



## Characterization and biodegradation study of polymer hydrogel composite based on natural fibers

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### Abstract

Polymer hydrogel composites of poly acrylic acid based on plant natural fibers were characterized using Fourier-transform Infrared Spectroscopy. The effect of plant natural fiber on thermal stability and biodegradation of polymer hydrogels was investigated using thermogravimetric analysis and burial test respectively. Surface morphology of polymer hydrogel composites was studied using scanning electron microscopy. Polymer hydrogel based on cotton natural fiber seems to have higher thermal stability and biodegradation rate than plain and oil palm empty fruit bunch based hydrogels. Bigger pores sizes were observed with polymer hydrogel grafted cotton fiber. Fiber size distribution revealed that cotton fiber has higher aspect ratio than oil palm empty fruit bunch. However, 65 % of cotton fiber has the size of less than 30 micron in contrast to 60 % of oil palm empty fruit bunch of range 90-70 micron

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### 1. Introduction

Biodegradability is defined as decomposition or deformation of the materials by microorganism's attack such as fungi, bacteria, yeasts and their enzymes. These microorganisms consume the substance as a food under appropriate condition [1]. The biodegradation of synthesized polymer is mainly depended on the polymer molecular weight (MW). High MW prevents the polymer to pass through the plasma membrane of microbial cells. There is one way to enhance the biodegradation of synthesized polymer of high MW, and that is to insert highly biodegradable components into the main polymer backbone [2, 3]. Plant natural fibers (PNF) of high percentage of cellulose are highly biodegradable materials therefore they have the possibility to be used for enhancing the biodegradability of polymer hydrogels (PHG). Toshio Yoshimura and his colleagues have synthesized polymer hydrogel from cotton fiber and succinic anhydride without using cross linker via esterification process. This study stated that the hydrogel derived from cotton cellulose is biodegraded almost completely after 25 days in contrast to 10% degrade of

conventional sodium polyacrylate hydrogel by using biological oxygen demand (BOD) testing as illustrated in Figure 1. They describe the different in biodegradation of the hydrogels as a result of different networks chemical bonding. Sodium polyacrylate hydrogel has an ether linkage that is more stable and hard to degrade in contrast to ester linkage of cotton hydrogels [4]. Most of the earlier works on thermal stability of PHGC have been done on polymer hydrogel filled with minerals and a very few work on PHGC based plant natural fibers. The effect of microfibril of sodium humate (SH) of thermal stability of guar gum-g-polysodium acrylate (GG-g-PNaA) has been studied. The work has reported that SH has positive effect on thermal stability due to the formation of chemical bonds between SH and GG-g-PNaA polymer network [5]. The effect of cotton fiber on thermal stability of poly acrylic acid (PAA) has been investigated by Sunil K. Bajpai using TGA. The result of this work indicated that cotton fiber has higher thermal stability than PAA-g-cotton fiber. In addition, the works described that biphasic

decomposition of grafted fiber in contrast to one phase in plain cellulose fiber [6]. Another work has reported the effect of wheat straw (WS) on thermal stability of PAA. TGA graph shows decreasing in thermal stability of PAA via grafted with WS as shown in Figure 2. In this article, sample preparation and the material are paralleled with our previous work [7]. The samples formulations of polymer hydrogels throughout this work were 1.5, 0.15, 13.5 and 14.5 of APS, MBA, NaOH and natural fibers respectively.

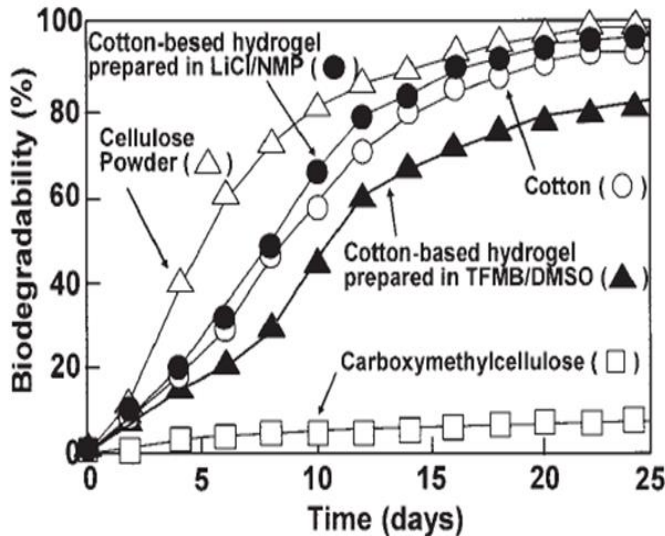


Figure 1: Biodegradability of various polymer hydrogel materials evaluated at 25 °C [6]

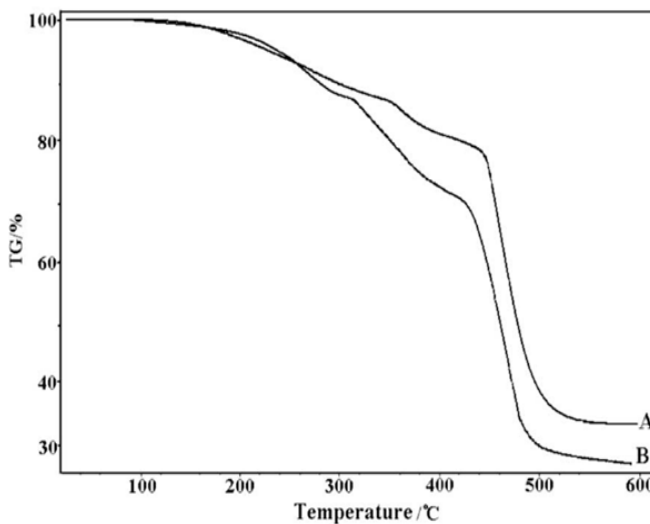


Figure 2: TGA curves of PAA (A) and WS/PAA (B) superabsorbent composite at a heating rate of 10 °C/min [6]

## 2. Characterization

### 2.1 Fourier-transform Infrared (FTIR) Spectroscopy

Fourier-transform infrared (FTIR) spectroscopy is used to perceive the existence of functional groups of the materials.

According to FTIR result the chemical compositions of the material were predicted before and after the compounding. The function groups of CTN, OPEFB, PHG-g-CTN, PHG-g-OPEFB and plain PHG samples were characterized using FTIR (Perkin-Elmer 180 spectroscopy. to identify the functional groups and match the chemical structure of PHG sample. Samples in a powder form were ground along with dried KBr powder in ratio of 1:10 and placed in the sample holder. FTIR spectrum was subjected from 4000 to 450  $\text{cm}^{-1}$ .

### 2.2 Thermal Stability

Thermal stability of the polymer is usually inspected using thermogravimetric analysis (TGA) which is depending on the weight change of a sample subjected to controlled temperature. TGA was used to study the thermal stability of CTN, OPEFB, PHG-g-CTN, PHG-g-OPEFB and plain PHG samples were and to analysis the effect of CTN and OPEFB microfiber on thermal stability of PHG. A Perkin Elmer Thermogravimetric Analyzer (TGA 7) was utilized to study the thermal stability in terms of temperature decomposition. Approximately 8 mg of the sample were heated from 35 to 700 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

### 2.3 Morphology Analyses

Scanning electron microscopy (SEM) was used to study the surface morphology qualities of PHG-g-CTN, PHG-g-OPEFB and plain PHG. The samples were immersed in distilled water for 24 hours and then filtered by sever to remove the unabsorbed water and scanning by SEM at 250 X magnification. Samples were examined using HITACHI TM3000 scanning electron microscopy (SEM). In addition, the physical appearances of the samples were observed and pictures snapped using digital camera.

### 2.4 Particle Size Distribution

This test was used to discover the size range distribution of the fibres partials. Sieves of 100-30 micron were used to separate the fibres then the percentage of each size was calculated.

## 3. Biodegradation Study

Soil burial test was used to simulate the natural biodegradation of PHG-g-CTN, PHG-g-OPEFB and plain PHG. Certain weights ( $W_0$ ) of the Samples were buried in sandy and multipurpose compost soil for interval time 1-16 weeks. The compost materials that attached to the specimen's surface were removed and washed in running water. After that the samples were dried till constant weight ( $W_1$ ). Weight loss of the buried samples was calculated using Equation 1.

$$\text{weight loss \%} = \frac{W_0 - W_1}{W_0} \times 100 \quad (1)$$

Where  $w_0$  is initial samples weight,  $w_1$  is samples weight after interval time.

#### 4. Result and Discussion

##### 4.1 FTIR Analysis

FTIR spectroscopy is considered an effective way for identifying the chemical composition of inorganic and organic materials. FTIR spectroscopy has been used for many decades to characterize the polymers chemical structure and showed a sufficient result particularly in newly formed chemical bonds. FTIR spectrums OPEFB, PHG-g-OPEFB, CTN, PHG-g-CTN and plain PHG are shown in Figure 3. The multiband at 3300-3846  $\text{cm}^{-1}$  which corresponded to different kind of O-H stretching groups (water, cellulose and lignin) and N-H stretching of MBA. The bands at 2917 and

2923  $\text{cm}^{-1}$  are corresponding to C-H stretching. The bands at 1635  $\text{cm}^{-1}$  are corresponding to C=O groups of PAA, MBA. The bands at 2917-2895.18  $\text{cm}^{-1}$  in sample OPEFB, PHG-g-OPEFB, CTN and PHG-g-CTN are corresponding to C-H stretching vibration from cellulose molecules. This band is absent in the plain PHG sample.

The broads from 1450-1700  $\text{cm}^{-1}$  in all samples are corresponded to N-H binding C=O and C=C of MBA and PAA and aromatic groups of plant natural fiber respectively [8, 9]. The sharp bands 1057 and 1052 in spectrum of CTN and OPEFB respectively are corresponding to C-O-C of the aromatic rings of the cellulose. However, similar bands can be seen in the spectrums of PHG-g-OPEFB and PHG-g-CTN at 1053  $\text{cm}^{-1}$  which is not existence in plain PHG spectrum which is considered the main evidence for the grafting between PAA and the natural fibers [10].

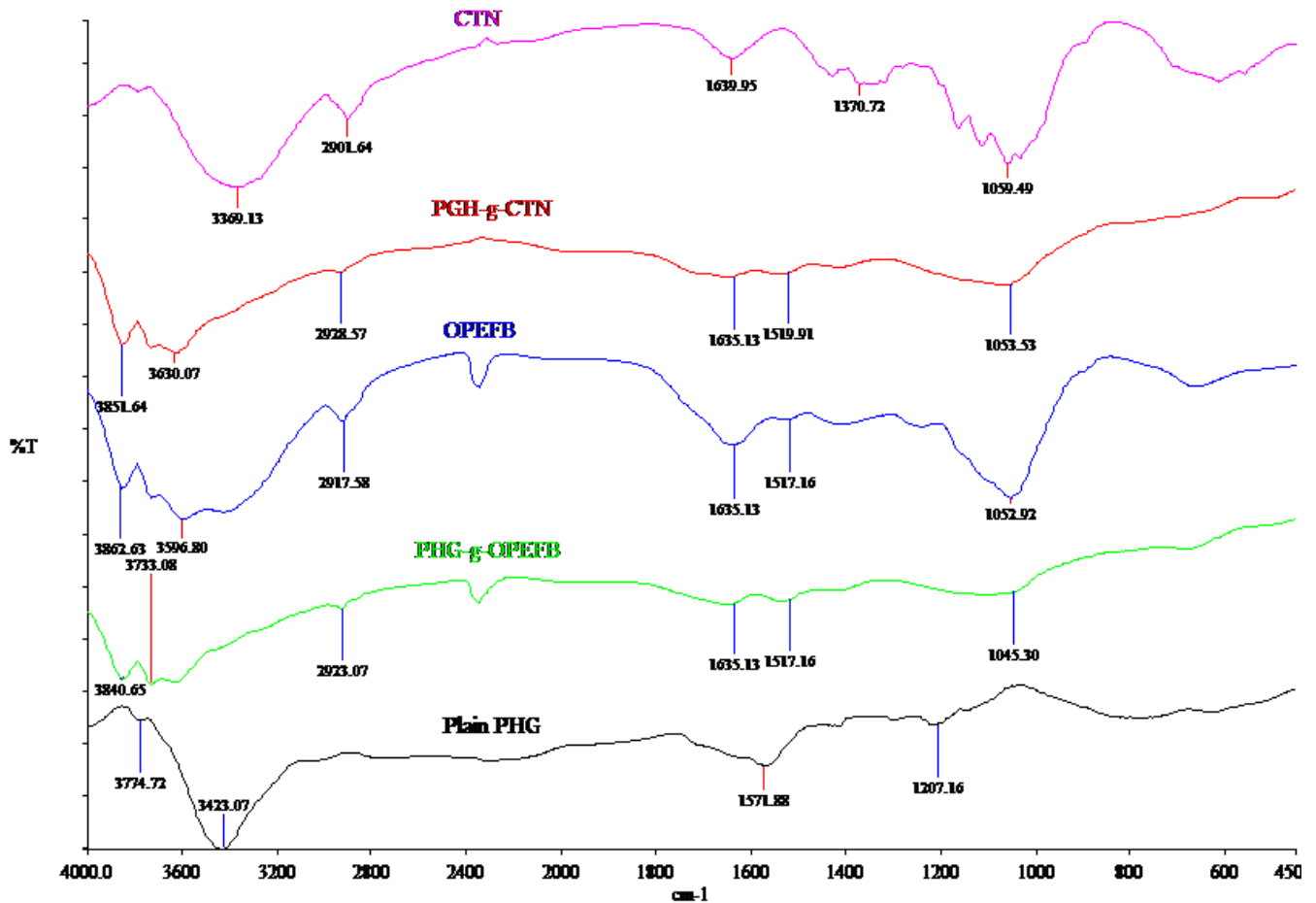


Figure 3: FTIR spectrums of OPEFB, PHG-g-OPEFB, CTN, PHG-g-CTN and plain PHG.

##### 4.2 Thermal Stability

The result of thermo-gravimetric analysis of CTN, OPEFB,

plain PHG, PHG-g-OPEFB and grafted PHG-g-CTN are shown in Figure 4. The initial weight loss of the samples is representative of dehydration process which indicates the

percentages of moisture in each sample. The result indicated that CTN fiber begin to decomposed at 350 °C with rapid thermal degradation and the sample lost more than 90% of its weight at 400 °C in contrast with OPEFB fiber which begin to decomposed at 250 °C with rapid thermal degradation and the sample lost more than 60 % of its weight at 350 °C which means CTN fiber has more thermal stability than OPEFB fibers. Plain PHG and grafted PHGs exhibited initial decomposition temperature of 150 °C and multiphase decomposition in contrast with the natural fibers. Multiphase degradation is attributed to decomposition of different groups of the composite. Moreover, grafted PHG shows higher thermal resistant than PHG as a result of enhancement of thermal stability via using CTN and OPEFB fiber. The improvement in the thermal stability of PHG via using OPEFB is an indication for grafting between the fiber and the polymer chains. Moreover, PHG-g-CTN is more stable thermally than PHG-g-OPEFB as a result of the chemical composition of the natural fiber which natural fiber of high cellulose constant is higher thermal stability than that of less cellulose content. Fiber of high cellulose content might lead to increase the crosslinking density which enhances the thermal stability. In addition, DTG diagrams of the samples in Figure 5 indicated the single and multiphase transition point. Both fibers have a single transition point in contract to multi point in polymer hydrogel samples [11, 12].

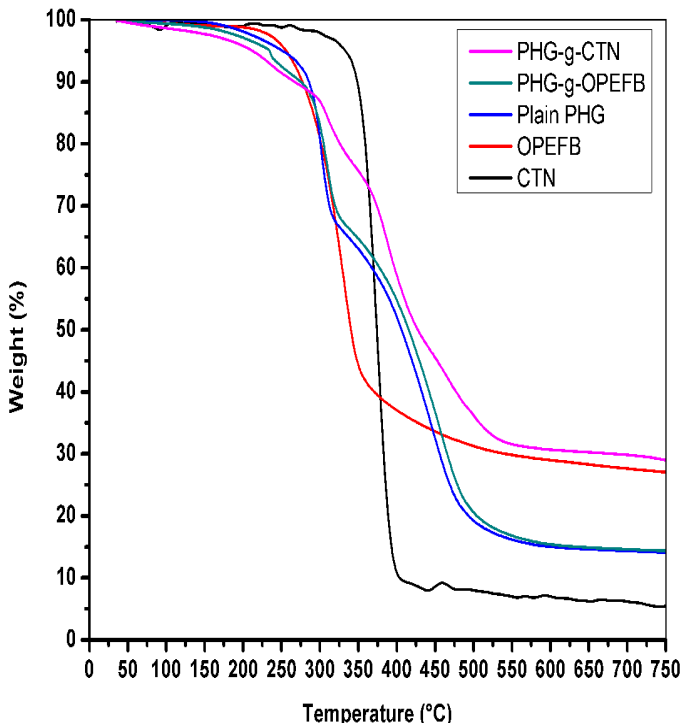


Figure 4: Thermo-gravimetric analysis of CTN, OPEFB, plain PHG, PHG-g-OPEFB and grafted PHG-g-CTN.

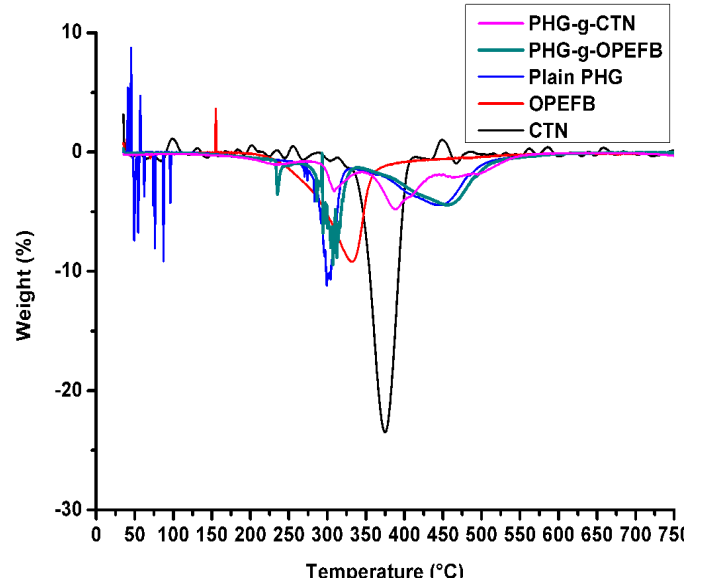


Figure 5: DTG diagrams of CTN, OPEFB, plain PHG, PHG-g-OPEFB and grafted PHG-g-CTN.

#### 4.3 Morphology Study

Scanning electron microscopy (SEM) is regularly used to analyze the pore structure and to observe the three dimensional network of polymer hydrogels. Surface morphology study result indicated that the grafted PHG-g-CTN has bigger pore size approximately 100-208  $\mu\text{m}$  in diameter follow by PHG-g-OPEFB of 74-100  $\mu\text{m}$  than that of plain PHG 20-70  $\mu\text{m}$  as shown in Figure 6 (a),(b) and (c). Bigger pore size allowed more water to penetrate the network and enhance the final swelling rate and absorption capacity. Water absorption capacities of the samples are in the same order as a result of porous size of each sample. In addition, the digital image in Figure 6(d) shows the outer physical appearance of swollen samples of grafted and plain PHG. Plain PHG seems to have transparence structure in contrast with grafted ones.

#### 4.4 Fiber Size Distribution

The result in Figure 7 revealed that 64 % of CTN in the range of 0-30 micron and 61 % of OPEFB fiber in the range of 60-70 micron. This means, the enhancement of water absorption capacity (WAC) of PHG-g-CTN might be as a result of small size fiber. Fiber of small size led to produce hydrogel with homogenous pore size. In addition, fiber of small size has an advance of more surface area which led to increase the amount of trapped water molecules. Moreover, bigger fiber size of OPEFB led to produce heterogenous pore size as shown in SEM images in section 4.3 and low WAC hydrogel. CTN fiber give the impression to has high aspect ratio over OPEFB fiber as illustrated in SEM images of Figure 8.

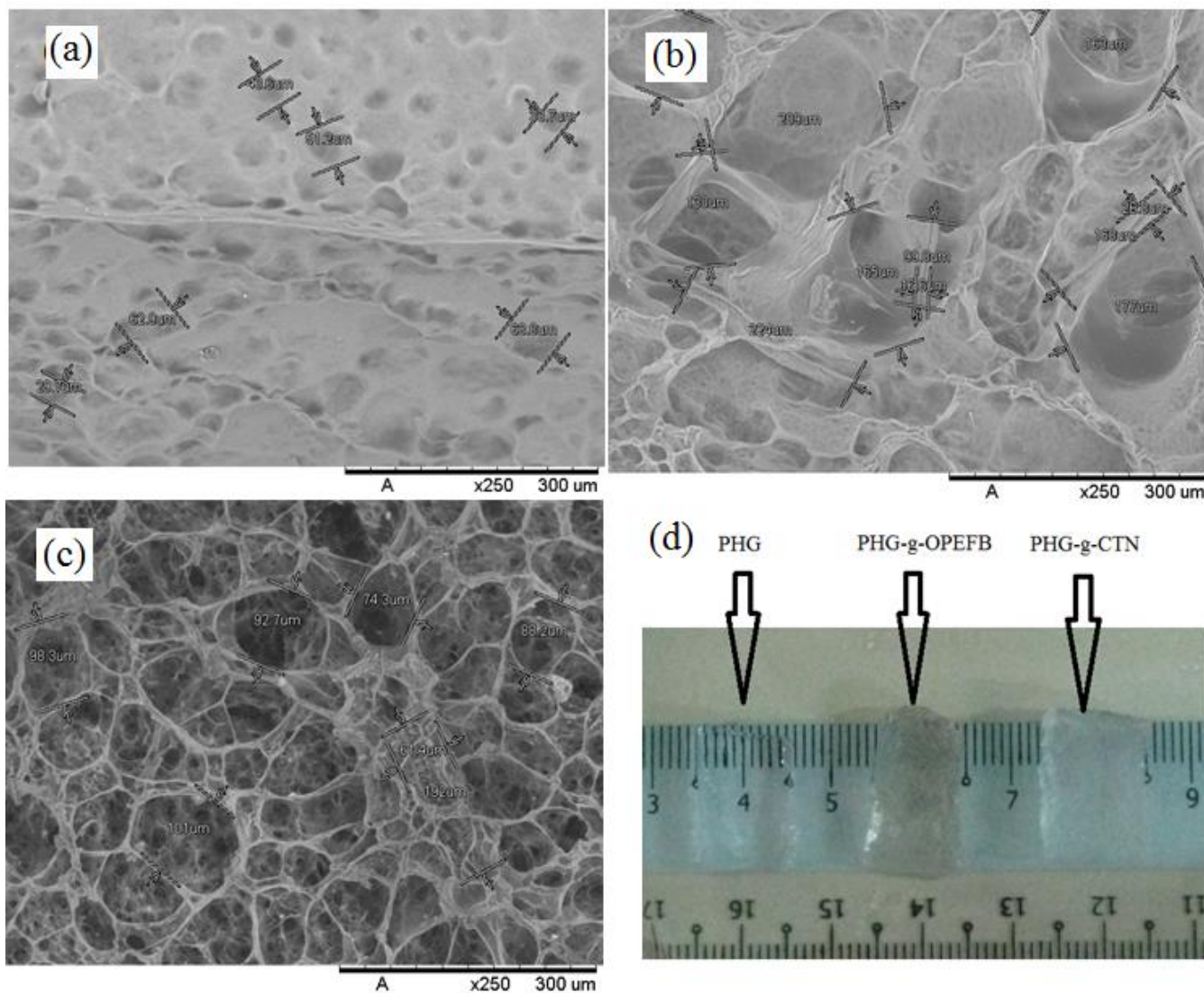


Figure 6: SEM and digital image of a) Plain PHG, b) PHG-g-CTN, c) PHG-g-OPEFB, d) digital image.

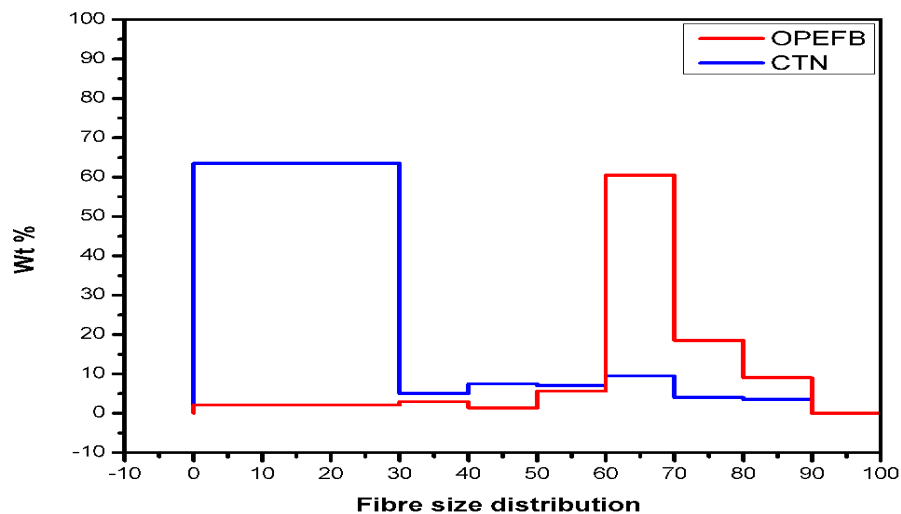


Figure 7: Fiber size distribution of CTN and OPEFB

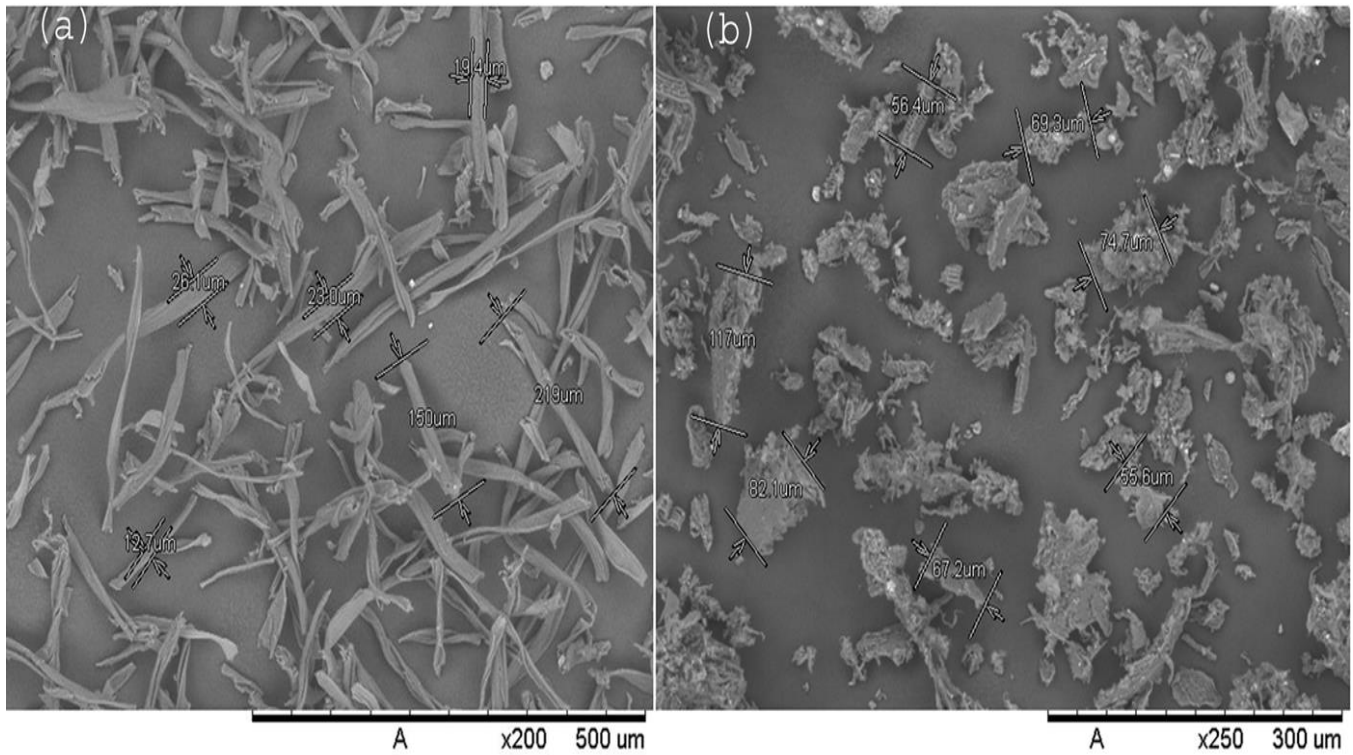


Figure 8: SEM images of OPEB and CTN fiber

#### 4.5 Biodegradation of PHG Composites

First step of biodegradation mechanism is chain cleavage which the polymer chains are converted into their oligomers and monomers (depolymerization). The resulting oligomers and monomer are smaller in size which can be easy to transported into the cytoplasmic cells of the microorganism and get completely mineralized. In the mineralizing process, various byproducts such as carbon dioxide, water, methane are formed. During these steps, the microorganism attached the surface of the hydrogels by the enzymes which led to change the surface morphology as can be seen in Figure 9. The results of biomass biodegradation are carbon dioxide and water under aerobic condition, and carbon dioxide methane and water under anaerobic condition. Microorganisms are capable to degrade cellulose and producing a set of enzymes. Generally, first step of polymer biodegradation is transforms the long polymeric chains into monomeric and oligomeric products which can be easily absorbed by microorganisms [13]. Results in Table 1 show that there is no loss in samples weight for first three weeks. PHG-g-CTN was the first sample started loses weight and degrade followed by PHG-g-OPEFB and PHG. As it can be observed from the results after 16 weeks, the amount of weight loss is 13.9 % in PHG-g-CTN, 4.7 % in PHG-g-OPEFB and 0.1 % in PHG. In addition,

same order was observed in terms of degradation rate. The higher degradation rate in the hydrogel composites is a result of the initiation of enzymatic degradation of the fiber cellulosic chains. Furthermore, the higher cellulose content of CTN fiber led to higher water adsorption which has a synergetic effect on the rate of biodegradation of PHG-g-CTN comparing to PHG-g-OPEFB. Moreover, the percentage of ash or low biodegradable contents in the natural fiber reduces the biodegradation of the polymeric materials. The high molecular weight and insolubility of lignin reduce its biodegradation which means PHG-g-OPEFB has lower biodegradation rate in contrast to PHG-g-CTN due to high content of lignin in OPEFB. Biodegradation of plain PHG and PHGC in compost result in Table 2 show similar trend with the burial in sandy soil in terms of biodegradation rate of the samples. The maximum weight loss of 23.6 % was recorded with PHG-g-CTN followed by 9.3 % for PHG-g-OPEFB and 0.1 for plain PHG after 16 weeks from the burial. Using compost as burial medium enhanced the biodegradation of PHGCs due to the high microorganism species are living in this kind of medium. In addition, Plain hydrogel sample shows resistance to the microorganism in the compost medium and that is similar result of the burial in sandy soil.

Table 1: The result of biodegradation burial test in compost soil

Sample	Weight loss %						
	week						
	2 <sup>nd</sup>	4 <sup>th</sup>	6 <sup>th</sup>	8 <sup>th</sup>	10 <sup>th</sup>	12 <sup>th</sup>	16 <sup>th</sup>
Plain PHG	0	0	0	0.01	0.01	0.1	0.1
PHG-g-CTN	0	0.11	0.23	1.9	14.7	18.1	23.6
PHG-g-OPEFB	0	0.03	0.07	0.52	1.8	5.6	9.3

Table 2: The result of biodegradation burial test in sandy soil

Sample	Weight loss %						
	week						
	2 <sup>nd</sup>	4 <sup>th</sup>	6 <sup>th</sup>	8 <sup>th</sup>	10 <sup>th</sup>	12 <sup>th</sup>	16 <sup>th</sup>
Plain PHG	0	0	0	0	0	0.1	0.1
PHG-g-CTN	0	0.053	0.1	0.9	3.4	9.1	13.2
PHG-g-OPEFB	0	0.01	0.09	0.3	0.8	1.5	4.7

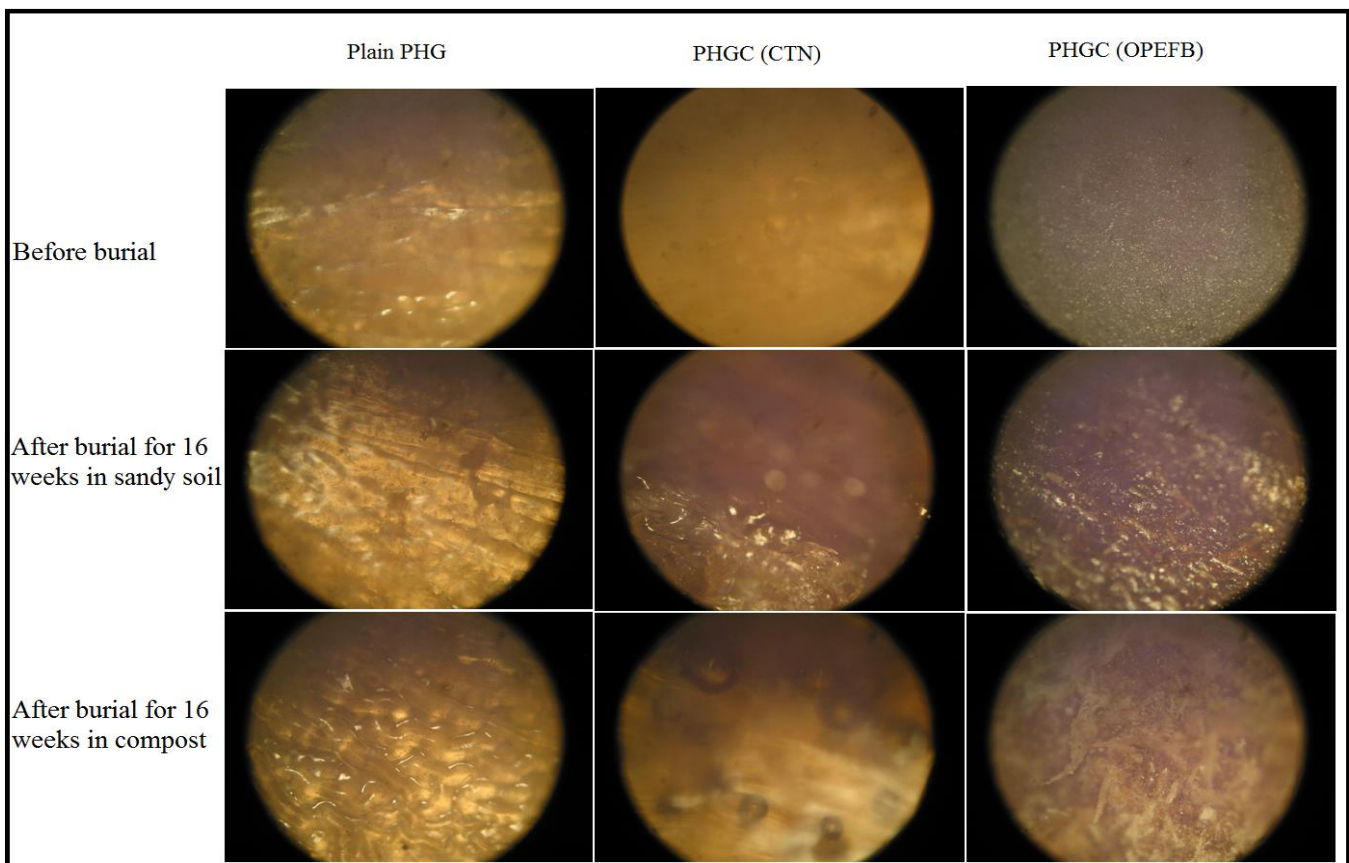


Figure 9: Biodegradation of PHG-gCTN, PHG-g-OPEFB and plain PHG in sandy soil and compost for 16 weeks.

## 5. Conclusion

Plant natural fibres of OPEFB and CTN have remarkable effect on biodegradation of polymer hydrogels of poly acrylic acid. Biodegradation rates were increased via using plant natural fibres. Polymer hydrogel composite based high cellulose content fibre has high biodegradation rate and thermal stability than that of less cellulose content based. Both fibres have narrow size distribution and different

particle size range which CTN fibre had smaller particle size than OPEFB.

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