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Effect of Adipic Acid as Crosslinking Agent in Polyvinyl Alcohol / Nanocellulose from Rice Straw Biocomposites

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ABSTRACT

A study was conducted to investigate the biodegradable polymers by adding natural polymers into non-degradable plastics material. Therefore in this research, an attempt was made by incorporating natural polymer, which is cellulose nanocrystal (CNC) into polyvinyl alcohol (PVA) matrix. This study was also investigated the effect of adipic acid as a crosslinking agent to PVA/CNC film with different CNC content. CNC was extracted from agricultural waste, which is rice straw by sulphuric acid hydrolysis at 45ºC for 60 minutes. The CNC was characterized by Fourier Transform Infrared (FTIR). The result shows that hemicellulose and lignin break down after undergoes several pre-treatments. The PVA/CNC biocomposites films were prepared by casting with different concentrations of CNC (0%, 2%, 6%, 10% wt) and the addition of 5 wt % (0.1 g) of adipic acid (AA) to the respective concentrations. The tensile test and FTIR analysis were used to investigate the properties of these biocomposites films. The result of PVA/CNC/AA film showed a higher tensile strength and elongation at break (E_b) compared to PVA/CNC film. Thus, the presence of AA enhanced the properties of PVA/CNC biocomposites film.

Keywords: Adipic Acid, Cellulose Nanocrystal, Polyvinyl Alcohol, Rice Straw.

1. INTRODUCTION

Biocomposite composed of natural fiber, a biopolymer that offers reductions in cost, weight and less dependence on fossil resources as the future of green composites (1). Generally, there are two types of biocomposite materials mainly formulated by biomass-based filler or biopolymers with organic fillers and petroleum-based polymers with biomass-based filler. Biocomposites are widely used in many industries which are construction, automobile, furniture and packaging industries (1). There are varieties of biomass-based reinforcement materials have been used for biocomposite formulation such as agro-industrial wastes, bamboo fiber, chitin, cellulose and wheat gluten (2).

Due to the environment and sustainability issues, this century has witnessed remarkable achievements in green technology through the development of biocomposites. Agricultural wastes are materials from the harvested crops that have different usages. Nanocelluloses that can be extracted from agricultural waste ie, rice straw have unique properties, such as renewability and biodegradability; they are harmless to human health and can even be considered as appropriate alternatives to many petroleum products and other industrial products (3-4). Rice straw is one of the agricultural wastes that deserve further research in order to overcome poor agricultural waste handling and management and it is abundantly available. Nanocellulose can be extracted in a high yield from rice straw as rice straw contains a high amount of cellulose. Isolation of cellulosic nanomaterials from rice straw and their use in novel bionanocomposites having the potential to be used in different applications have been recently studied (5).

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Polyvinyl alcohol (PVA) is a hydrophilic semicrystalline polymer produced by polymerization of vinyl acetate to polyvinyl acetate (PVAc), and the subsequent hydrolysis of PVAc to PVA. This polymer is widely used industrially and also has the advantages of being biocompatible, biodegradable and non-toxic (6). Toward this end, several biopolymers have been modified in order to be competitive with petroleum-based polymers in term of performance and cost. Incorporating nanosized reinforcement into the polymer is one way to improve and enhance their properties of biopolymers and their commercial potential (7). The application of cellulose nanocrystals (CNC) as a nanosized reinforcement in polymer matrixes has attracted considerable attention in this field, since it offers a unique combination of desirable physical properties and environmental benefits (8). The adipic acid is used as a crosslinking agent to improve the properties of hydrophilic composites due to its capability to interact with alcohol (OH) groups of the polymer and its filler material.

This research is to study the best formulation for biocomposites by extracting the nanocellulose from rice straw. Polyvinyl alcohol (PVA) will be incorporated into a natural fiber which is cellulose nanocrystals and the addition of adipic acid is to enhance the properties of the composites compared to neat polymer.

2. MATERIAL AND METHODS

2.1 Material Preparation

The rice straw from paddy residues was chosen as a raw material in this research as it is abundantly available and contains a high amount of cellulose. The rice straw was collected from Kampung Batu Pahat, Perlis. Firstly, rice straw was cut into pieces and ground into a fine powder. Then, rice straw fiber was sieved to 63 μm in size before purification process.

2.2 Purification of Rice Straw

The rice straw fiber was purified according to the method described by Silverio et al., (2013). The untreated rice straw fiber was first treated with an alkaline treatment by using 32 g sodium hydroxide (NaOH) (4% w/w NaOH, pellet, Sigma-Aldrich) for 4 hours at 80 °C distilled water. Then, the fiber was filtered and washed until neutrality with distilled water. After that, the treated fiber was dried in an oven at 50 °C for 24 hours.

2.2.1 Extraction of Cellulose Nanocrystals (CNC)

The resulting material from purification process was used for the isolation of CNC. The acid hydrolysis treatment was performed by added 23.4 ml sulphuric acid (H_2SO_4) (64% v/v H_2SO_4, Sigma-Aldrich) into a distilled water under vigorous stirring at 45°C for 60 minutes. After that, 200 ml of distilled water (cold) was added to the solution to stop the reaction. The solution was kept at room temperature for 24 hours to get the suspension. Next, the suspension was centrifuged at 10000 rpm for 5 minutes. The precipitate was then dialyzed against water and CNC suspension was obtained. Finally, CNC was characterized through Fourier Transform Infrared (FTIR) analysis.

2.2.2 Preparation of CNC/PVA Biocomposites Film

A matrix suspension of PVA was obtained by stirring 2 g of PVA granules (5% w/w, Sigma-Aldrich) at 90°C distilled water for 2 hours under mechanical stirring at 150 rpm. After that, 0.8 ml of CNC (2 % v/v CNC) suspension was added into the prepared PVA solution and the final suspension was cast in an acrylic mold (30 cm x 30 cm) and adjusted to 1 mm spacing. Then, the step of preparation biocomposites film was repeated with different proportions of CNC by adjusting its concentration to 4, 6, 8, 10 % wt. The film was dried in an oven for 24 hours at 50 °C before further testing.

2.2.3 Preparation of CNC/PVA/AA Biocomposites Film

The CNC/PVA/AA solution was prepared by dissolving 2 g of PVA granules (5 % w/w, Sigma-Aldrich) in distilled water and stirred at 90 °C for 2 hours under mechanical stirring. At the same time, 0.1 g of adipic acid (99 % adipic acid, Sigma-Aldrich) was added to the solution. The proportion of CNC was added equivalent to the prepared PVA/adipic acid solution by adjusting the CNC concentrations to 0, 2 (0.8 ml), 4 (1.6 ml), 6 (2.4 ml), 8 (3.2 ml), 10% wt (4 ml), respectively. The final suspension was cast in an acrylic mold (30 cm x 30 cm) and was adjusted to 1 mm spacing. The film was dried in an oven at 50°C for 24 hours before further testing.

2.3 Characterization

2.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to characterize the presence of the functional group. The sample in powder form was prepared in KBr method. FTIR spectrometer was operated at 4 cm^{-1} resolution level, over wave number interval of 4000-650 cm^{-1} to investigate the changes of structural. The samples were tested by using attenuated and total reflectance (ATR) technique.

2.3.2 Tensile Testing of Biocomposites Film

According to the Silvério et al. (2013), the ultimate strength of the nanocomposites film and neat PVA film was measured with the aid of a Universal Tensile Machine (UTM) (Instron 5569). The sample was cut into 1 cm width and 10 cm length and tested using a crosshead speed of 50 mm/min using ASTM D882 with a load cell of 1 kN at 25 ºC. Five measurements were tested for each sample to ensure reproducibility of the results

3. RESULTS AND DISCUSSION

3.1 Comparison of CNC/PVA Biocomposite Film with the Incorporation of Adipic Acid

Figure 1 presents the effect of adipic acid (AA) as a cross linker on the tensile strength of PVA/CNC biocomposite films at different CNC contents. From the graph shown as the content of CNC increases with 2 %, 6 %, and 10 %, the tensile strength of both PVA/CNC film with the incorporation of AA the tensile strength was decreased. The tensile strength of PVA/CNC film decreased from 30.2 MPa to 18.8 MPa while PVA/CNC/AA was decreased from 41.3 MPa to 29.3 MPa. Thus, PVA/CNC/AA film shows a higher tensile strength than PVA/CNC film. This indicates that the strengthening of the tensile strength of PVA/CNC/AA films is due to the formation of intermolecular hydrogen bonds between PVA matrix and CNC filler.

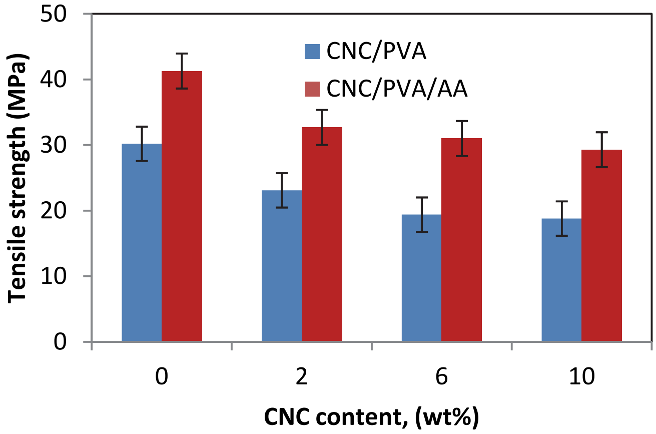

Figure 1. Tensile strength of PVA/CNC and PVA/CNC/AA film.

Figure 2 illustrates the effect of AA content on the modulus of elasticity of PVA/CNC and cross-linked adipic acid of PVA/CNC biocomposite films at different contents of CNC loading. The results indicated the modulus of elasticity of PVA/CNC film was increased from 20.6 MPa to 37.6 MPa and PVA/CNC/AA film increased from 30.4 MPa to 49.4 MPa. The modulus of elasticity is an indication of the relative stiffness of biocomposite films. The increase in modulus of elasticity was expected as the CNC contents increases, due to more crosslinking reaction occurs between PVA matrix and leads to stiffness of the biofilms. In addition, the values of modulus of elasticity also depend on many factors such as the ratio of filler to the matrix, adhesion between filler and matrix.

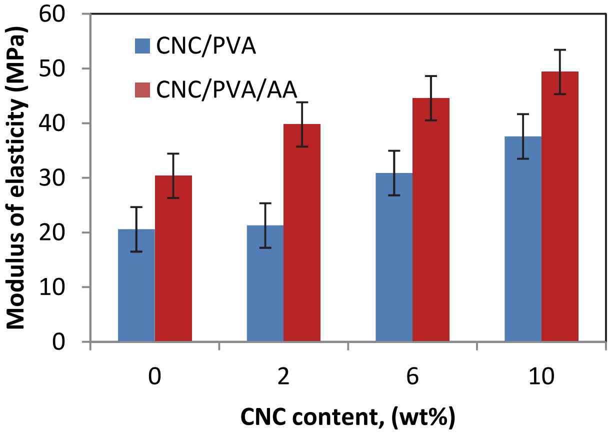

Figure 2. Young modulus of PVA/CNC and PVA/CNC/AA biocomposites film.

3.2 FTIR Spectra of CNC/PVA Biocomposite Film with the Incorporation of Adipic Acid

The effect of addition AA in term of spectra was shown in Figure 3 compared to neat PVA and PVA/CNC film at 10 wt % of CNC content. The sample of neat PVA showed that it was quite similar to the sample of PVA/CNC. The infrared spectra of neat PVA exhibit C-H stretching bands at 2918 and 2849 cm^{-1}. The spectral bands and wave number of neat PVA were in general agreement with the results of Raj et al. (2004) (9). From Figure 3, it is clearly shown that the broad and strong peak ranges from 3000 to 3700 cm^{-1} which represent the overlapping hydroxyl (OH), silanol and amine stretching vibration. The peak at 1574 cm^{-1} represents for alcohol primary $–CH_2OH$. Based on the observation, in the same spectra, the presence of broad hydroxyl group (OH) group peak at 3500

cm^{-1} indicates the presence of CNC in the film. The presence of a peak at 1645 cm^{-1} can be related to carboxyl (COOH) group as the addition of AA to PVA/CNC film.

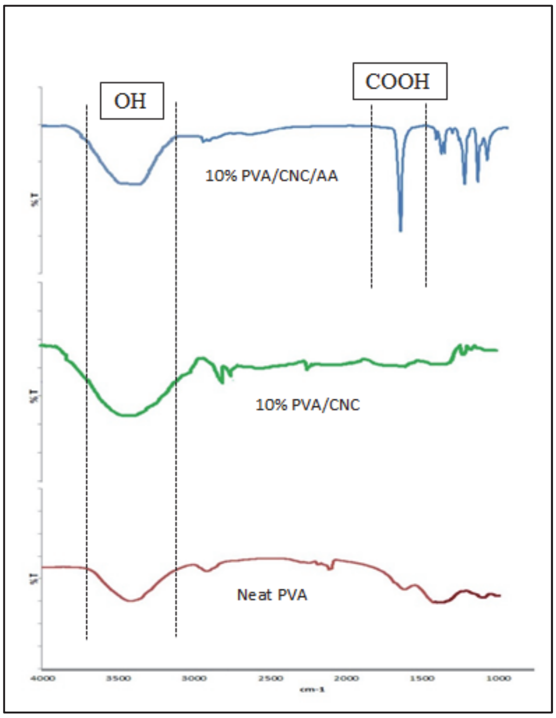

Figure 3. FTIR spectra of neat PVA, 10% PVA/CNC and 10% PVA/CNC/AA.

The effect of adipic acid has been proven in term of hydrophilic properties as it can see in Figure 4. The properties of PVA/CNC biocomposites film have the disadvantage of poor water barrier properties due to the hydroxyl groups present in PVA. However, by incorporation of adipic acid has shown that it can improve the properties of hydrophilic composites due to its capability to interact with alcohol (OH) group of the polymers and its filler materials.

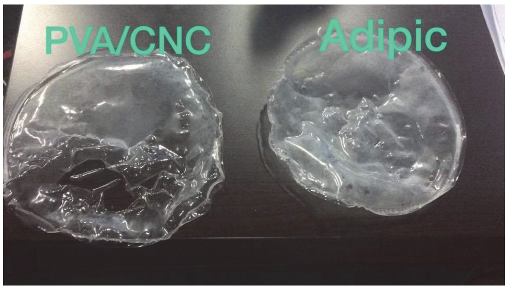

Figure 4. Comparison between PVA/CNC and PVA/CNC/AA film in term of hydrophilic properties.

4. CONCLUSION

The result shows that the tensile strength, break elongation and modulus of elasticity of PVA/CNC biocomposite films with the incorporation of adipic acid increased with the increasing CNC content from 0% to 10 %. The AA was used as a crosslinking agent in the PVA/CNC biocomposite films. AA has improved the tensile strength of the film due to its capability to interact with a hydroxyl group (OH) that present in PVA. The presence of AA enhanced the adhesion between the PVA matrix and the CNC filler was proven by SEM study. Overall, the CNC/PVA/AA shows a better performance compared to CNC/PVA biocomposites film.

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