause an error in the quantification. Therefore, extra precautions, such as washing, were carried out in methanol solution at 40°C in a few repeated cycles to ensure excessive monomer and homopolymer were removed before the quantification. Throughout the entire extensive washing processes, the grafted kenaf fibers were placed into a tea bag in order to avoid the loss of any strand of the fibers. The grafted fibers with PG higher than 150% were found to be brittle and difficult to separate to obtain a single-filament for testing. Due to this, only grafted samples up to 50 kGy were used for tensile tests.

Figure 5 shows the tensile strength and tensile modulus of grafted fibers at different doses. Only kenaf fibers pre-treated at the concentration of 0.5% $NaClO_2$ and subsequently irradiated at 10 to 50 kGy for grafting process were used in this part of the experiment. The result showed no significant differences of tensile strength and tensile modulus between each doses. This result contradicted the previous results pertaining to effects on mechanical strength at different irradiation doses, which are exhibited in Figure 4. Although radiation affected the fibers and lowered the tensile properties, the presence of grafted layers some how compensated these effects. As PG increased with dose, thicker grafted layers were formed. Graft polymerization of the fibers helped in improving chemical bonding between the monomers and fibers. Therefore, it can be concluded grafting of GMA onto kenaf fibers can improved the mechanical properties of the radiated fibers.

Dose (kGy)	10	30	50	70	100
PG (%)	7.3	97.5	154.7	165.4	192.8

Table 1. Percentage of grafting, PG (%) for each sample

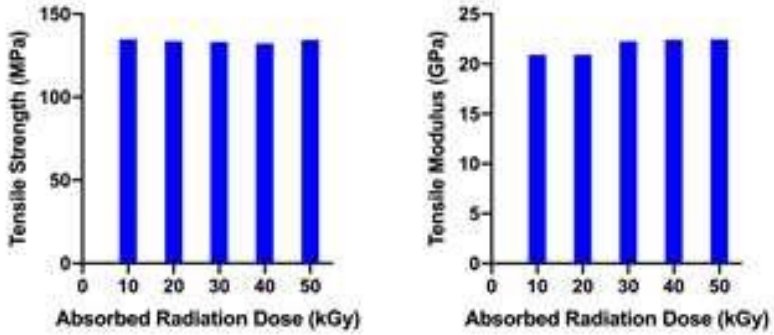
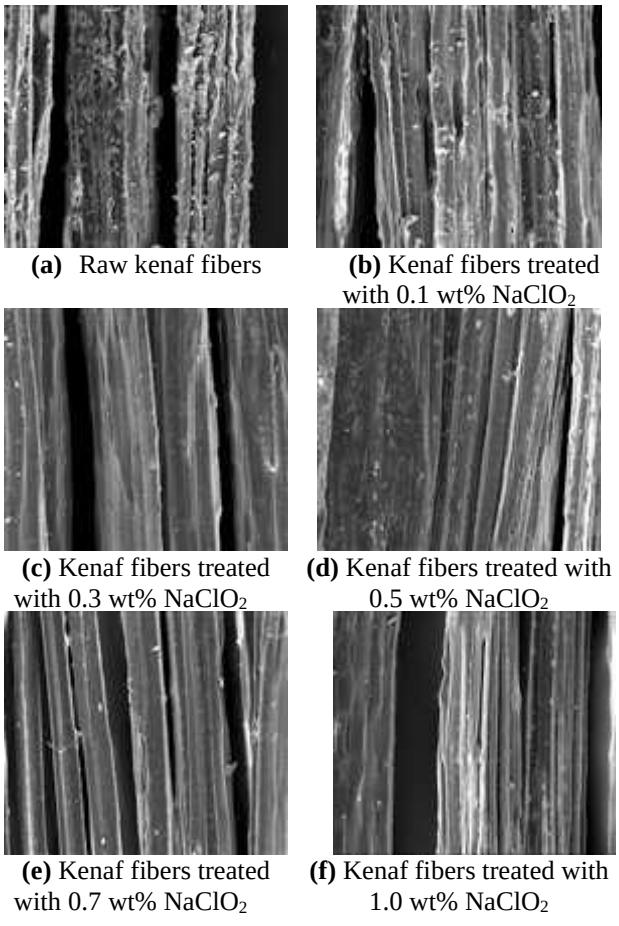


Figure 5. Tensile strength and tensile modulus of grafted kenaf at different doses

2. Surface Morphology

Figures 6(a) – (f) present the morphological changes of kenaf fibers after treatment with $NaClO_2$ at different concentrations. Pertaining to raw kenaf fibers, single fibers were linked and bundled up together by lignin, resulting in fiber bundles, as seen in Figure 6(a). The surface layer exhibited coarse morphology where it could be seen clearly that the fibers were coated with surface impurities, probably waxy substances of lignin and hemicellulose. It could be seen that the fibers became cleaner after treatment using 0.1 wt% $NaClO_2$. However, the presence of surface impurities still could be seen, indicating that the treatment using 0.1 wt% $NaClO_2$ was insufficient. It is clear in Figures 6(b) – (f) that treatments using 0.3 wt% $NaClO_2$ onwards gave smoother fiber surfaces, which indicated the removal of surface impurities, mainly lignin and hemicellulose. This finding matches the results obtained in the delignification of banana fibers for radiation grafting polymerization study performed by Selambakkannu *et al*. [8].

Morphological changes of kenaf fibers that occurred after graft polymerization were analysed with SEM, as shown in Figure 7. From the cross-section micrographs of the fibers, it was observed that the kenaf fibers before graft polymerization consisted of hollow microfibrils. The ungrafted kenaf fibers had undergone $NaClO_2$ treatment, therefore all impurities in the fibers had been removed, resulting in smooth and clean surfaces, as evidenced in the micrographs. In comparison to the ungrafted kenaf fibers, the extent of filling of cellular cavities of the kenaf fibers was observed in the grafted kenaf. It is clearly shown in Figure 7 that the kenaf fibers were coated with GMA copolymer layer and there is no indication of PGMA homopolymer on the surface of the fibers. It is believed that the monomer penetrated into the fibers and formed a layer within and on the surface of the fibers. Therefore, several grafted layers were formed and could be seen in the micrographs. The changes of physical appearance of the grafted kenaf were the additional physical evidence to confirm the presence of grafted polymer layers on the fibers. The SEM analysis on grafting of GMA onto cotton fibers by Sekine *et al*. had exploited results which favor the finding in this study as well [10].



(a) Raw kenaf fibers
(b) Kenaf fibers treated with 0.1 wt% $NaClO_2$
(c) Kenaf fibers treated with 0.3 wt% $NaClO_2$
(d) Kenaf fibers treated with 0.5 wt% $NaClO_2$
(e) Kenaf fibers treated with 0.7 wt% $NaClO_2$
(f) Kenaf fibers treated with 1.0 wt% $NaClO_2$

Figure 6. SEM images of kenaf fibers treated with different concentrations of $NaClO_2$ (EHT = 2.0 kV, Magnification : 500x)

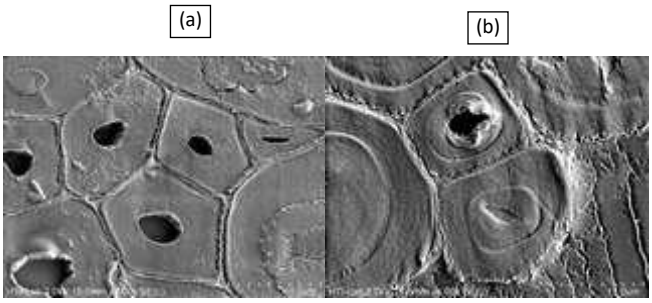


Figure 7. SEM micrographs of cross-section kenaf fibers: (a) before graft polymerization and (b) after graft polymerization

3. Fourier Transform Infra-red (FTIR)

FTIR spectra for raw and pre-treated kenaf fibers at the concentration of $NaClO_2$ ranging from 0.1% to 1.0% are shown in Figure 8. The transmittance bands which appeared signify the major functional groups which act as the backbone in the lignocellulosic kenaf fibers. O-H stretching absorption at 3345 cm^{-1}, C-H stretching at 2914 cm^{-1}, C=O stretching at 1731 cm^{-1}, C=C stretching for lignin at 1632 cm^{-1}, and C-O stretching at 1239 cm^{-1} and 1029 cm^{-1} were observed in both raw and pre-treated kenaf fibers [15]. The main peaks which existed in raw and pre-treated kenaf fibers didn't indicate any major changes. But, the intensity of the peaks present at 1731 cm^{-1}, 1239 cm^{-1}, 1029 cm^{-1}, and 1632 cm^{-1} devoted to hemicellulose and lignin, reduced as the concentration of sodium chlorite used during pre-treatment increased [8]. Reduction in peak intensity at 1632 cm^{-1} denoted the removal of lignin from the fibers via treatment with sodium chlorite [16]. Meantime, the reduction in peak intensity at 1731 cm^{-1} designated the occurrence of de-esterification process, which was responsible for the removal of carboxylic groups [17]. The peak intensity reduction at 1239 cm^{-1} and 1029 cm^{-1} indicated diminishing of C-O stretching of acetyl group in lignin [8]. This finding matched the results obtained in the delignification of kenaf fibers for radiation grafting polymerization study performed by Jamaliah *et al.* [6].

FTIR spectra for ungrafted and grafted fibers are shown in Figure 9. A similar backbone for both ungrafted and grafted fibers was observed, indicating that the chemical composition of the substrate sustained after the graft polymerization process. However, a strong vibration frequency was observed at about 1720 cm^{-1} attributed to the C=O group of GMA monomer and another distinctive vibration at 800 – 900 cm^{-1} associated with the epoxy ring. This proved the successful grafting of GMA onto the kenaf fibers.

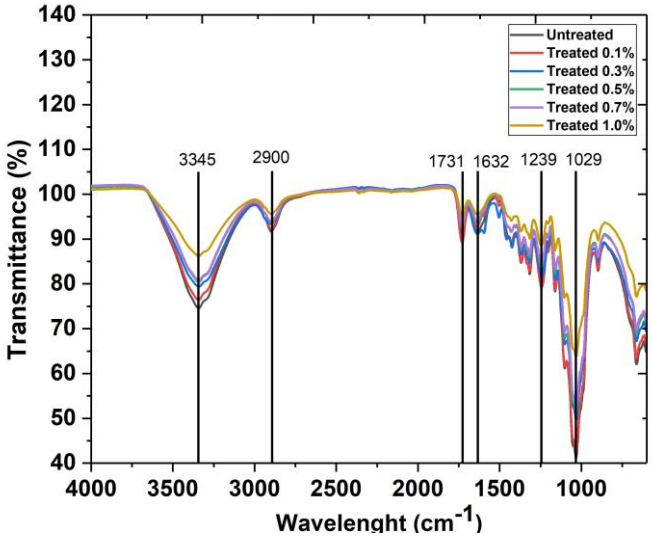


Figure 8. FTIR spectra of (a) raw kenaf fibers, (b) kenaf fibers treated with 0.1 wt% $NaClO_2$, (c) kenaf fibers treated with 0.3 wt% $NaClO_2$, (d) kenaf fibers treated with 0.5 wt% $NaClO_2$, (e) kenaf fibers treated with 0.7 wt% $NaClO_2$, and (f) kenaf fibers treated with 1.0 wt% $NaClO_2$

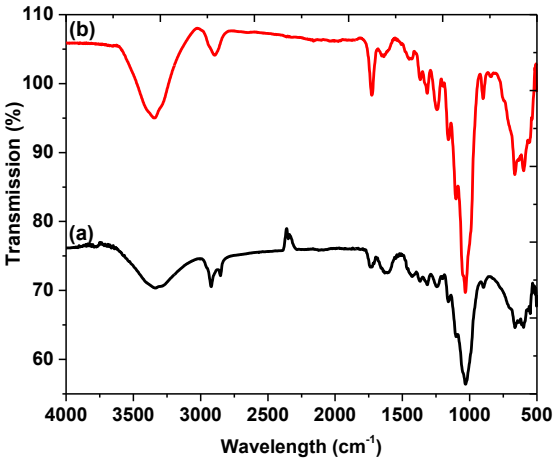


Figure 9. FTIR spectra of (a) ungrafted and (b) grafted kenaf fibers, P.G. ~100%

CONCLUSION

This study focused on changes in tensile strength and tensile modulus of kenaf fibers after pre-treatment with $NaClO_2$, upon being exposed to electron beam irradiation at different doses and finally grafting with GMA thereafter. The results obtained clearly indicated that all the three processes actually imposed greater impact onto tensile strength and tensile modulus of the kenaf fibers, which significantly affected the mechanical properties of the kenaf fibers as well. Among all the process, electron beam irradiation at higher dose led to substantial reduction in the tensile strength and tensile modulus of the kenaf fibers. Thus, it is essential to use a lower dose for the preparation of radiation-induced grafted kenaf adsorbent in order to preserve the mechanical properties of kenaf fibers.

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REFERENCES

1. Yan, H., et al. (2011) Sorption of methylene blue by carboxymethyl cellulose and reuse process in a secondary sorption. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **380(1-3)**, 143–151.

2. O'Connell, D. W., C. Birkinshaw and T. F. O'Dwyer (2008) Heavy metal adsorbents prepared from the modification of cellulose: A review. *Bioresource technology*, **99(15)**, 6709–6724.

3. Rimdusit, S., et al. (2012) Comparison of gamma radiation crosslinking and chemical crosslinking on properties of methylcellulose hydrogel. *Engineering Journal*, **16(4)**, 15–28.

4. Selambakkannu, S. et al. (2018) A kinetic and mechanistic study of adsorptive removal of metal ions by imidazole-functionalized polymer graft banana fiber. *Radiation Physics and Chemistry*, **153,** 58–69.

5. Jopony, M., et al., Kenaf Fibres (Hibiscus Cannabinus) As a Potential Low-Cost Adsorbent for Wastewater Treatment.

6. Sharif, J., et al. (2013) Graft copolymerization of glycidyl methacrylate onto delignified kenaf fibers through pre-irradiation technique. *Radiation Physics and Chemistry*, **91**, 125–131.

7. Babatunde, O. E., et al. (2015) Potentials of kenaf fibre in bio-composite production: A review. *Jurnal Teknologi*, **77(12)**.

8. Mohamed, N. H., et al. (2013) Effect of partial delignification of kenaf bast fibers for radiation graft copolymerization. *Journal of applied polymer science*, **127(4)**, 2891–2895.

9. Mohamed, N. H., et al. (2013) Emulsion graft polymerization of 4-chloromethylstyrene on kenaf fiber by pre-irradiation method. *Radiation Physics and Chemistry*, **82**, 63–68.

10. Sekine, A., et al. (2010) Biodegradable metal adsorbent synthesized by graft polymerization onto nonwoven cotton fabric. *Radiation Physics and Chemistry*, **79(1)**, 16–21.

11. Madrid, J. F., G. M. Nuesca and L. V. Abad (2013) Gamma radiation-induced grafting of glycidyl methacrylate (GMA) onto water hyacinth fibers. *Radiation Physics and Chemistry*, **85**, 182–188.

12. Barbosa, A., et al. (2012) Effect of electron beam irradiation on the mechanical properties of buriti fiber. *Matéria (Rio de Janeiro)*, **17(4)**, 1135–1143.

13. Machnowski, W., et al (2013) Effects of gamma radiation on the mechanical properties of and susceptibility to biodegradation of natural fibers. *Textile Research Journal*, **83(1)**, 44–55.

14. Lee, J. S. (2013) The effect of electron beam irradiation on chemical and morphological properties of Hansan ramie fibers. *Fashion & Textile Research Journal*, **15(3)**, 430–436.

15. Sarala, S., et al. (2014) Delignification studies of banana fibers for radiation graft copolymerization. *Australian Journal of Basic and Applied Sciences*, **8(15)**, 112–118.

16. Kabir, M., et al. (2012) Chemical treatments on plant-based natural fibre reinforced polymer composites: An overview. *Composites Part B: Engineering*, **43(7)**, 2883–2892.

17. Adel, A. M., et al. (2011) Characterization of microcrystalline cellulose prepared from lignocellulosic materials. Part II: Physicochemical properties. *Carbohydrate Polymer*s, **83(2)**, 676–687.