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Effect of Chemical Treatment on Tensile Properties of Oil Palm Empty Fruit Bunch (OPEFB)-based All Cellulose Composite (ACC) Films

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Abstract. This study explored the potential of using oil palm empty fruit bunch (OPEFB) in the production all-cellulose composite (ACC) films. The isolation process of the raw OPEFB fiber was carried out using chemical process to extract the OPEFB nanocellulose. The ACC films from the OPEFB and microcrystalline cellulose (MCC) were prepared using dimethylacetamide (DMAC) and lithium chloride solvent system whereby the partially dissolved cellulose was transformed into the matrix phase surrounding the remaining non-dissolved fiber. The ACC films containing 1, 2, 3 and 4 % (wt/vol) OPEFB cellulose and 3 % (wt/vol) microcrystalline cellulose (MCC) were prepared and the effects of 2-ethylhexyl acrylate chemical treatment of the OPEFB cellulose on tensile properties of the ACC film were investigated. Results indicate that the chemical treatment using 2-ethylhexyl acrylate has reduced the hydroxyl group composition in the cellulose and allowing greater dissolution of the cellulose during the formation of the ACC film. As a result, the tensile strength and modulus of elasticity of the ACC film were significantly enhanced. However, both untreated and treated ACC films experienced the reduction in both properties when the cellulose concentration was increased from 1 % to 4% (wt/vol), due to the saturation of the cellulose particles and non-homogeneity of the ACC system.

1 Introduction

Synthetic plastics are daily used materials by billions number of human being from all over the world. However, these petroleum-based plastics can cause several negative impacts to the environment and ecosystem [1]. Due to these ecological concerns, there is an increasing effort to replace the conventional synthetic plastics with the natural based plastics (biodegradable and biorenewable) by undertaking significant number of research and development and translating them into commercial products [1- 4]. Some natural polymers that have been used for packaging application include starch, cellulose and chitin [1, 2, 4]. The addition of natural elements from lignocellulosic fibers (flax, ramie, sisal) as an

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alternative to the traditional glass fibers can have a much gentler effect to the surrounding [4, 5]. These natural fibers are also economical and have good mechanical properties [5].

In Malaysia, the plantation of palm oil produces large amount of residues like oil palm empty fruit bunch (OPEFB), oil palm shell and other biomass wastes [2, 6]. These lignocelluloses wastes can be generated into something useful for example to produce biomass feedstock, bioconversion and also utilize in composite fields [2, 6, 7]. Lignocelluloses like OPEFB consists a vast amount of cellulose which can be utilized in the production of biocomposite films. Our research group has investigated the utilization of OPEFB derived cellulose in the production of all-cellulose composite (ACC) [2, 6]. ACC is a composite whereby both the matrix and fiber are from the same component; in this case they are from cellulose sources. ACC can be produced by "surface selective dissolution" whereby part of the cellulose fiber is partially dissolved using cellulose solvents which is regenerated to form the matrix surrounding the non-dissolved fiber (which act as the reinforcement for the composite). Part of the cellulose fiber that are dissolved, becomes the matrix of the composite [8, 9]. The main advantage of ACC process is that it simplify the composite's method and can produce composite with good mechanical properties [8, 9].

In the production of polymer composite, processing method and route may affect the morphology and properties of the resultant composite material [10]. This fact also applies to the ACC material. Suitable cellulose solvents are required in order to properly dissolved the cellulose since the dissolution of cellulose can be quite difficult due to the structure of the cellulose itself which consist of their inter and intra hydrogen bond [2, 6, 11, 12]. Some solvents that are known to participate in the dissolution of cellulose include N-methylmorpholine-N-oxide (NMMO) [11], NaOH/urea solution [12] and N-dimethylacetamide/lithium chloride (DMAC/LiCl) [2, 6]. Furthermore, pre-treatment in the form of chemical, need to be introduced to optimize the cellulose dissolution process. In addition, ideal nanocellulose content should be determined to optimize the performance of the resultant regenerated cellulose composite film.

In this communication, we report the production of the ACC films from the OPEFB-derived cellulose and microcrystalline cellulose (MCC). DMAC/LiCl solvent system was used, whereby the partially dissolved cellulose were transformed into the matrix phase surrounding the remaining non-dissolved fiber. The effect of the cellulose chemical treatment by 2-ethylhexyl acrylate on tensile properties of the ACC films were studied and reported herein.

2 Materials and Method

The raw materials used in this study were oil palm empty fruit bunch (OPEFB) which was used as received from Malaysian Palm Oil Board (MPOB) Bangi, Selangor and microcrystalline cellulose (MCC) from cotton linters (Aldrich Chemistry) with the average size of 51 μm. The chemicals used for the production of ACC films were; sodium hydroxide (NaOH), ethanol (C_3H_3OH) and acetone (C_3H_6O), which were supplied by HmbG® Chemicals. Sodium Chlorite ($NaClO_2$) was supplied by Sigma-Aldrich (Germany) and was used in the bleaching treatment of the OPEFB fiber. Sulfuric acid was used during the hydrolysis step of OPEFB and has a molar mass of 98.10 g/mol. 2-ethylhexyl acrylate was used to treat the OPEFB nanocellulose and this chemical was supplied by Merck. N,N-Dimethylacetamide (DMAC) was also manufactured by Merck, Germany and was used to dissolve the cellulose. Lithium chloride (LiCl) was supplied by Across, Belgium and was used together with DMAC to dissolve the cellulose.

2.1 Chemical Isolation Processes of OPEFB Fiber to Obtain the Nanocellulose

Firstly, the OPEFB fiber was treated in 4 % NaOH solution at the temperature of 80 °C for 1 hour under stirring conditions. Then, the filler was subjected to distilled water and filtered in order to remove the alkaline. This step was repeated in a count of four times to assure substantial removal of the hemicellulose. The bleaching treatment was employed on the OPEFB fiber after it was dispersed in distilled water. The resultant OPEFB suspension was then bleached using the diluted $NaClO_2$ and mechanically stirred for 1 hour at 80 °C. The step was repeated three times to assure the removal of the lignin and hemicellulose. The treated fiber was subsequently washed with distilled water and filtered. The acid hydrolysis using 65 % H_2SO_4 was conducted under stirring condition at a temperature of 45 °C. The suspension of OPEFB was washed with cold distilled water in order to stop the reaction. The OPEFB suspension was then centrifuged at the speed of 7500 rpm for about 15 minutes and was repeated about 10 times. The produced nanocellulose was homogenized for 30 seconds at 5000 rpm before being dried in an oven at the temperature of 50 °C for one day.

2.2 Chemical Treatment of OPEFB Nanocellulose using 2-ethylhexyl acrylate

The chemical treatment of the nanocellulose was conducted by employing 3 % (v/v) of 2-ethylhexyl acrylate which was dissolved in ethanol and stirred. Then, OPEFB nanocellulose was added into the solution and was stirred for a while. After stirring, the solution was left overnight. The next day, the treated OPEFB nanocellulose was filtered and dried in an oven at a temperature of 70 °C.

2.3 Preparation of All Cellulose Composite (ACC) Films

Prior to the dissolution of cellulose, the OPEFB nanocellulose and MCC were activated in the following solvents firstly; in acetone (for 1 hour and dried in oven) followed by DMAC (for 1 hour and dried in oven). This activation step was conducted to ensure the cellulose swell before the dissolution process. For the dissolution step, the activated OPEFB nanocellulose and MCC were dissolved in DMAC for 10 minutes. Next, LiCl at 8 % (wt/vol) was added to the mixture. The mixture was constantly stirred for 30 minutes until the LiCl completely dissolved in the solution. The cellulose solution was then poured onto a glass plate and left to develop overnight. The next day, the resultant composite films were washed with distilled water to remove the residual of DMAC/LiCl before letting it dried at room temperature for a day.

2.4 Fourier Transform Infrared (FTIR) Analysis

Perkin Elmer spectrum FTIR spectrometer was used to analysis the functional groups of raw OPEFB fiber, OPEFB nanocellulose and acetic acid-treated OPEFB nanocellulose. The wavenumber range was between 500 - 4500 cm^{-1}. The spectra were recorded with 16 scans and resolution of 4 cm^{-1}.

2.5 Tensile Test

Instron Universal Testing Machine, model 5590, was used to conduct the tensile test which was based on ASTM D882. The cross-head speed of the testing was at 10 mm/min. Five replicates were tested for each samples. The mean values of the tensile strength, elongation at break and modulus of elasticity were recorded.

3 Results and Discussion

Fig. 1 exemplifies the FTIR spectra of the untreated and 2-ethylhexyl acrylate-treated OPEFB nanocellulose. The peaks at 3340 cm^{-1} (untreated nanocellulose) and 3338 cm^{-1} (treated nanocellulose) are assigned to the stretching vibrations of –OH group. The bands at 2888 cm^{-1} for both nanocelluloses correspond to the stretching vibration of C-H group [13-15]. The peaks between 1035 – 1036 cm^{-1} indicate the C-O-C pyranose ring stretching vibration in the nanocellulose [15].

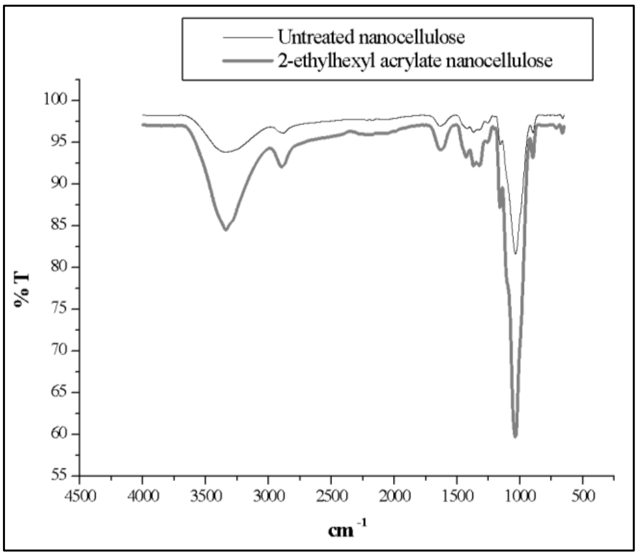

Fig.1. FTIR spectra of the untreated and 2-ethylhexyl acrylate-treated nanocellulose.

The band that is observed on 2-ethylhexyl acrylate-treated OPEFB nanocellulose at 1630 cm^{-1} can be described as the characteristic of carbonyl group (-C=O) [13]. Furthermore, the intensity and strength of the treated nanocellulose peaks as opposed to the untreated nanocellulose suggest that the chemical treatment have led to the substitution of hydroxyl group (OH) from nanocellulose with the carbonyl group (-C=O) originated from acrylate compound [14]. Fig. 2 illustrates the proposed molecular interaction between the nanocellulose and the 2-ethylhexyl acrylate treatment.

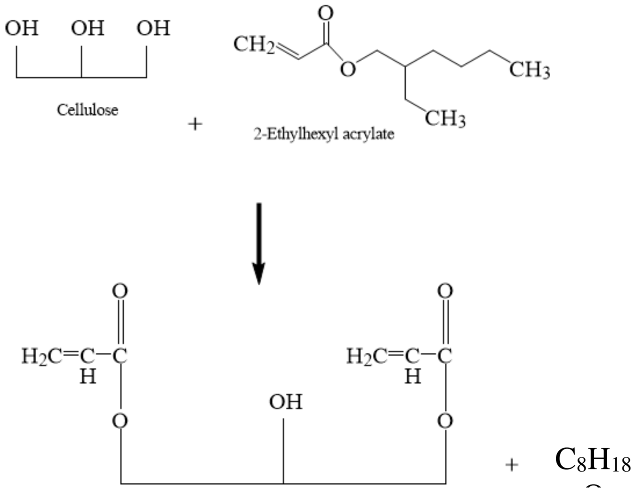

Fig. 2. Proposed molecular interaction between the nanocellulose and 2-ethylhexyl acrylate.

Fig. 3 demonstrates the tensile strength of both untreated and 2-ethylhexyl acrylate-treated ACC films incorporating fix amount of MCC (3 % (wt/vol)) plus OPEFB in the various amounts of 1, 2, 3, 4 % (wt/vol). Both ACC films exhibit similar results whereby the tensile strength decreased as the OPEFB contents increased from 1 % (wt/vol) to 4 % (wt/vol). Although both types of ACC films tend to show similar trend, 2-ethylhexyl acrylate-treated ACC films exhibit greater tensile strength than the untreated counterparts. Apparently, the 1 % (wt/vol) of 2-ethylhexyl acrylate treated OPEFB ACC film displays the highest tensile strength with the value of 14.8 MPa. As compared to the untreated film at 1 % (wt/vol), the increment of 85 % was obtained. In general, the treated ACC films showed better tensile strength than the untreated ACC films. The reason for this could be due to the treatment of the OPEFB nanocellulose with 2-ethylhexyl acrylate that reduced the intra and inter molecular bonding of the nanocellulose by replacing its hydroxyl group with the carbonyl group of the 2-ethylhexyl acrylate. This induced greater dissolution of the nanocellulose in the solvent, thereby more homogeneous composite structure was formed. This can be correlated with the findings of Zailuddin et al. [6] by which the presence of butylmethacrylate (BMA) treatment has led to the increment of the interfacial interactions between the dissolved cellulose matrix and the non-dissolved cellulose fiber in the biocomposite films.

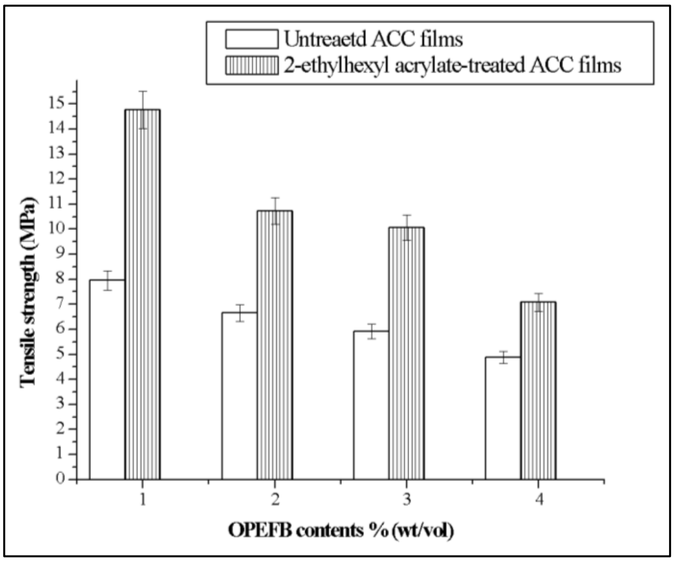

Fig. 3. The effect of OPEFB nanocellulose contents on the tensile strength of the untreated and 2-ethylhexyl acrylate-treated ACC films.

The effect of modulus of elasticity of the untreated and treated ACC films consisting consistent amount of MCC at 3 % (wt/vol) and different amounts of OPEFB nanocellulose (1, 2, 3, 4 % (wt/vol)) is illustrated in Fig. 4. The modulus of elasticity for 2-ethylhexyl acrylate-treated films is higher than the untreated composite films. However, it is observed that both ACC films exhibit similar trend of results in which the modulus of elasticity decreased as the OPEFB contents increased from 1 % (wt/vol) to 4 % (wt/vol). The modulus of elasticity for OPEFB content at 1 % (wt/vol) of 2-ethylhexyl acrylate-treated ACC film is 534.9 MPa while for the 1 % (wt/vol) untreated OPEFB ACC film is 179.8 MPa. The chemical treatment using 2-ethylhexyl acrylate has led to the improvement of the interfacial interactions between both filler and matrix phases of the composite film, hence the stiffness of the material increased. Apparently, both types of ACC films exhibit reduction in the modulus of elasticity when the OPEFB content increased from 1 % to 4% (wt/vol) due to cellulose particle aggregations or saturation that induced the formation of stress concentrated area and non-homogenized composite structure.

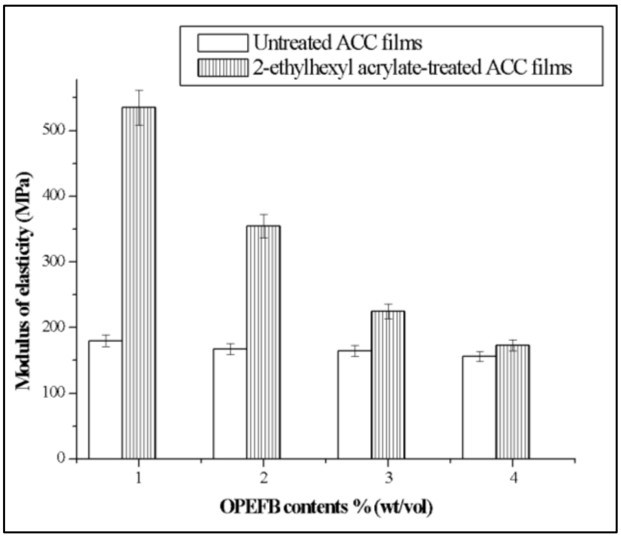

Fig. 4. The effect of OPEFB nanocellulose contents on the modulus of elasticity of the untreated and 2-ethylhexyl acrylate-treated ACC films.

4 Conclusion

In this study, we have investigated the use of 2-ethylhexyl acrylate for chemical treatment of the OPEFB cellulose and analyzed its efficiency to improve the tensile properties of the OPEFB cellulose-derived ACC film. Based on the FTIR spectra, it can be proved that the chemical treatment resulted in the substitution of hydroxyl group (OH) from nanocellulose with the carbonyl group (-C=O) from the acrylate compound. This reduction in hydroxyl group of the cellulose assists in better dissolution of cellulose during the formation of the ACC film. Both treated and untreated ACC films show the highest value of tensile strength and modulus of elasticity when 1 % (wt/vol) of OPEFB was used to form the composite. However, both types of ACC films exhibit reduction in tensile strength and modulus of elasticity when the OPEFB content increased from 1 % to 4% (wt/vol). This could be due to cellulose particle aggregations and saturation that induced the formation of stress concentrated area along the composite structure. Nevertheless, the treated ACC films showed higher tensile strength and modulus of elasticity as compared to the untreated ACC films due to improved interfacial interactions between the dissolved cellulose matrix and the non-dissolved cellulose fiber in the biocomposite films.

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