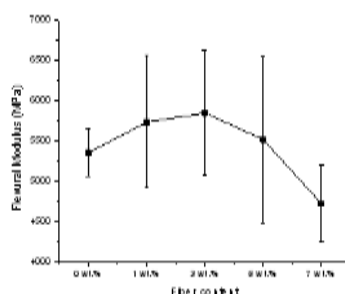# THERMAL AND FLEXURAL PROPERTIES OF REGENERATED CELLULOSE(RC)/POLY(3-HYDROXYBUTYRATE)(PHB)BIOCOMPOSITES

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Graphical abstract

Abstract

Regenerated cellulose (RC)/ poly(3-hydroxybutyrate) (PHB) composite was prepared via melt compounding with different RC contents from 1 to 7 wt.%. Regenerated cellulose fiber was prepared in NaOH/urea aqueous solution. The properties of the cellulose and the regenerated cellulose were compared using Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric analysis (TGA), and Differential Scanning Calorimetry (DSC). The results of TGA and DSC revealed that the regenerated cellulose had lower thermal properties than cellulose. Meanwhile, the FTIR of regenerated cellulose showed that the intensity portrayed by a few peaks had reduced or disappeared as compared to cellulose. Besides, PHB composites were characterized using TGA and flexural testing. Moreover, thermal stability of the composites insignificantly changed with the incorporation of RC. Improvement in flexural strength and modulus were observed, whereas 3 wt.% was found to be the optimum RC content.

Keywords: Poly(3-hydroxybutyrate)(PHB), regenerated cellulose (RC), cellulose, NaOH, urea, biocomposite, thermal properties, mechanical properties, TGA, DSC, FTIR, flexural.

Abstrak

Selulosa dibangunkan semula (RC) / poli (3 - hydroxybutyrate) (PHB) dengan komposit telah disediakan dengan pencairan pengkompaunan dengan kandungan RC berbeza 1-7 wt . %. Serat selulosa dijana semula dalam NaOH / urea larutan akueus. Sifat selulosa dan selulosa yang dijana semula dibandingkan dengan menggunakan Fourier Transform Infrared Spektroskopi (FTIR), analisis Termogravimetri (TGA), dan Kalorimeter Pengimbasan Perbezaan (DSC). Hasil kajian melalui TGA dan DSC mendedahkan bahawa selulosa yang dibangunkan semula mempunyai sifat haba yang lebih rendah daripada selulosa. FTIR daripada selulosa yang dijana semula menunjukkan bahawa keamatan beberapa puncak telah dikurangkan atau hilang berbanding dengan selulosa. Tambahan pula, komposit PHB telah dicirikan menggunakan TGA dan ujian lenturan. Selain itu, kajian ini mendapati bahawa kestabilan terma bagi komposit yang tidak ketara berubah dengan penubuhan RC. Peningkatan dalam kekuatan lenturan dan modulus diperhatikan dan 3 wt . % didapati dalam kandungan RC yang optimum.

Kata kunci: Poli (3 - hydroxybutyrate) (PHB), selulosa dibangunkan semula (RC), selulosa, NaOH , urea, biokomposit , sifat haba , sifat mekanik , TGA , DSC , FTIR , lenturan .

1.0 INTRODUCTION

Poly(3-hydroxybutyrate) (PHB) is a type of biopolymer. It is produced by saturated aliphatic polyester. It is synthesized by a variety of bacteria as a metabolism of stored energy molecule [1]. PHB is biodegradable and it is mainly used in: helping relieve environmental pollution due to the disposal of non-biodegradable petroleum-based polymer; while another is to provide new-types of materials in the use of biomedical field [2].

Cellulose is a semicrystalline polysaccharide. Large amounts of hydroxyl groups are responsible for the hydrophilic properties of the natural fibers [3]. In original form, cellulose is classified as cellulose I, which is also called native cellulose. After mechanical or chemical treatment, the cellulose is now classified as cellulose II, which is also called as regenerated cellulose [4]. Cellulose application and development are limited due to its difficulty to dissolve in most of the common solvents. This is because of its strong inter-molecular force, van der Waals, and intra-molecular force of hydrogen bonds [5]. Hence, processing approaches that prevent toxic byproducts and complicated processing routes are important [6]. Sodium hydroxide (NaOH)/urea aqueous solvent system has been reported as a good alternative and a green solvent for regeneration of cellulose. NaOH and urea are inexpensive and can function as non-toxic chemical agents. Nevertheless, there is no evaporation of any toxic byproducts at the time of cellulose dissolution at low temperature [7].

In this study, the preparation and the characterization of regenerated cellulose fiber, as well as the incorporation of different contents of regenerated cellulose fiber into PHB biocomposite, had been looked into. Regenerated cellulose was regenerated by NaOH and urea mixture solvent. Cellulose and regenerated cellulose were compared via Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric analysis (TGA), and Differential Scanning Calorimetry (DSC). On top of that, thermal and mechanical properties of the regenerated cellulose/PHB biocomposites were characterized with TGA and flexural testing.

2.0 MATERIALS AND METHODS

Poly(3-hydroxybutyrate) (PHB), Y3000 grade from Tianan Biologic Material Co. Ltd, microcrystallite cellulose, Avicel PH-101grade, 50 μm particle size from Sigma-Aldrich, natrium hydroxide AR (analytical reagents) grade from QREC, urea AR (analytical reagents) grade from QREC and distilled water.

The regenerated cellulose was prepared in NaOH/urea aqueous solvent. A ratio of 7 wt.% NaOH/12wt.% urea solvent was prepared by mixing 31.85g of NaOH, 54.6g of urea, and 368.55g of distilled water (7:12:81 by weight). A total of 455g of solvent was prepared to a desired temperature at ice refrigerator of -12 °C. Then, 9 wt.% (45g) of cellulose powder was added immediately into 91 wt.% of solvent(455g), and then, it was stirred vigorously for around 30 min to dissolve the cellulose. The cellulose solution was then poured into a flask. 4500g of distilled water was added into the flask with 500g of cellulose solution to remove the remaining NaOH and urea with 5 flasks of 1000ml capacity. The solution was stirred for 4 hours on plate magnetic-stirrer at room temperature.

Next, the solution was filtered with filter paper. The remaining residue of cellulose was centrifuged at 5000 rpm for 20 minutes and the process was repeated thrice. Finally, the regenerated cellulose was dried at room temperature before compounding it with PHB. PHB was mixed with regenerated cellulose at different loadings of 1, 3, 5, and 7 wt. % in internal mixer at a temperature of 178 °C at 10 rpm for around 15 minutes. After that, the samples were compress molded by using a hot press machine that was pre-heated for 5 minutes before the samples were compressed at 178 °C for 15 minutes in a suitable mold. Lastly, the sample was cooled to room temperature.

2.1 Thermogravimetric Analysis (TGA)

TGA test was performed by using Perkin Elmer – TGA 7. The flow rate of nitrogen was 50 ml/min and the heat rate was 10 °C/min. The samples weighed at around 5 mg. The samples were heated from room temperature of 30 °C to 600 °C.

2.2 Differential Scanning Calorimetry (DSC)

DSC testing samples had been prepared between 6 and 12 mg. The test was conducted based on ASTM standard D3418-08 using Perkin-Elmer DSC-6. The weighed samples were placed and sealed in an aluminum pan. The heating rate was 10 ˚C/min in the presence of nitrogen gas with a flow rate at 20 ml/min. The glass transitions and the melting temperatures of the material were recorded.

2.3 Fourier Transform Infrared Spectroscopy (FTIR)

The material structures were evaluated by using Perkin-Elmer, a model of Spectrum 1, FTIR spectrometer. The samples were prepared in less than 10 mg. 64 consecutive scans for each spectrum was carried out in the range of 4000-400 cm-1. FTIR determined the infrared absorption spectrum and the molecular functional group in the material.

2.4 Flexural Testing

Flexural testing was performed by using the Universal Testing Machine Lloyd LRX Material Testing Machine (Lloyd Instruments Ltd, Fareham, UK), based on ASTM D790. The testing method was three-point bending. The load was 10 N, deflected at 10 mm, and the length of the spam was 5 cm. Meanwhile, the

constant crosshead speed was 3 mm/min, whereas the size of the samples in length, width, and thickness was 122 mm x 12 mm x 3 mm. 5 samples were tested for each formulation.

3.0 RESULTS AND DISCUSSION

3.1 Characterization Of Cellulose And Regenerated Cellulose

3.1.1 Thermogravimetric Analysis (TGA)

TGA and DTG of cellulose and regenerated cellulose are shown in Figures 1 and 2. Thermal decomposition of the samples had been investigated via TGA from 30 °C to 600 °C at 10 °C/min. Thermal decomposition of the cellulose and regenerated cellulose was divided into two weight loss stages, corresponding to the slow pyrolysis and fast pyrolysis stages. At the early and slow pyrolysis stage of the curve, weight loss was associated with volatilization and vaporization of water. Cellulose and regenerated cellulose were hydrophilic and were subjected to dehydration, in which water was released. From 50 °C to 250 °C, the mass of cellulose was almost unchanged, however, regenerated cellulose showed continuous weight loss in that temperature range due to lower intermolecular forces and hydrogen bonding after the regeneration process.

Meanwhile, fast pyrolysis occurred at 250 °C to 350 °C. Further weight loss was relatively fast, which was due to dehydration and decomposition of the cellulose. Onset decomposition temperature is the temperature in which oxidation process begins. The onset temperature of regenerated cellulose was lower than the cellulose, that was 270 °C and 305 °C respectively. During this stage, cellulose and regenerated cellulose were almost completely burnt due to oxidative thermal degradation, and destruction of the crystallite structure. As shown in DTG curve in Figure 2, the maximum decomposition temperature was 338 °C for cellulose, and 343°C for regenerated cellulose. Both peaks show the insignificant difference in the maximum decomposition temperature. The percentage weight residue for the cellulose was 13.92%, whereas 30.1% for regenerated cellulose (Figure 1). Higher weight residue was discovered probably due to the impurities that remained in the regenerated cellulose during the regeneration process.

Other than that, the onset decomposition temperature for regenerated cellulose was 35 °C lower than the cellulose. Thermal stability of regenerated cellulose was reduced after regeneration process. This can be explained as most of the hydrogen bonds and the cellulose molecular chains were degraded by NaOH, thus reduced the molecular weight and crystallinity[8]. Besides, low molecular weight accelerated the thermal degradation process. This is consistent with the result

obtained from Chen et al. (2011). They found that the regenerated cellulose membrane prepared with ionic liquid had lower thermal stability than the original cellulose. Even though regenerated cellulose had lower onset decomposition temperature, it contributed to a higher residual mass after the decomposition process. This result indicated that the regenerated cellulose gave higher char yield (non-volatile carbonaceous material) during the pyrolysis stage[8].
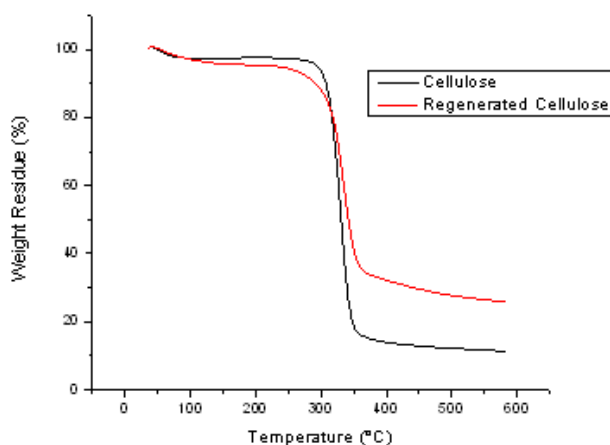

Figure 1 TGA of Cellulose and regenerated cellulose.
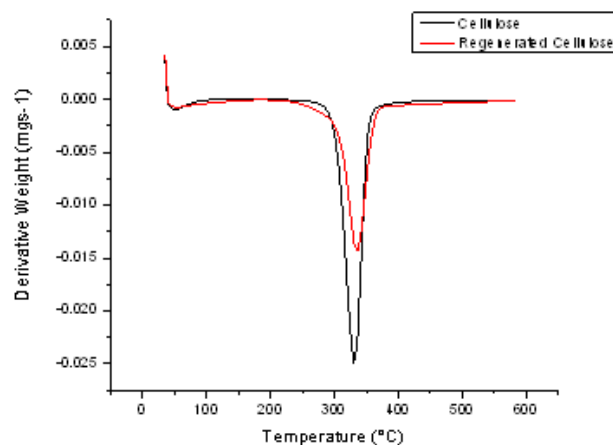

Figure 2 DTG of Cellulose and Regenerated Cellulose.

3.1.2 Differential Scanning Calorimetry (DSC)

Figure 3 shows the DSC thermogram of cellulose and regenerated cellulose from 30 °C to 450 °C. The first endotherm of cellulose started at 40 °C to 80 °C, while the regenerated cellulose ranged around 60 °C to 120 °C. It is believed that this ranges of endotherm transitions corresponds to amorphous component, which caused the rearrangement of the molecular chains. Besides, regenerated cellulose have a higher amount of amorphous component than cellulose, thus increases the temperature of endotherms transition. Besides, Mahato et al. (2013) have reported

the two endothermic transitions at cellulosic coir fiber[9].

The second endotherm transition corresponded to the crystallite part of cellulose and regenerated cellulose. In cellulose, the endothermic transition at 319.67 °C was attributed to cellulose melting, which corresponded to the breakage of glicosidic bonds, and the depolymerization of the cellulose [10]. This indicated that the molecular structure changed as observed in TGA curves, being related to thermal decomposition as well. Moreover, the thermal transitions in this temperature range are associated with the onset of thermal degradation of cellulose, which consists of the rearrangement of molecular chains, followed by molecular chain cleavage of glucosidic bonds and intermolecular cross-linking. This is in agreement with Miranda's et al. (2013) work, which used simultaneous differential thermo analysis (simultaneous DSC-TGA). They also observed an endothermic peak for maize straw cellulose at 330 °C[11].

On the other hand, regenerated cellulose had its endothermic transition temperature at around 314.83 °C, which was slightly lower than cellulose. It can be explained by the breakage of more intra-molecular and inter-molecular hydrogen bonding in the molecular chain during the regeneration, resulting in the decrease of crystallinity and endothermic transition. Besides, Liu et al. (2011) also identified the regenerated cellulose film to have a lower endothermic peak than original cotton pulp, due to the breakage of hydrogen bonding[12].
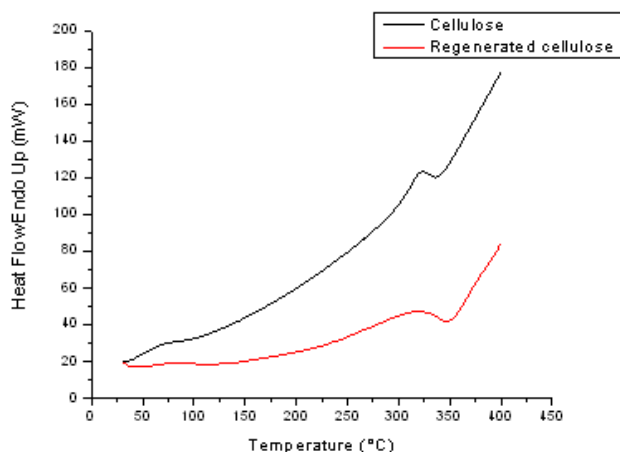

Figure 3 DSC of cellulose and regenerated cellulose.

3.1.3 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 4 shows the FTIR spectra of cellulose and regenerated cellulose. In the cellulose, n(C-O) around 1114.25 cm-1 was the ether linkages, while the n(OH) of the hydroxyl groups was around 3393.49 cm-1. A certain amount of bound water hydroxyl groups, n(OH) around 3400 cm-1 and n(OH) at 1640.60 cm-1 also contributed to pure cellulose FTIR peaks. The peak of 1028.70 cm-1 was the C-OH stretching, 1054.82 cm-

1 was the OH bending, while 1162.36 cm-1 was the C-O stretching or C-OH deformation. Meanwhile, peaks of 1318 cm-1 belonged to C-H deformation, 1337.81 cm-1 was the OH in plane deformation, 1375.04 cm-1 was attributed by the C-H deformation. In addition, CH2 symmetric bending was observed in 1425.53 cm-1.

In comparison of the two spectra in Figure 4, many bands present in the cellulose spectra were flattened out in the regenerated cellulose. This is an indication of transformation of cellulose I to cellulose II. The peaks from 894 cm-1 to 1430 cm-1 reduced in intensity and some peaks disappeared. Peaks that were located between 1430 cm-1 and 894 cm-1 were sensitive to the amount of crystallite versus amorphous structure, whereby broadening of these peaks meant that more disordered structure was present in the regenerated cellulose [13].

On top of that, peak 1114.25 cm-1 appeared strongly in cellulose, but in regenerated cellulose, this peak only appeared as a shoulder, which also confirmed the transformation from cellulose I to cellulose II. Besides, the peak at 1425.53 cm-1 (CH2 bending vibration) disappeared in regenerated cellulose, which depicted the reduction in crystallinity, and the destruction of intramolecular hydrogen bond in regenerated cellulose [14]. Meanwhile, the absorption bands of 3000–3600 cm-1 in regenerated cellulose were assigned by the free OH and bonded OH stretching in the structure, whereas the peak at 2912.18 cm-1 was contributed by the C–H stretching vibration. In addition, the CH2 symmetric bending and C–O stretching vibration of C–O–C groups were located at 1405.72 cm-1 and 893.52 cm-1, respectively.
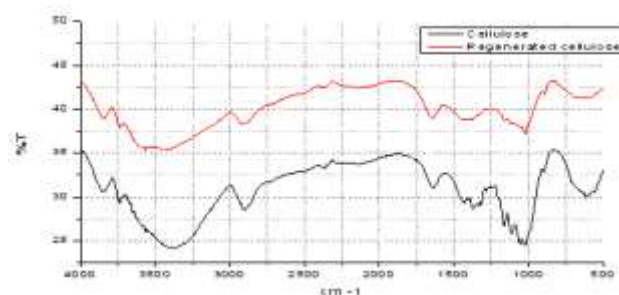

Figure 4 FTIR of pure cellulose and regenerated cellulose.

3.2 Characterization Of Regenerated Cellulose/PHB Composites.

3.2.1 Thermogravimetric Analysis (TGA)

Figure 5 shows the TGA results of the composites. The composites showed good stability from 30 °C up to 240 °C. Thermal decomposition of the composites and pure PHB only started at around 240 °C to 300 °C. Figure 5 also shows insignificant variation in the onset temperature for all the composites. When above 350

°C, there was also an insignificant change in the weight residue of the composite with different RC loading. In fact, 7% of impurities were detected in pure PHB, as supposedly it would be fully decomposed at temperature above 300 °C.

On top of that, El-Shekeil et al. (2012) found that the thermal stability of polyurethane composite decreased with the addition of kenaf fiber. The easy decomposition could be attributed by the dehydration and the degradation from the cellulose unit, with the thermal cleavage at the glycosidic linkages of cellulose. High temperature also caused the aromatization that involved dehydration in cellulose [15].
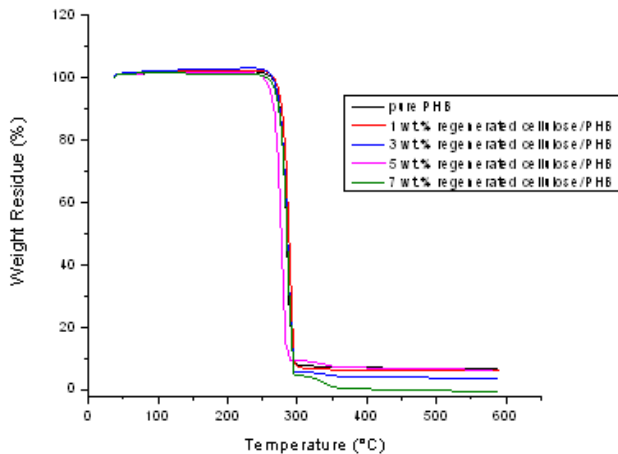

Figure 5 Curves of the regenerated cellulose/PHB composite

3.2.2 Flexural Testing

Based on Figure 6, the flexural strength continued to increase with the increment of the RC fiber up to 3 wt.% of RC loading with the optimum value of 62.65 MPa. Flexural strength of the composites increased because of the hardness character of the regenerated cellulose fibers, as compared to brittle PHB. Moreover, some studies proved the efficiency of natural fibers as a good reinforcement for polymers, for instance, based on a research conducted by Rao et al. (2010) [16] in natural fiber composites and Asumani et al. (2012) in kenaf reinforced polypropylene [17]. However, the flexural strength decreased with 5 wt.% of RC. Meanwhile, at high loading of regenerated cellulose fiber, the load from PHB matrix could not be transferred effectively to RC fiber due to agglomeration that occur at high fiber content. On top of that, Ren et al. (2014) also observed that the flexural strength was reduced when the bamboo fiber was increased up to 50%, and this might be due to the fiber agglomeration, which reduced the contact area between the fiber and the matrix [18].

Apart from that, uneven distribution of the fibers or the failure of PHB to form a continuous phase in the biocomposites might also contribute to the decrease in flexural strength at high fiber loading. This was due

to poor interaction between PHB and fiber, which was insufficient to cover all the surfaces of the fibers[19]. Moreover, it was predicted that the interfacial bonding of regenerated cellulose to PHB matrix was weak.
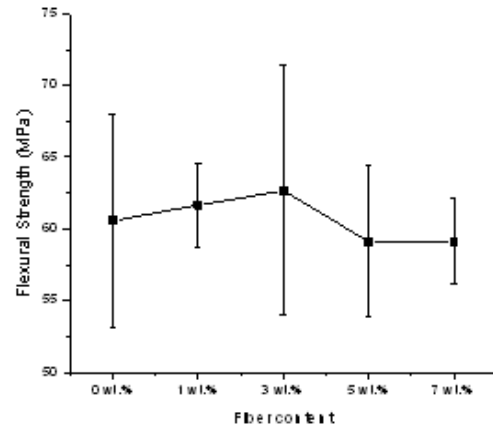

Figure 6 Flexural strength of pure PHB and regenerated cellulose/PHB.

From Figure 7, it can be seen that the flexural modulus increased steadily until 3 wt.% RC loading. Further increase in the RC loading slightly decreased the flexural modulus. This increment could be explained by the efficient load transfer from matrix to RC in the compressive load bending testing. In addition, Sawpan et al. (2012) reported that the value of flexural strength increased with the increment of untreated hemp fiber in the polylactic-acid (PLA) composite[20].
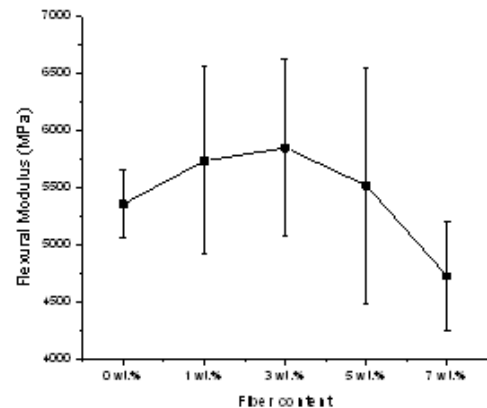

Figure 7 Flexural modulus of bending in pure PHB and regenerated cellulose/PHB

4.0 CONCLUSION

Regenerated cellulose was prepared by using NaOH/urea aqueous solution. Besides, TGA analysis revealed that the regenerated cellulose had lower thermal stability than the cellulose, while DSC results showed that the cellulose had higher endothermic peak at 319.67 °C, and the exothermic peak for regenerated cellulose was at 314.83 °C. Moreover, the

regeneration process of cellulose led to a change in the FTIR spectra, in which some of the bands reduced in intensity, whereas some disappeared in the regenerated cellulose. In addition, the regenerated cellulose (RC)/poly(3-hydroxybutyrate)(PHB) composites melted when compounded with various RC contents. In fact, TGA analysis revealed that the incorporation of RC fiber into PHB did not give any significant improvement in the thermal stability of the composite. Furthermore, flexural testing of composite was observed to increase. 3 wt. % of RC/PHB indicated the maximum loading, contributing to the flexural strength as high as 62.65 MPa, and flexural modulus at 5848.08 MPa.

Acknowledgement

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