Delignification Studies of Banana Fibers For Radiation Graft Copolymerization

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INTRODUCTION

Banana is the common name of the fruit and herbaceous plant which belongs to genus Musa (Musa sapientum) (Pothan et al., 2003). Banana is recognized as food; a commonly eaten fruit and fodder crop. Apart from that, it is also acknowledged as the source of lignocelluloses fibers. More than 100 countries such as Brazil, India and Ecuador cultivate banana on a large scale throughout the year due to their favorable climate and nature (Satyanarayana et al., 2007). After harvesting of the fruits, the banana stalk would be rejected as waste which serves no purpose. The stalk consists of mostly cellulose, hemicellulose, pectin, tannin, wax and lignin. Thus, in all likeliness, it is considered as waste and a pollutant to the environment (Shibi and Anirudhan, 2005). The constituents of the banana trunks induce them to degrade naturally on the soil, after the harvesting of the fruits. Unfortunately, this process causes several problems such as proliferation of fungi and the production of methane (CH4) gases. Fungi cause the spreading of diseases to banana plants whereas the methane (CH4) gases are one of those gases which are responsible for the green-house effect (Barreto et al., 2010). Hence, every attempt to reuse the banana trunk will be sensible.

Lignocellulosic fibers possess a few advantages as they are low in density, biologically degradable, renewable, non-toxic, and ultimately cheap. In addition, they have good mechanical properties and high resistance. Moreover, these fibers could easily be modified with chemical agents (Joesph et al., 1996). With the concern of low environmental impact, procedures via reuse of by-product which could bearably represent a sustainable alternative for new materials endorse the approach of radiation-induced graft co-polymerization for the preparation of an adsorbent. Radiation-induced graft polymerization technique holds the merits on modifying chemical and physical characteristic of polymeric materials without changing their natural properties (Mohamed et al, 2012). Furthermore, biomass and agriculture byproducts exhibit very good binding and absorption capacity which was reported in a review by Abia et al. 2003. But, the leading obstruction found in radiation graft polymerization on lignocellulosic fibers is the existence of phenol in lignin molecular structure. Phenol could turn into quinone structures by the exposure to radiation which in turn, hinders graft polymerization on fibers and favors mostly the homopolymer formation (Ghosh et al, 1994). Thus, prior to
grafting, banana fibers would need to undergo partial delignification for inductive grafting yield. Out of common approaches for delignification, sodium chlorite was used in this study as it’s capable of removing lignin selectively without serious degradation of cellulose fibers in acidic condition (Liao et al., 2008). This study is vital to determine the required optimum reaction parameter in order to achieve reproducible grafting yield on fibers. In this investigation, optimum conditions, pertaining to temperature, time and NaClO2 concentrations were analyzed, for delignification of banana fibers. At last, the effect of residual lignin in banana fibers on radiation graft copolymerization with glycidyl methacrylate (gma) was examined as well.

2. Methodology:

MATERIALS AND METHODS

The lignocellulosic banana fiber used in this study was supplied by Innovation Pultrusion Sdn Bhd. Analytical Grade Chemicals such as NaClO2, nitric acid, glycidyl methacrylate and surfactant polyoxyethylene sorbitan monolaurate (Tween 20) were purchased from Sigma Aldrich Malaysia.

2.2 Delignification of banana fiber:

The whole delignification process of banana fibers was carried out with NaClO2 solution at pH 4 which was adjusted with nitric acid in a fume chamber. The selected concentration of NaClO2 for this study was 0.2%, 0.6%, 0.8%, 1.0%, 3.0%, 5.0% and 10.0%. The prepared solution of NaClO2 was placed on a hot plate stirrer and heated up to 40°C and 70°C. The banana fibers were added into the solution and remained in it for the chosen reaction hours of 1, 3 and 6. Soon after reaction was over, the subjected banana fibers were removed from the NaClO2 solution and washed thoroughly with distilled water. Later, the fibers were dried in an oven at 60°C overnight.

2.3 Characterization of fibers:

Lignin content of both virgin and delignified banana fibers was determined based on standard method of TAPPI T222 om-02. Morphological studies of fibers conducted with Scanning Electron Microscope (SEM) using FEI Quanta 400. Gold coating was spattered on samples via Bio Rad system. Nicolet IS10 FTIR spectrometer (Thermo Scientific) machine was used for Fourier transform infrared spectroscopy (FTIR) spectrum at a resolution of 4 cm⁻¹ with single reflection diamond universal attenuated total reflection (ATR) accessory at frequency in the range of 4000-400 cm⁻¹. Shimadzu XRD 600 X-ray diffractometer was used for X-ray diffraction analysis at room temperature. The instrument operating condition was nickel filtered CuKα (λ=1.542Å) at 30kV and 30mA. Data were collected from 20 of 2° to 30° at rate of 1°/min.

2.4 Radiation Graft Copolymerization:

0.2g of delignified banana fibers, packed in polyethylene zipper bag, was purged with nitrogen and sealed. The bags were then placed on dry ice blocks and exposed to electron beam irradiation. The selected irradiation dose was 60kGy at the energy of 2 MeV and 10mA of current. Right after the irradiation session, the sample was transferred into an ampoule. 100ml of gma-water emulsion containing 3% of gma, 1% of Tween 20 and 96% of deionised water was transferred into the ampoules with samples in a vacuum condition. Prior to grafting, the emulsion was purged with nitrogen for an hour. The allowed reaction time for grafting process was 3 hours at 40°C in a water bath. After the fixed reaction hours, the samples were removed from the ampoules and washed continually with methanol in order to remove homopolymer and excess monomer. After drying overnight in an oven set at 50°C, the weight of gma-grafted banana fibers were measured. Grafting yield (GY) was determined gravimetrically based on the formula stated below:

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\text{Grafting yield(%) = } \frac{(W_f - W_i)/W_i} \times 100 \%
\]

Whereby, \(W_i\) is the initial weight of banana fiber and \(W_f\) is weight of banana fiber after grafting process had taken place.

Results:
Fig. 1: Residual lignin contents as the function of chlorite concentration at different reaction temperature, (a) 40°C (b) 70°C

Fig. 2: Effect of delignification time on lignin removal (%), at different chlorite concentration, (a) 6hrs, (b) 3hrs, and (c) 1hrs.

Fig. 3: SEM imaging of banana fibers with different lignin residual after delignification, (a) virgin fiber: (b) fiber with 19.9% lignin residual, (c) fiber with 15.0% lignin residual, (d) fiber with 5.8% lignin residual.
Fig. 4: FTIR spectra for (1) virgin fiber, (2) delignified fiber (19.9% lignin residue), (3) delignified fiber (5.8% lignin residue)

Fig. 5: XRD pattern for (a) virgin fiber, (b) delignified fiber (5.8% lignin residue), (3) delignified fiber (2.86% lignin residue)

Fig. 6: Lignin content effect of delignified banana fibers on grafting yield thru radiation grafting copolymerization technique.
Discussion:

Effect of Chlorite Concentration, Temperature and Time on Residual Lignin:

Chlorite concentration and temperature played the most crucial roles in removal of lignin. Lignin content of virgin banana fiber which was used in this study was 22.45%. The predetermined reaction temperature was 40°C and 70°C showed two regions on residual lignin content as shown in Figure 1. In the first region (40°C), the delignification is quite low and slow in comparison to the second region (70°C). The second region exhibits a remarkably faster reduction in lignin as NaClO₂ concentration increases. At 70°C, the delignification was enhanced steadily when the concentration of NaClO₂ approached 3.0%, with minimum lignin content of 2.86% at 10.0%. This result indicates that, at higher temperature, chlorine dioxide had reacted extensively with lignin present in fibers (Gupta et al, 2011). A few previous studies on delignification had reported that, increase in concentration of NaClO₂ is capable of reducing the lignin on lignocellulosic fibers (Yu et al, 2011)(Hubell, C.A. and Ragauskas, A.J., 2010). Extended delignification had shown massive reduction in lignin content (Archibald, 1997). Lignins are incorporated with hemicellulose through radical crosslink and this network holds the cell walls together stiffly (Buranov, A.U. and Mazza, G., 2008). But extensive removal of lignin would impart bond cleavage between lignin and polysaccharides molecules which will lead to rupture or weakening of cell wall. This makes the fibers to become very brittle and lose their natural form. Under this circumstance, the fibers are unfit to play a part in radiation grafting co-polymerization. Therefore, combination of mild concentration of NaClO₂ with longer reaction hours could improve the process.

Figure 2 exhibits the outcome on removal of lignin versus reaction time of banana fibers delignification 0.2%-1.0% NaClO₂ at 70°C. Higher delignification was observed at 6hrs. The delignification was comparatively slower at 1hr and 3hrs of duration. At 6hrs of treatment, the removal percentage of lignin was 48% for chlorite concentration of 0.8%. This stands for almost partial delignification of banana fiber which might be very suitable for radiation grafting co-polymerization process. This finding is slightly higher than proposed standard (0.7%) by Ghosh et al of lignin removal in jute. The result obtained demonstrates that the chemical loading can be minimized by extending the reaction hours in order to obtain the same lignin removal.

SEM analysis:

Delignification actually refers to the removal of lignin which is highly deposited in between microfibrils. Thus, delignification basically separates the layer from fibers into finer fibrils (Revol, J.F. and Goring, D.A.L., 1981). SEM micrographs illustrated in Figure 3 align with this explanation. It is clearly seen that the binding material covers the virgin banana fibers thoroughly. As a result, the individual fibers are held together as in a bundle form (Khalil et al, 2010). Partially delignified fiber with remaining lignin content around 19.9-15.0% seems to have some slight changes in its arrangement. Prominent changes in micro fibril arrangement were seen on those fibers with remaining lignin content around 5.8% at extensive delignification state. During the delignification process, solubilization of cemented layers occurs which makes the fiber narrow in size with more open well-defined fibrils and it holds the explanation behind this observation (Saha et al, 1991).

FTIR analysis:

Figure 4 exhibits the identified peaks of interest which is significant to this study. The virgin fiber and delignified fibers with different lignin residue were subjected to this analysis. Both virgin and delignified fibers show O-H stretching absorption at 3345cm⁻¹, C-H stretching at 2914cm⁻¹, C=O stretching at 1731cm⁻¹, C=C
stretching for lignin at 1632cm\(^{-1}\) and 1033cm\(^{-1}\) stretching vibration assigned for C-O groups from cellulose unit (Sharif et al, 2013). The occurrence of major peaks doesn’t appear to have any changes but it is obvious that the peak intensity at 3345cm\(^{-1}\), 1731cm\(^{-1}\) and 1632cm\(^{-1}\) reduces with NaClO\(_2\) treatment. The peaks at 1731 cm\(^{-1}\) and 1632 cm\(^{-1}\) ascribed to hemicellulose and lignin which exist in lignocellulosic fibers (Mwaikambo and Ansell 2002). Thus, reduction in peak at 1632cm\(^{-1}\) designates the removal of lignin with NaClO\(_2\) treatment (Sgriccia et al, 2008). Meanwhile, the peak intensity reduction at 1731cm\(^{-1}\) after the treatment implies removal of carboxylic groups via de-esterification process (Adel et al, 2010).

**XRD analysis:**

X-ray diffraction analysis was performed on virgin and delignified fiber in order to observe the changes in crystalline structure owed by NaClO\(_2\) on fibers after the process. The XRD pattern of virgin and delignified fiber with different lignin residue is illustrated in Figure 5. Crystallinity peak for virgin and delignified fibers appears at the same angle, 20 which indicates that the delignification process exhibits no changes on the fiber’s crystalline structure. But, the reflection peak intensity of delignified fibers is lower and decreases as the lignin residue decreases further. This finding signifies that the crystallinity content of delignified fibers decreases as the lignin content reduces. Reduction in crystallinity content might be due to dilution of inherent crystallinity by incorporation of NaClO2 with lignin in amorphous phase which also causes cellulose, a semi-crystalline component, to decrease at extensive delignified condition (Periera et al, 2013). This clarifies the obtained XRD spectrogram for delignified fibers.

**Radiation Grafting Copolymerization:**

Figure 6 portrays the effect of lignin content of banana fiber on grafting yield. The grafting yield depicts a decreasing trend with increase in lignin content. Grafting was found to be in negligible amount on virgin banana fibers which denotes that the existence of lignin naturally inhibits graft copolymerization. Grafting yield obtained at mild delignification happens to be little and this might be due to the trapping of growing polymer radical in lignin network. Therefore, the possibilities of grafting chain propagation remains limited (Rizk et al, 1984). Fibers with residual lignin ranging 3.9-1.4% are capable of generating high grafting yield because they are highly reactive and proficient of accessible surface area by crystal regions of cellulose exposure at secondary layer (Ghosh et al, 1998). In agreement, fibers with 2.86% of lignin residue had generated grafting yield about 308%. The occurrence of grafting was confirmed with FTIR analysis (Figure 7). Apart from the common peaks which exist in fibers, there was seen an elongated peak at 1733cm\(^{-1}\) which was assigned to C=O vibration indicating the presence of ester group –COO- contribution from gma having been used. Appearance of epoxy characteristic peak at 1237 and 901 cm\(^{-1}\) in grafted fibers suggests successful grafting of gma onto banana fibers as well. Few researchers had reported the presence of these three peaks in their studies on radiation grafting too (Jordan et al, 2013; Wojnarovits et al, 2010). Another prominent evidence of grafting is clearly shown on SEM images in Figure 8. The grafted delignified fibers were coated with a thin layer of gma copolymer.

**Conclusion:**

The scope of this study was delignification of banana fibers at different varying parameters such as NaClO\(_2\) concentration, reaction time and temperature. The results achieved via the experiments strongly agree that the grafting yield steadily depends on lignin residue on banana fibers after the delignification process. Through the conducted test, it was revealed that partial delignification is sufficient in order to obtain desirable grafting yield. Although extensive delignification at high concentration of NaClO\(_2\) gives a very high grafting yield, it increases the porosity of the fibers which makes them unsuitable for further modification step. The most optimum condition chosen for delignification process was 0.8% NaClO\(_2\), 6h and 70°C. The lignin residue at this condition was 11.91% and attained grafting yield was about 190%. At this stage, the fibers were still intact with their original form and its votes for simplicity of the process as well.

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