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Effect of Partial Delignification of Kenaf Bast Fibers for Radiation Graft Copolymerization

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ABSTRACT: Malaysian kenaf bast fiber was treated by acidic chlorite to be applied for a trunk polymer radiation-induced graft copolymerization. The delignification conditions such as temperature, reaction time, and sodium chlorite ($NaClO_2$) loading were optimized from the viewpoints of density, tensile strength, and reactivity of grafting. It was found that delignification condition at 80°C for 6 h with 0.5% $NaClO_2$ gave 91% of lignin removal from the kenaf bast fibers. In this case, the density, fineness, and tensile strength of the kenaf fiber decreased about 46, 44, and 87%, respectively. Reactivity of grafting was evaluated using 4-chloromethyl styrene to obtain widely available precursor materials. The partial delignified kenaf with residual lignin less than 2% resulted in degree of grafting of 134%, which is enough for precursor materials. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Kenaf (*Hibiscus cannabinus L.*) is an annual herbaceous crop of the Malvaceae family with many environmental advantages, good mechanical properties, abundant, and relatively low price.[1–4] Strong interest is shown on this plant in Malaysia as it is fast growing and can be harvested twice a year in the local climate. In view of the immense potential generated by its fiber promising prospective for pulp and paper as well as reinforced composites for automotive industries, the Malaysian Government has pursued various efforts in promoting kenaf planting among local farmers.[3] In fact, in 2009, the United Nations Industrial Development Organization endorsed Malaysia's initiative by agreeing to examine the industrial and the commercial use of kenaf via funding provided by Netherlands-based Common Funds for Commodities. With such abundance, relatively low-capital investment and renewable sources, it is an advantage to explore the new utilization of kenaf as trunk polymer for grafting copolymerization. Especially, grafting polymer on kenaf surface can give many new specific properties including adsorption capacity, acid resistance, and wetting capability.[5,6]

In the recent years, the radiation-induced graft copolymerization is considered as important research subject, because it is known for its merits and potential in modifying the chemical and the physical properties of pre-existing polymeric materials without altering their inherent properties. At present, mass production of ion exchange nonwoven fabrics and ion-conductive spacer has been explored for the purification of air and water in semiconductor industry.[7] However, the major limitation found in the irradiation graft polymerization of lignocelluloses fiber is due to the presence of phenol in the molecular structure of lignin. It is reported that radiation can change phenol into quinone structures, thus protecting fiber from graft polymerization, and hence the graft polymerization was hindered, and instead homopolymerization occurs.[8] The common approaches for delignification are either by aqueous solutions of inorganic substances such as sodium hydroxide, sodium sulfite, ammonium oxalate, and hydrogen peroxide,[9–14] or by organic solvents such as ethanol.[15] Acidic chlorite has been reported as an effective method to control residual lignin in lignocellulose fiber as it is capable in selective removal of lignin without severely degrading cellulose fiber.[16–19] The great advantage of using acidic chlorite for lignin removal lies on the fact that such process offers the possibilities to oxidize the phenolic and nonphenolic structure of lignin at low $NaClO_2$ loading at a temperature ranged 70–80°C.[20]

No comprehensive work dealing with the effect of lignin content of partial delignified kenaf fiber on radiation graft

polymerization has been published. An investigation of such effect is essential for determining the optimum reaction parameters required to obtain reproducible degree of grafting in the fiber. In this present study, we report the preparation of partial delignified kenaf via acidic chlorite method. The optimum levels of delignification variables, for example, temperature, time, and $NaClO_2$ concentrations were established. It is known that the delignification may affect the fiber performance and mechanical strength. Hence, an assessment of density, fineness, and tensile strength of delignified kenaf was carried out. Finally, the effect of residual lignin in kenaf fiber on the radiation graft copolymerization of 4-chloromethyl styrene (CMS) was investigated to obtain widely available precursor material, because the chloromethyl moiety can be converted to the aiming functional group by chemical modifications.

EXPERIMENTAL

Material and Methods
The material used in this study was water-retted kenaf bast fiber supplied by Lembaga Kenaf dan Tembakau Negara (LKTN), Malaysia. Reagent grade chemicals such as nitric acid, $NaClO_2$, and CMS were obtained from Wako Chemical Co., Japan. The CMS was purified by passing through aluminum oxide prior using. The surfactant polyoxyethylene sorbitan monolaurate (Tween20) was supplied by Kanto Chemical Co. The deionized water from Milli-Q deionized system (Nihon Millipore K.K., Tokyo) was used as received.

Chemical Treatments
Acidic chlorite delignification of kenaf was performed in a fumed hood using aqueous $NaClO_2$ at pH 4[8] adjusted with nitric acid. $NaClO_2$ concentrations are 0.3, 0.5, 0.7, and 1.0%. $NaClO_2$ solution was placed on a hot plate stirrer and heated from 60 to 90°C. Kenaf was then added in the solution for the reaction to be carried out in time ranged between 1 and 6 h. After the reaction, the partial delignified kenaf was removed from $NaClO_2$ solution, washed repeatedly with distilled water, and air-dried.

Characterization of Fibers
The dry density of the kenaf was determined by toluene displacement and air comparison at 25°C. The technique used to measure the fineness or denier is mass in grams of 9000 m length of kenaf. The lignin content of the fiber was assessed according to TAPPI T222 om-02.[21] Tensile strength of single kenaf was measured using an Instron tensile testing with a gauge length of 25 mm and a crosshead speed of 20 mm/min. Scanning electron microscopy (Horiba Hitachi SEM-EDEX Type N X-ray microanalyzer) was used as a routine for microstructures analysis of the fibers after various stages of delignification. All images were taken at an accelerating voltage of 15 kV. The sample surfaces were coated with thin layer of gold using an ion sputter coater (Hitachi E-1010) to provide electrical conductivity prior analysis. Fourier transform infrared (FTIR) spectroscopic studies was performed using a Perkin Elmer Spectrum-One FTIR (USA).
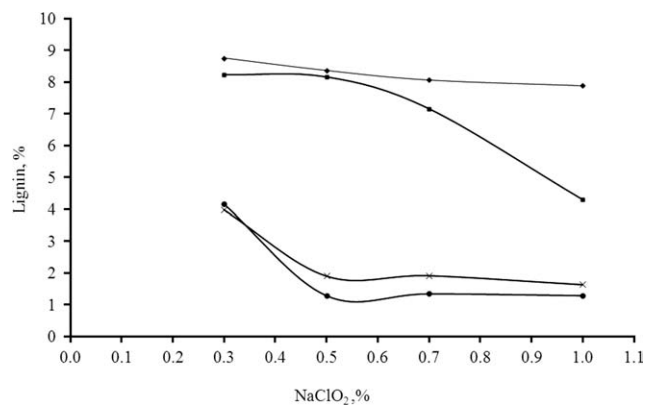
Figure 1. Residual lignin contents as a function of chlorite concentration at various reaction temperatures; [(◆) 60°C; (■) 70°C; (●) 80°C; (X) 90°C].

Radiation Graft Copolymerization
For radiation graft polymerization, the untreated and delignified kenaf bast fiber were dried to a constant weight under vacuum overnight at 30°C. About 400 mg fiber was purged with N_2 and then sealed in polypropylene zipper bag. The kenaf in the sealed bag was laid on dry ice and irradiated with electron beam energy of 2 MeV and 3 mA at a dose of 150 kGy. Graft polymerization of CMS on irradiated kenaf was carried out by adding 100 mL emulsion containing 3% of CMS, 0.3% Tween20, and 96.7% deionized water in vacuum condition. Before grafting, the emulsion is purged under N_2 for about 1 h. The grafting reaction was then allowed to react for 24 h at 30°C in water bath. After the reaction, the grafted kenaf was recovered from the emulsion and washed repeatedly with methanol to remove excess monomer and homopolymer. The weight of the CMS-grafted kenaf was determined after overnight dried in vacuum oven at 30°C.

The degree of grafting (D_g) was calculated according to the following formula:

$$D_g(\%) = \left[\frac{W_1 - W_0}{W_0}\right] \times 100$$

In the formula, W_0 is the initial weights of kenaf and W_1 is the weight of kenaf after grafting.

RESULTS AND DISCUSSION

Effect of Temperature, Time, and Chlorite Concentration
Temperature dependence on the residual lignin, in the range 60–90°C for a series of 0.3–1.0% $NaClO_2$ is presented in Figure 1. From this figure, two regions can be clearly delimited. In the first region (60–70°C), the residual lignin remained practically unchanged (8% lignin) at 60°C for all $NaClO_2$ concentration. However, at 70°C, the delignification steadily improved when $NaClO_2$ concentration approached 0.7%, with minimum lignin content of 4.3% at 1.0% $NaClO_2$. In the second region (80–90°C), the delignification showed a positive dependence at 80°C and a negative dependence at 90°C. At each temperature, reduction in lignin content is remarkably fast with the increase of $NaClO_2$, showing a plateau at 0.5% $NaClO_2$ with a minimum
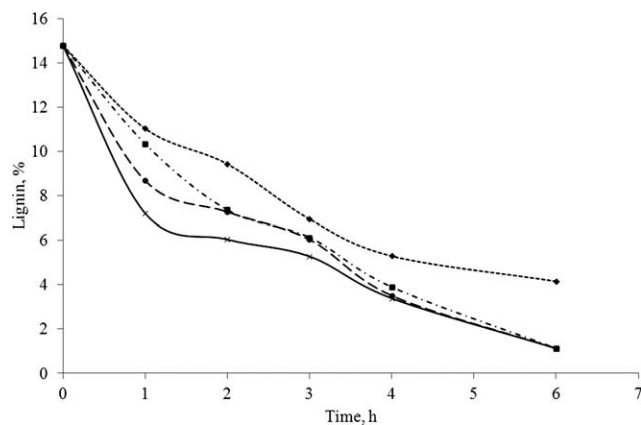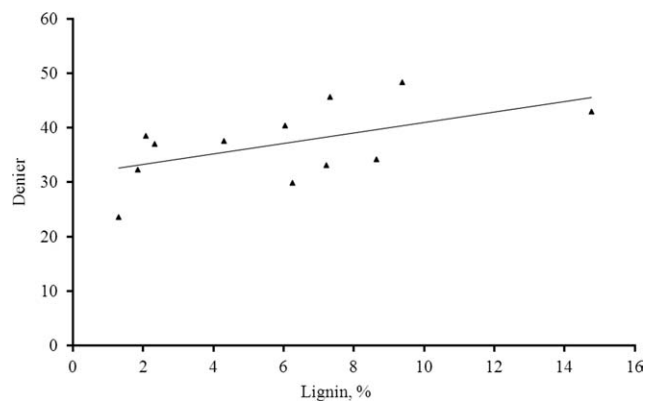
Figure 2. Effects of delignification time on residual lignin contents at various chlorite concentrations [($\blacktriangle$): 0.3% $NaClO_2$; ($\blacksquare$): 0.5% $NaClO_2$; ($\bullet$): 0.7% $NaClO_2$; (X): 1.0% $NaClO_2$].

Figure 3. Average denier of kenaf fibers in relation to the lignin content after chlorite treatment.

lignin content of 1.12%. The reduction in delignification at 90°C was marked up by 20% of the corresponding value at 80°C. This result indicated that at 80°C, chlorine dioxide extensively reacted with lignin.[22]

The reduction in lignin content on the lignocelullosic fiber can be reduced by the increase of $NaClO_2$ concentration.[23–25] However, Gupta et al.[22] have reported that the use of $NaClO_2$ between 1 and 5% did not cause any significant improvement on delignification. It is known that the extended delignification can lead to a massive reduction in lignin content.[26] Therefore, it was expected that a combination of mild $NaClO_2$ treatment and longer reaction time could improve the delignification.

Figure 2 illustrates the residual lignin against reaction time of kenaf delignified by 0.3–1.0% $NaClO_2$ at 80°C. Fast and highly selective delignification is observed during the first 2 h of the $NaClO_2$ treatment. However, the lignin degradation was rather slow during next 2 h with the same value of lignin content by 0.5 and 0.7% $NaClO_2$ loading. Then, the delignification accelerates again with the increase in reaction time. It is noted that the increase in $NaClO_2$ loading above 0.5% does not have any significant improvement in lignin removal especially after 4 h. At 6-h treatment, the residual lignin reached at 1.12% for the $NaClO_2$ concentration of 0.5–1.0%. It is clear that the use of
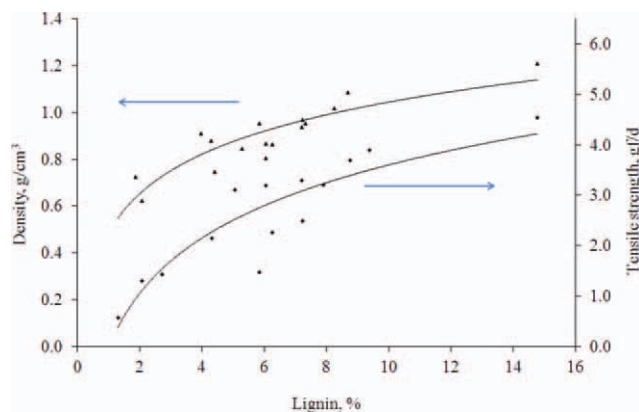
$NaClO_2$ at 0.5% is sufficient for the delignification of kenaf. This $NaClO_2$ dose is slightly lesser than the proposed standard (0.7%) used by Ghosh et al.[8] for the lignin removal in jute. Therefore, the findings indicated that $NaClO_2$ concentration can indeed be minimized, decreasing the chemical loading while at the same time maintaining the removal of lignin.

Fineness and Fiber Morphology
Figure 3 shows the effect of delignification on the fiber fineness. From the trend lines, the fiber denier decreased from 43 to 39 after the removal of about 50% of lignin. This value further reached 24 when 91% of lignin was removed. The reduction in denier after delignification could be attributed by two reasons. One is that during delignification, some volatile compounds[3] are released and resulted in mass reduction of the kenaf fiber, thereby reducing the fiber diameter. Alternatively, high concentration of lignin is positioned primarily between microfibrils,[27] and so the delignification should include the separation of the layers from fibers to form finer fibrils. These can be observed from SEM micrographs given in Figure 4. It is clear that the undelignified kenaf is indeed coated with binding material. Because of this, the individual fibers are held together as a bundle.[3] This is in contrast with the partial delignified kenaf of 4.19% residual lignin, where the surface of the kenaf was found to be rather smooth with prominent changes in its arrangement. This may be due to the solubilization of cemented layers during
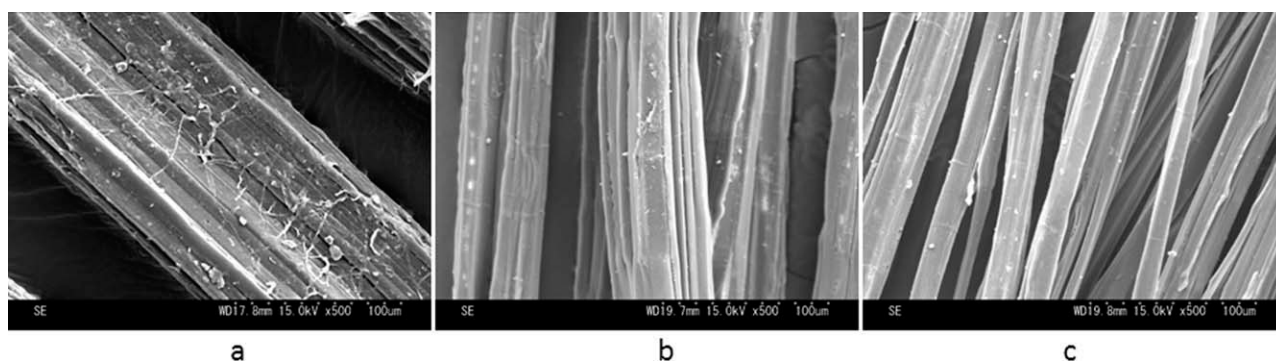
Figure 4. SEM micrographs of kenaf fibers with different residual lignin after delignification [(a): untreated kenaf with 14.77% lignin (b): kenaf with 4.19% residual lignin; (c): kenaf with 1.12% residual lignin].

Figure 5. Density and tensile strength of kenaf fibers in relation to the lignin content.

Figure 6. Effect of lignin contents on degree of grafting of radiation graft copolymerization on treated kenaf fibers.

the delignification.[28] Accordingly, the decrease in lignin content down to 1.12% caused the kenaf became narrow in size and more open with well-defined fibrils.
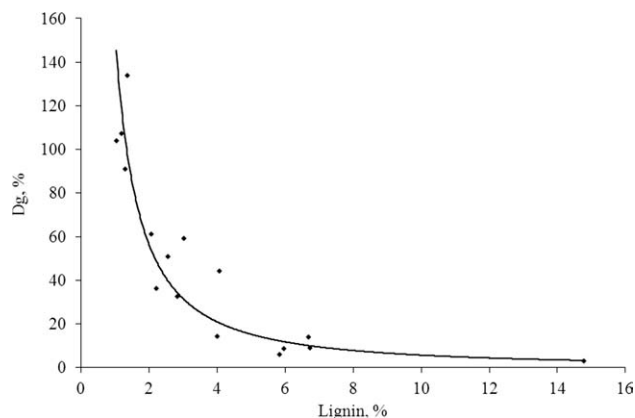
Density and Strength Capacity

The changes in the tensile strength and the density due to delignification are presented in Figure 5. As shown, tensile strength and density reduced steadily with the reduction of lignin content. Initially, the tensile reading was 4.5 gf/d with a density of 1.21 g/cm^3 at 14.77% lignin content. As delignification reached 40%, the tensile strength dropped to 3.6 gf/d accompanied by the reduction of density at 1.07 g/cm^3. Further delignification finally resulted in a sharp decrement of tensile strength with 0.58 gf/d, and the density dropped to 0.55 g/cm^3, which is 87% from the initial strength.

It should be noted that fiber cell walls are actively incorporated into lignin through radical crosslink of arabinoxylanes to lignin, and this crosslink networks impart to the stiffening of the cell walls.[29] The alteration in tensile strength after delignification is correlated to modification in residual lignin by ether bond cleavage, side-chain shortening and oxidation, and condensation reaction between lignin molecules and between lignin and polysaccharides.[26] Therefore, due to the continuous removal of lignin, the fiber cell walls weaken and rupture, lowering the density and finally deteriorating the tensile strength. This is in agreement with the simulation by Archibald et al.[26] that minor decrease of lignin would produce major pores of fiber cell walls and the advanced delignification leading to the infusion of these pores into larger cavities. The occurrence of these cavities not only reduce the density but also create multiple weak points in the fiber and finally form fatal voids, which almost covers almost the entire fiber and cause the tensile strength to decrease sharply.

Graft Copolymerization

Figure 6 depicts the influence of residual lignin in kenaf on the degree of grafting. Clearly, the declining trend in the degree of grafting is ascribed with the increase in lignin content. The absence of degree of grafting was noted when the undelignified kenaf was used, suggesting that the presence of lignin inhibits

the graft copolymerization. The retardation by lignin appeared to be due to the trapping of growing polymer radicals within lignin network and therefore limited the graft propagation.[30] The point in which the partial delignified kenaf begins to graft to the greater extend was at lignin content below 4%. According to Ghosh et al.,[31] fiber in the range of 3.9–1.4% residual lignin can generate high degree of grafting due to high reactive and accessible surface area on fiber. Further removal of lignin up 86% (2% residual lignin), the increased in degree of grafting can be attributed to the expose of crystal regions of cellulose at secondary layers, swelling behavior, and the porosity of the fibers.[3,17,26] This circumstance is more pronounced in partial delignified kenaf with 1.03% residual lignin, which showed the highest value of degree of grafting of about 134%.

FTIR Analysis

The absorbance peaks of interest in this study have been identified and shown in Figure 7. Although the occurrence of majority peaks did not change, it is noted that the peak intensity at
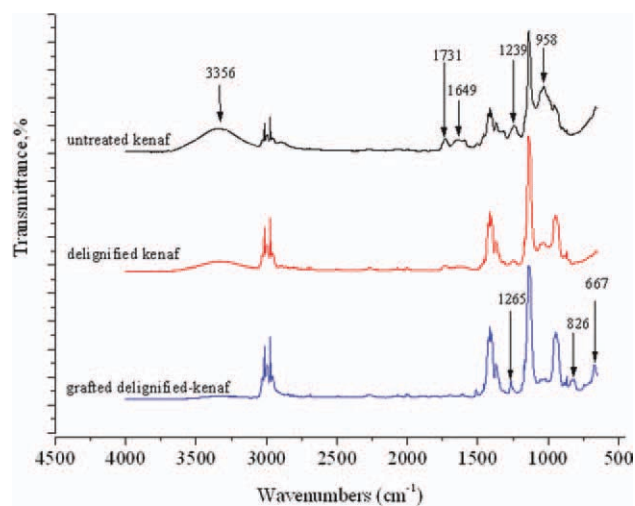
Figure 7. Infrared spectra of untreated kenaf (14.77% lignin), delignified kenaf fiber (1.12% residual lignin), and grafted delignified-kenaf fiber (134% degree of grafting). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$3356\ cm^{-1}$ is reduced because of $NaClO_2$ treatment. Peak at $1731\ cm^{-1}$ seen in undelignified fiber is also reduced upon $NaClO_2$ treatment. This is due to the removal of carboxylic groups by the process called de-esterification.[32] The peak at $1239\ cm^{-1}$ in the obtained spectra is much smaller for the delignified kenaf. This peak is due to a C—O stretching of acetyl groups in lignin.[33] The reduction of this peak from the spectra of the delignified kenaf is attributed to the partial removal of lignin.[34] The observed peak at $1649\ cm^{-1}$ shows diminishing intensity as the kenaf is subjected to delignification by $NaClO_2$ treatment. This peak represents the C═O bonds on hemicelluloses.[35] Peak at $958\ cm^{-1}$ originated from β-glycosidic linkages $(1 \rightarrow 4)$ of hemicelluloses also reduced.[36] Thus, it is the evidence that hemicelluloses are partially removed from kenaf surface. As the probable sites of grafting occurred at —OH, the distinct reduction of peak at $3356\ cm^{-1}$ is observed. Another evidence of grafting could be seen from additional peaks at 1261, 826, and $667\ cm^{-1}$, which assigned to the CH_2Cl groups of CMS.

CONCLUSION

In this study, the delignification of Malaysian kenaf bast fiber was investigated under different conditions such as varying temperature, reaction time, and $NaClO_2$ loading. The effect of delignification temperature showed that the mild condition at $80°C$ is sufficient for delignification. The delignification results revealed that the reaction condition of 0.5% $NaClO_2$, 6 h, and $80°C$ is capable in reducing the lignin content down to 1.12%. It was also found that the delignification reduced fiber fineness from 1.21 to 0.65 g/cm^3 and degraded tensile from 4.54 to 0.58 gf/d. It was demonstrated that the degree of grafting is strongly dependent on the amount of residual lignin in the kenaf fiber. At relatively low content of lignin, particularly less than 2%, displayed high degree of grafting up to 134%. Thus, present investigation promises the wide application of kenaf bast fiber as a trunk material for graft products that are available as precursors for tailoring functional materials.

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