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Effect of Butyl Methacrylate on Properties of Regenerated Cellulose Coconut Shell Biocomposite Films

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Abstract

In this study, butyl methacrylate acid (BMA) is used as chemical modifier of regenerated cellulose (RC) coconut shell (CS) biocomposite films. The effect of CS content and BMA on tensile properties and crystallinity index (CrI) of RCCSbiocomposite films were investigated. It is found that the increasing of CS content up to 3 wt% increased the tensile strength and modulus of elasticity but decreased at higher content of CS. Elongation at break decreased with increasing of CS content and increased at 4 wt% of CS. Cystallinity index (CrI) of biocomposite films also increased with increasing CS up to 3 wt% content. At similar CS content, treated RC CS biocomposite films with BMA were found to have higher tensile properties and crystallinity index (CrI) than the untreated biocomposite films. The modification by BMA improved interfacial interaction and dispersion of CS in RC biocomposite films.

*Keywords:*Coconut shell; Butyl methacrylate acid; Regenerated cellulose; Biocomposite films; Chemical modification

1. Introduction

In recent years, cellulose biocomposite materials which also known as green materials has generate enormous attention and interest in research and industrial area because it comes with features of biocompatibility, environmentally friendly, biodegradability, availability and sustainability. With the serious environmental issues

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from the non-biodegradable materials, this could be an alternative towards new developing environmentally safe eco-design materials. The emerging of cellulose as a substitute polymer is one of the approaches to curb the dependence on fossil fuel since cellulose is the most sustainable biopolymer on earth[1,2]. However, cellulose does not dissolve in water and any other common conventional solvent due to its crystalline structure that consist of strong inter- and intramolecular hydrogen bonds thus limiting its applications[3].

Lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) represent well established non-derivatizingsolvent system that has been commonly used in cellulose modification. This solvent can dissolve cellulose with a molecular weight of more than 10^6 under ambient conditions without degradation. LiCl/DMAc also has been used as medium for cellulose derivatizing under homogenous conditions. Moreover, this solvent was actively employed in the preparation of regenerated cellulose by using water as coagulant[4-6]. Coconut shell (cocosnucifera) is one of the hard lignocellulose filler which is abundantly found as it's an agricultural co-product. Besides of its wide availability and outstanding properties, coconut shell is also low cost and environmentally in nature. Lignocellulose biomass is a potential source of starting materials for industrial process that are less expensive than petroleum and does not effects food supplies[7-8]. Nowadays, there are many chemical used in modification of filler to improve the interfacial adhesion between filler and matrix such as alkaline treatment, silane treatment, esterification and with other chemical compund[9].

In this study, the effect of CS content and the butyl methacrylate acid on tensile properties and crystallinity index (CrI) of RC CS biocomposite films.

2. Experimental

2.1. Materials

Coconut shell (CS) was obtained from a market at Perlis, Malaysia. The CS was cleaned, dried, crushed and grounded into powder. The particle size of CS, 63 μm was measured by Malvern Particle Size Analyzer Instrument. Microcrystalline cellulose (MCC) and sodium chlorite was provided by Sigma-Aldrich while DMAc and LiCl were supplied by Merck and Acros Organic. Sodium hydroxide (NaOH) andsulphuric acid were supplied by HmbG Chemicals. Glacial acetic acid was provided by BASF.

2.2. Pretreatment of coconut shell

The alkali treatment of coconut shell (CS) with 4% (w/v) sodium hydroxide solution at 70 ºC for 3 hours was conducted three times under mechanical stirring. Bleaching treatment was conducted with equal part of acetate buffer (sodium hydroxide, glacial acetic acid and sodium chlorite) at 70 ºC for 1 hour under mechanical stirring and was repeated for eight times. 65% of sulphuric acid was used in acid hydrolysis. This process was conducted at 45 ºC for 1 hour. Cold water is used to dilute the solution after the acid hydrolysis process to stop the reaction. CS is washed, filtered and dried in oven at 80 ºC for 24 hours.

2.3. Chemical treatment of coconut shell

Butyl methacrylate (BMA) with 3% (v/v) was dissolved in ethanol. The CS was added slowly into the solution and then stirred for 1 hour and stay overnight. The CS was filtered and dried in oven at 80 ºC for 24 hours.

2.4. Preparation of RC CSbiocomposite films

MCC/CS required activation before dissolution in DMAc. The MCC and CS were first dissolved in distilled water, followed by acetone and DMAc for 1 hour at room temperature. The LiCl at 8% (w/v) was used in the cellulose dissolution. The MCC/CS together with LiCl/DMAcwere stirred for 1 hour until transparent viscous solution was obtained. Solution was then casted on the glass plate and leaved overnight for regeneration process to take place. RC biocomposite film was washed with distilled water and dried at room temperature for 24 hours. The formulation of RC CSbiocomposite films with different filler content is shown in Table 1.

Table 1. Formulation of untreated and treated RC CS biocomposite films.

Materials	Untreated RC CSfilms	Treated RC CSfilms
Microcrystalline cellulose (MCC) (wt%)	3	3
Coconut shell (CS) (wt%)	1, 2, 3, 4	1, 2, 3, 4
Butyl methacrylate acid (BMA) (%)[a]	-	3

[a] 3% based on weight of CS

2.5. Tensile testing

Tensile properties such as tensile strength, modulus of elasticity and elongation at break can be obtained from tensile test. Tensile testing was conducted using Instron 5569 Universal testing system by referring to ASTM D 882. A cross-head speed of 10 mm/min was used and test was carried out at room temperature. Five samples were tested with size of 50 x 15 mm was cut from each of RC biocomposite films.

2.6. X-Ray diffraction

Crystallinity index (CrI) of RC biocomposite film samples was determined by X-ray diffraction method by using Bruker Advance model system. The pattern with Cu Kα1=1.5406Å at 30kV and 10mA were recorded from 2° to 35°. CrI as defined by Segal was used as a measurement of crystallinity.

$$CrI (\%) = (I_{002}-I_{AM})/I_{002} \times 100 \tag{1}$$

Where I_{002} is the maximum intensity of the (022) lattice diffraction peak and I_{AM} is the intensity scattered by the amorphous part of the sample. The diffraction peak for plane (002) is located at the diffraction angle of around 2θ=21°-22° and the intensity scattered by amorphous part was measured at lowest intensity at a diffraction angle around 16°

3. Results and discussion

3.1. Tensile properties

Fig. 1 (a) shows the tensile strength and modulus of elasticity of untreated and treated RC CS biocomposite films. The incorporation of CS increased tensile strength of RC biocomposite films. The addition of CS up to 3 wt% was found to have increased the tensile strength for untreated RC biocomposite films. This is due to good dispersion and interaction between CS and regenerated cellulose matrix. At 4 wt%, tensile strength was reduced because of high concentration of CS that leads to poor dispersion thus cause agglomeration in RC biocomposite films. Treated RC biocomposite show higher tensile strength compared to untreatedbiocompositefilmsdue to better filler-matrix interaction thus promotes strong interaction between CS and RC matrix.

At similar CS content, modulus of elasticity also increased with increasing CS content up to 3 wt% and decreased with further addition of CS. Addition of CS promotes stiffness of regenerated cellulose biocomposite films. On the other hand, treated biocomposite films exhibit modulus of elasticity at similar content, 3 wt% of CS. The improvement was attributed to strong interaction between hydroxyl groups of celluloses which then improves CS dispersion and adhesion with regenerated cellulose matrix.

Fig. 1(b) illustrate the effect of CS content on elongation at break of regenerated biocomposite films. It was found that elongation at break was decreased with increasing CS content up to 3 wt% and increased at higher CS content. This is due to CS which acts to confine the movement of RC biocomposite films chains thus decreased the elongation at break of untreated RC CS biocomposite films. Nevertheless, treated RC CS biocomposite showedlower elongation at break compared to the untreated biocomposite films. Strong interfacial interaction can be expect between celluloses matrix, thus improves the stiffness of treated biocomposite films.
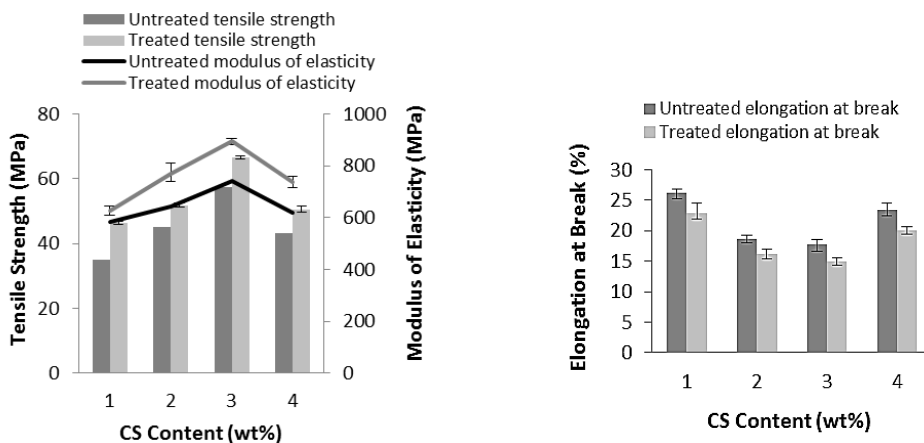
Fig. 1. (a) Tensile strength and modulus of elasticity; (b) elongation at break of untreated and treated RC CS biocomposite films.

3.2. X-Ray diffraction

Fig. 2 showed the XRD patterns of untreated and treated RC biocomposite films with BMA as modifier. Table 2 showed the effect of CS content on crystallinity index (CrI) of biocomposie films. It was observed that the addition of CS in RC bicomposite films increased the crystallinity up to 3 wt% and further addition decreased the crystallinity of RC biocomposite films. The crystallinity increase as the addition of CS in the system increased the cellulose crystallization. Further addition of CS in the system could restrict the dissolution process thus prevent the cleavage of inter- and intra-molecular hydrogen bond of cellulose. At similar CS content, treated RC CS biocomposite films exhibit higher crystallinity compared with the untreated biocomposite films. BMA promotes strong interaction between CS and regenerated cellulose thus enhanced the crystallinity of treated RC CS biocomposite films.
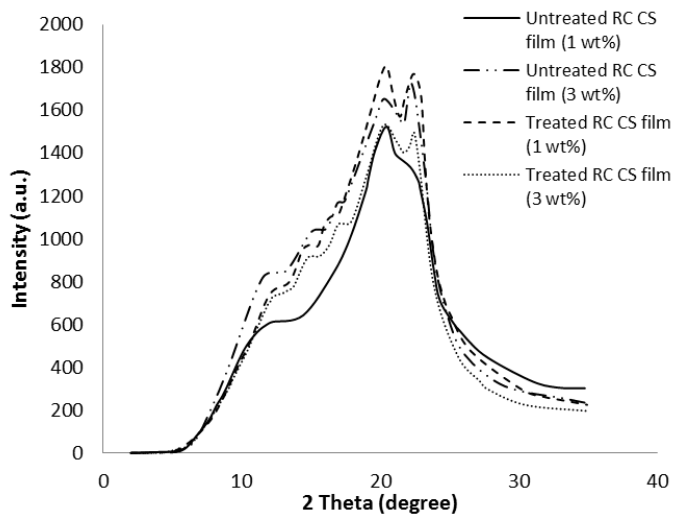

Fig. 2. XRD patterns of untreated and treated RC CS biocomposite films at 1 and3 wt% of CS.

Table 2.Crystallinity index (CrI) ofuntreated and treated RC CS biocomposite films.

CS content	CrI (%) Untreated RC CS films	CrI (%) Treated RC CS films
1	39.9	42.5
2	40.8	43.7
3	42.5	44.9
4	34.1	36.1

4. Conclusions

The tensile strength and modulus of elasticity of biocomposite films increased with the increasing of CS up to 3 wt% and decreased at higher of CS content. Elongation at break decreased upon addition of CS and increased at higher CS content. Crystallinity index also increased up to 3 wt% of CS content. The treated biocomposite films with BMA improved the tensile strength, modulus of elasticity and crystallinity index (CrI) of biocomposite films, but lower elongation at break.

Acknowledgements

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