

Tapioca Starch Based Green Nanocomposites with Environmental Friendly Cross-linker

Wei Tieng Owi^a, Ong Hui Lin^{*,a}, Sung Ting Sam^b, Al Rey Villagrancia^c, Gil Nonato C. Santos^c

^aSchool of Material Engineering, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 2, 02600 Arau, Perlis, Malaysia.

^bSchool of Bioprocess Engineering, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 3, 02600 Arau, Perlis, Malaysia.

^cDe La Salle University Manila, Physics Department, College of Science, Taft Avenue, Manila 0922, Philippines. hlong@unimap.edu.my

Starch based films have drawn considerable attention on food packaging owing to their attractive combination of price, environmental friendliness, and abundance. Nevertheless, the use of starch based films in industrial application were restricted by its poor mechanical properties and naturally intractable behavior. The aims of this work were to develop starch green composite films prepared with sustainable materials in agreement with ecology and economic requirements including environmental satisfactory disposal and to investigate the effects of nanocellulose and citric acid on tensile properties, and thermal properties of tapioca starch green composite films. Through the advance of nanotechnology, nanocellulose recovered from oil palm empty fruit bunches (EFB) by chemical approaches acted as reinforcing material incorporated into tapioca starch green composites. Citric acid was a cross-linking agent added to crosslink the tapioca starch molecules in the films. A series of tapioca starch green composite films with varying amount of nanocellulose (0.5, 1, 2, 3, 4, and 5 phr) as per dry weight of tapioca starch were produced by casting method. Plasticizer such as glycerol was added to improve the processing of tapioca starch green composite films by softening the polymer matrix. Confirmation of nanocellulose characteristics were carried out by using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy (TEM). Whereas the effects of nanocellulose and citric acid on tapioca starch green composite films were performed by Instron Universal tensile testing machine and thermogravimetric analyzer (TGA). FTIR analysis on nanocellulose verified that the chemical treatments and acid hydrolysis removed non-cellulosic constituents including hemicelluloses and lignin from empty fruit bunches. XRD diffractograms revealed that the crystallinity of nanocellulose increased from 43.1 % of raw EFB to 65.8 %. TEM images confirmed the diameter of nanocellulose was in nano-sized with needle like structure. The tensile strength and modulus of elasticity of tapioca starch green composite films were enhanced significantly as the amount of nanocellulose increased from 0.5 to 3 phr and decreased for further addition of nanocellulose. While the value of break elongation sharply increased from 9.08 % for neat tapioca starch (TS) films to 109.36 % for crosslinked TS films. Therefore, these results reasonably remarked that nanocellulose from empty fruit bunches and citric acid could improve the tensile of tapioca starch green composite films. However, crosslinked TS/NC films using citric acid slightly lower the thermal stability.

1. Introduction

The rising concern towards environmental issues created by petroleum products and non-renewability of fossil resources had led the researches focussing more on new bio-based materials to develop edible and biodegradable films as a big effort to extend shelf life and improve quality of food while at the same time reducing packaging waste. This century has witnessed remarkable green technology achievements in the field of materials science via the development of green composites because of the environment and sustainability issues. The properties of green composites are manipulated by a number of variables comprising the fiber type,

environment aspects, and processing methods. Recently, there has been an increase of interest in the industries of composites involving biofibers and biopolymers. The greatest challenge dealing with natural fibers green composites is their variation in properties and characteristics. Nevertheless, the worldwide capacity of biopolymers such as starch-based plastics, polylactide (PLA) and polyhydroxyalkanoate (PHA) is expected to rise from 0.36 Mt in 2007 to 3.45 Mt in 2020 (Faruk et al., 2012).

Starch-based polymer formed from variety of crops such as wheat, corn, potato, and tapioca can be a possible alternative for production of green composites since they are low cost, widely available, renewable, and total compostable without toxic residue (Xie et al., 2013). Plasticizer like glycerol are usually added to improve the processing by softening the polymer. However, starch-based substances is greatly inhibited by its naturally intractable, brittleness, and poor mechanical properties. Nanocellulose is appealing to substitute the man-made fibers as reinforcement materials to overcome the limitation use of starch-based polymer (Abdul Khalil et al., 2012). Similar chemical structure of starch and cellulose made their combination a strong adhesion through hydrogen bonding. Nanocellulose has no harmful impact on human health and is used as additive to enhance product quality in many applications such as foodstuffs, biomedical and cosmetic.

Another approach to mitigate the shortcoming of starch-based polymer is by modifying the starch. Chemical modification such as crosslinking using phosphorus oxychloride, boric acid, sodium trimetaphosphate, glutaraldehyde, sodium tripolyphosphate and epichlorohydrin have long been studied as a method to overcome the poor properties of starch. However, some of these cross-linkers are relatively toxic and expensive. Therefore, an alternative way to make the starch-nanocellulose composites environmental friendly while improving its properties is by adding citric acid as the cross-linker. Citric acid is a natural polycarboxylic acid (with three carboxylic groups) present in fruits like lime, pineapples and lemon. Generally, citric acid is classified as safe for food usage owing to its biodegradable and renewable properties (Olsson et al., 2013). Many food products for example jams, juices and soft drinks include citric acid. The carboxyl groups of citric acid can form stronger hydrogen bonds with the hydroxyl groups from starch molecules resulting the improvement of starch films mechanical properties. According to Ghanbarzadeh et al. (2011), citric acid could enhance the tensile strength and thermal stability of the starch films.

In this study, green composites based on tapioca starch (TS) with nanocellulose extracted from empty fruit bunches (EFB) was developed and citric acid was added for fabrication of cross-linked green composites. The evaluation of the influence of citric acid and nanocellulose on the TS/nanocellulose green composites was conducted. Among the various types of starch, TS is chosen as polymer matrix because it is abundant in Southeast Asia and low cost. Whereas for nanocellulose, oil palm waste such as EFB has been considered as attractive raw material for its production since it has high cellulose content (around 40-60 %) and widely available in Malaysia. All the TS/nanocellulose green composites films were plasticized using glycerol.

2. Experimental

2.1 Materials

Empty fruit bunches (EFB) were provided by United Oil Palm Industries Sdn. Bhd., Nibong Tebal, Malaysia. Tapioca starch (TS) was acquired from Thye Huat Chan Sdn. Bhd. The chemicals, sodium hydroxide, acetic acid glacial, sulphuric acid and glycerol were obtained from HmbG Chemicals (Germany); sodium chlorite was procured from Acros (Belgium); and citric acid was purchased from Sigma Aldrich (US). All the chemicals were used as obtained from the suppliers.

2.2 Nanocellulose preparation

Cellulose (micro-sized) was first extracted from raw EFB by undergoing alkaline treatment and bleaching process for three cycles prior to acid hydrolysis for nanocellulose. The detailed procedures of cellulose extraction was described in Owi et al. (2016). In brief, ground EFB was treated with 4 wt % sodium hydroxide solution to remove the hemicelluloses then subsequently bleached with 1.7 wt % sodium chlorite in an acetic acid buffer solution for delignification. 5 g of dried cellulose obtained earlier was acid hydrolysed in pre-heated 100 mL of 64 wt % sulfuric acid solution. Acid hydrolysis process was performed at temperature of 45 °C for 45 min under strong agitation. Hydrolysis was then quenched by adding cold distilled water (100 mL) into the reaction mixture. High concentration of sulfuric acid was drained using centrifugation at 10,000 rpm for 10 min and repeated until the solution became turbid (pH of suspension obtained around 5). Nanocellulose suspension was sonicated for 15 min and stored in refrigerator at 4 °C until further use.

2.3 Green Nanocomposites preparation

Tapioca starch (TS) composite without citric acid (CA) were prepared by dispersing the nanocellulose in 100 mL of distilled water and 0.8 g of glycerol using ultrasonicator for 30 min before adding 4 g of TS. The amount of nanocellulose added into the mixture were 0.5, 1, 2, 3, 4, and 5 phr based on the dry weight of TS. Gelatinization of TS occurred when the mixture was heated to 80 °C and it is stirred vigorously for 30 min. The

gelatinized TS composite was cast into a 15 cm-diameter Teflon coated mould and dried in an air circulating oven at 40 °C for 24 h. Same procedure was carried out for making composite with inclusion of 0.4 g of CA before gelatinization. Dried composites with CA were cured subsequently at 105 °C for 15 min. While TS film produced without nanocellulose served as control. All the films prepared were then stored in humidity chamber at 50 % relative humidity for at least 2 days prior to characterization. The TS and nanocellulose green composite films were denoted as TS/NC whereas after cross-linked were denoted as crosslinked TS/NC.

2.4 Characterizations

Functional groups of cellulosic specimens were examined through Perkin Elmer Spectrum RX FTIR spectrophotometer (USA) by employing potassium bromide (KBr) pellet method which the dried powder specimens were blended with KBr at a ratio of 1:99 (%). FTIR spectra were overwritten in the range of 4000-500 cm^{-1} at a resolution of 4 cm^{-1} with 32 scans. While Attenuated Total Reflection (ATR) method was used for green composite films and its spectra were recorded in the range of 4000-650 cm^{-1} at a resolution of 4 cm^{-1} with 32 scans. Bruker Desktop D2 Phaser X-ray diffractometer (USA) was used to determine the crystallinity of cellulosic specimens with $\text{CuK}\alpha$ radiation operating at 30 kV and 10 mA. The data was recorded at 2θ angles between 10 to 30 ° with a scan rate of 2 °/s. Crystallinity index (CI) for each specimens were calculated according to Segal et al. (1959) applying Eq(1) as shown below (I_{002} represents both the crystalline and amorphous parts and I_{AM} represents only the amorphous part).

$$CI = [(I_{002} - I_{AM}) / I_{002}] \times 100\% \quad (1)$$

Morphological properties of nanocellulose was observed with TEM JEOL-1200EXII (Japan). Nanocellulose suspension was dropped on a carbon coated copper grid and stained by using 2 % uranium solution. Tensile properties of TS films were tested using Instron Universal (USA) tensile testing machine which followed a standard of ASTM D882-12 (ASTM, 2012). Specimens were cut into rectangular shape using a sharp scissor with a dimension of 100 mm x 10 mm. Thickness of the films were measured by Mitutoyo IP65 digimatic micrometer (Japan). The initial gauge length was set at 50mm and test speed at 10mm/min. A Perkin Elmer Pyris Diamond TG/DTA instrument (USA) was used to evaluate the thermal stability of the TS films. Approximately 8 mg of each specimen was heated from 30 to 800 °C at a heating rate of 10 °C/min under nitrogen gas environment.

3. Results and discussion

3.1 Nanocellulose properties

Fourier transform infrared (FTIR) spectroscopy analysis was performed to determine the chemical changes from raw EFB to nanocellulose obtained after chemical treatments and acid hydrolysis. Figure 1(a) displays the FTIR spectra of raw EFB, its microcellulose and nanocellulose. Specifically, there were three changes found on the spectra of microcellulose and nanocellulose compared to raw EFB which represented by the dotted line in Figure 1(a) while other peaks were similar for all three spectra shown. The sharp peak presented at 1,735 cm^{-1} on raw EFB is attributed to acetyl and ester groups from hemicellulose or C=O stretching of linkage of carboxylic acid from lignin but this peak disappeared for both microcellulose and nanocellulose. Whereas the peak at 1,511 cm^{-1} for raw EFB corresponded to C-C stretching vibration of lignin aromatic ring and the peak at 1,250 cm^{-1} corresponded to C-O out of plane stretching due to aryl group of lignin. Drastic reduction of these two peaks revealed the effectiveness of the chemical treatments applied to the raw EFB (Kumar et al., 2012).

The X-ray diffractograms of raw EFB, microcellulose and nanocellulose by comparison were shown in Figure 1(b) with two well defined peaks at around $2\theta=15^\circ$ (001 peak) and $2\theta=22.5^\circ$ (002 peak). The peaks obtained from XRD intensities were peaks for cellulose I characteristic. After treatment, 002 peaks for microcellulose and nanocellulose were more intense compared to raw EFB owing to removal of hemicellulose and lignin which corroborates the FTIR results. The CI of microcellulose was increased from 43.1 % of raw EFB to 52.1 % and further increased to 65.8 % for nanocellulose. The nanocellulose obtained in this work had higher crystallinity compared to cellulose nanofiber produced by Fahma et al. (2010) since its CI value was just 59 %.

Figure 1(c) captured by TEM illustrates the morphology of nanocellulose produced after acid hydrolysis which acted as scissors to cut the cellulose into nano-sized and at the same time remove some of the lignin. Nanocellulose shown in the figure was needle like structure and ranged in nanometer verifying the success of acid hydrolysis. Based on TEM micrograph, the diameter of cellulose was observed to be around 5-20 nm while its length to be around 20-60 nm. Moreover, it is well-known that nanocellulose is stable in suspension form which proven in Figure 1(d) by its physical appearance after set up for 3 months.

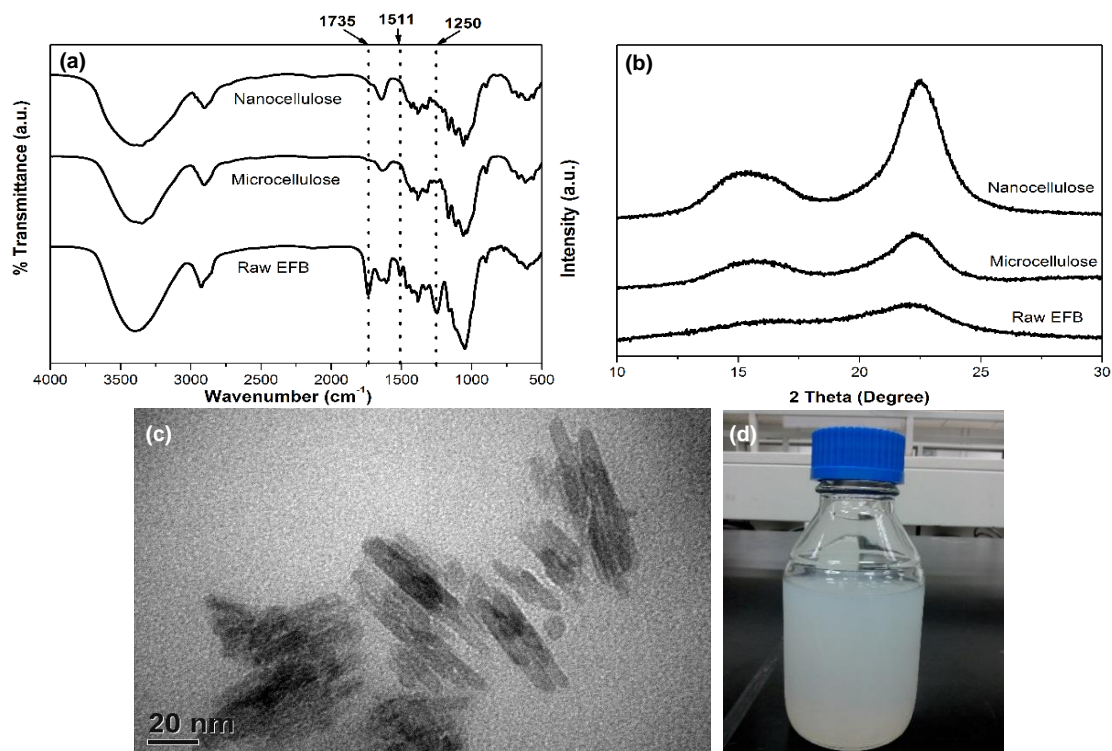


Figure 1: (a) FTIR spectra and, (b) XRD diffractogram of raw EFB with its micro-, nano-sized cellulose, (c) TEM image of nanocellulose at magnification of 100kX, and (d) Nanocellulose suspension

3.2 Tensile properties

The effect of nanocellulose from EFB incorporated into the TS films and crosslinked TS films containing CA on tensile properties are displayed in Figure 2. Generally, sufficient amount of nanocellulose added into starch matrix would enhance the tensile strength and modulus of elasticity E but lower the value of break elongation (ϵ). Figure 2(a) shows that the tensile strength increased from 8.18 MPa (neat TS film) to the highest tensile strength among all the films produced of 14.82 MPa when incorporated 3 phr nanocellulose but then tensile strength decreased for TS films with 4 and 5 phr nanocellulose. After the optimum content of filler, further addition of nanocellulose into these green composites system, the tensile properties of the materials could gradually decrease (Soykeabkaew et al., 2012). From these results, 3 phr of nanocellulose was considered as the optimum amount of filler added into TS films since tensile strength in the series of crosslinked TS films containing CA with 3phr nanocellulose was also recorded as the highest tensile strength of 13.3 MPa. Figure 2(b) exhibits that by increasing the amount of nanocellulose, the modulus of elasticity of the TS/NC films continuously increase while the value of break elongation continuous decrease. High tensile strength and modulus of elasticity values indicate that nanocellulose is well dispersed in the starch matrix because of similar chemical structure between nanocellulose and TS which stimulate a good interaction while the decrease in break elongation is owing to the rigidity nature of the cellulose. Similar to TS/NC, the trend of modulus of elasticity recorded for crosslinked TS/NC was increased till the optimum condition applied. However, break elongation increased sharply from 9.08 % till the highest value of 109.36 % and then gradually decreased. Sharply increased of break elongation might because of the role of CA as plasticizer that increases the interstitial volume of the material or macromolecular mobility of the polymer thus polymeric network become less dense owing to the lowering in intermolecular forces. Hence, the extensibility and flexibility of the green composite films are enhanced (Wang et al., 2014). Overall, both nanocellulose and citric acid affected the tensile properties by increasing its tensile strength and modulus of elasticity when incorporating appropriate amount of nanocellulose. The improvement of tensile properties of crosslinked TS/NC was supported by the FTIR results as shown in Figure 3 which confirmed the successfulness of CA cross-linking. FTIR spectra of TS, TS/0.5 phr NC and crosslinked TS/0.5 phr NC films have identical peaks except for additional peak in crosslinked film at 1721 cm^{-1} . The peak at $1,721\text{ cm}^{-1}$ is attributed to carboxyl and ester carbonyl group. Since CA cross-linking proceeds through esterification, the presence of the ester carbonyl peak verifies the chemical linkages between CA and TS.

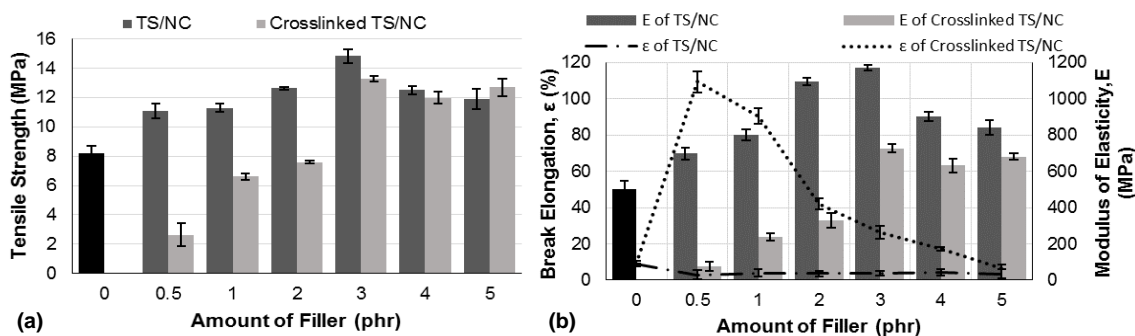


Figure 2: (a) Tensile strength of TS/NC and Crosslinked TS/NC, and (b) Break Elongation and modulus of elasticity of TS/NC and Crosslinked TS/NC.

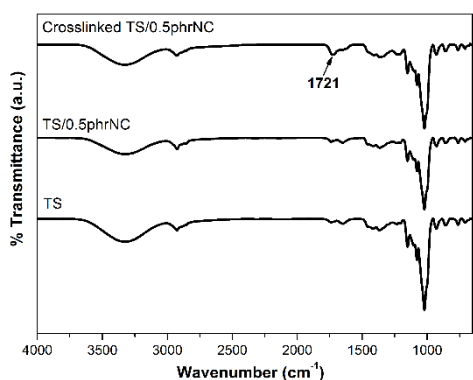


Figure 3: FTIR spectra of TS, TS/0.5phr NC and Crosslinked TS/0.5 phr NC.

3.3 Thermal properties

Thermal degradation (TGA) and derivative thermogravimetric (DTG) curves of chosen TS/NC and crosslinked TS/NC green composite films are shown in the Figures 4(a) and (b). Initial weight loss for all chosen green composites including neat TS film at around 150 °C on both TGA and DTG curves were due to water vaporization. The summary of thermal properties including temperature at 20 % weight loss (T_{20}) and degradation temperature (T_{deg}) of all selected TS green composites are listed in Table 1. Among tested films, TS/0.5 phr NC film had the highest T_{deg} of 318 °C. Based on the results shown in the table and figures, the incorporation of nanocellulose enhanced the thermal stability while crosslinked TS/NC films slightly lower the thermal stability. In fact, the addition of CA on starch-based composites might lower its thermal stability which can be ascribed to the ester bonds from the substitution that break at lower degradation temperature (Ma et al., 2009).

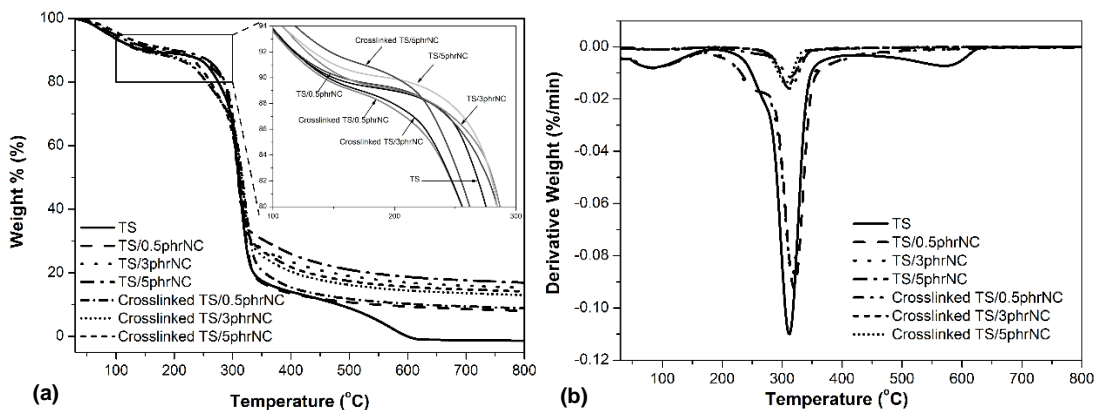


Figure 4: (a) TGA curves, and (b) DTG curves of TS/NC and Crosslinked TS/NC

Table 1: Thermal Properties of TS/NC and Crosslinked TS/NC

| Specimen | T ₂₀ (°C) | T _{deg} (°C) |
|---------------------------|----------------------|-----------------------|
| TS | 275 | 311 |
| TS/0.5 phr NC | 284 | 318 |
| TS/3 phr NC | 286 | 317 |
| TS/5 phr NC | 285 | 313 |
| Crosslinked TS/0.5 phr NC | 255 | 311 |
| Crosslinked TS/3 phr NC | 256 | 309 |
| Crosslinked TS/5 phr NC | 261 | 306 |

4. Conclusions

Generally, the tensile properties in term of tensile strength and break elongation of crosslinked TS/NC films using CA had been improved. Among the tested crosslinked green composite films, crosslinked TS/3 phr NC had the highest tensile strength of 13.3 MPa. However, crosslinked TS/NC films had lower thermal stability compared to both TS and TS/NC films.

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