The National and International Graduate Research Conference 2017
March 10, 2017 : Poj Sarasin Building, Khon Kaen University, Thailand

IPMP2

Liquid Absorption using 3D Carbon Nanofiber Scaffolding Derived from Bacterial Cellulose

Surachat Sombat* Nipaporn Sriplai** Dr.Supree Pinitsoontorn***

ABSTRACT

3D carbon nanofiber scaffolding was produced from the pyrolysis of freeze-dried (FD) bacterial cellulose (BC). The thermogravimetry and differential thermal analysis (TG/DTA) showed the weight loss of BC during the pyrolysis process. The X-ray diffraction technique showed the high crystallinity of the FD-BC and the high amorphousness of the carbon nanofibers. Both FD-BC and the pyrolyzed carbon nanofibers consisted of tiny fibers with the size of<100 nm. The liquid absorption capacity using FD-BC and carbon nanofibers was tested by measured the weight before and after absorption. It was found that the FD-BC was good for water absorption due to the hydrophilic nature of the sample. For the organic solvent, ethanol, methanol, benzene, and palm oil, the hydrophobic carbon nanofibers had the absorption capacity of nearly hundred times of their own weight.

Keywords: Bacterial cellulose, Carbon nanofiber, Liquid absorption

*Student, Master of Science Program in Materials Science and Nanotechnology, Department of Physics,Faculty of Science, Khon Kaen University

**Student, Doctor of Philosophy Program in Materials Science and Nanotechnology, Department of Physics, Faculty of Science, Khon Kaen University

*** Associate Professor, Department of Physics, Faculty of Science, Khon Kaen University

The National and International Graduate Research Conference 2017
March 10, 2017 : Poj Sarasin Building, Khon Kaen University, Thailand

IPMP2-2

Introduction

Cellulose is one of the most important natural polymers. It is an almost inexhaustible raw material and a key source of sustainable materials on an industrial scale(Klemm et al. 2005). Recently, a special natural cellulose, i.e. bacterial cellulose (BC) has gained particular interest. BC is commonly produced from the Gluconacetobacterbacteria. Although the chemical constitution of BC is the chain molecules linked by cellobiose, same as other celluloses, it is free of contaminant molecules, such as lignin, hemicelluloses, and pectin, etc., which are normally found in plant-derived cellulose(Huang et al. 2014). Fibril networks of BC consisting of well-arranged three-dimensional nanofibers with extremely high surface area and porosity (Katepetch et al. 2011). Moreover, the degree of polymerization(DP) of BC is very high, with DP values of 2000-8000. Crystallinity is also high, with values of 60 – 90% (Klemm et al. 2005). As-synthesized BC contains extremely high water content of 90% or more, and remains always wet unless drying process is applied, making it naturally never-dried hydrogels.

Due to its unique structures and properties, BC has been applied to a variety of fields, which can be broadly classified into medical applications and non-medical applications. For non-medical applications, BC has been used as diaphragms for loudspeakers(Iguchi et al. 2000), food packaging films (Wanichapichart et al. 2012), silk fabrics reinforcement for storage and display (Wu et al. 2012). Moreover, BC have been extended in diverse fields such as electronics (Shah and Brown 2005), paper industry (Surma-Slusarska et al. 2008), sewage purification (Chen et al. 2010), photocatalyst (Zhang et al. 2011) and biosensor (Zhang et al. 2010).

In particular, the sewage purification is very important for solving environmental problem. It was reported that BC could be used to separate heavy metal ions,e.g. Cu^{2+} and Pb^{2+}, from wastewater or aqueoussolutions(Chen et al. 2010). On the other hand, carbon-based aerogelswere demonstrated as the organic liquid absorbents. For example, carbon nanotube (CNT) sponge, synthesized by chemical vapor deposition, formed a three-dimensionally interconnected framework of nanotubes(Gui et al. 2010). The sponges were very light, highly porous, hydrophobic in pristine form, and could float on water surfaces and absorb large-area spreading oil films. Furthermore, another research showed that graphene framework architecturecould be used as an absorbent for oils and organic solvents, with a high absorption capacity (Zhao et al. 2012).

In this paper, we demonstrate the liquid absorption capacity of the three dimensional(3D) carbon nanofiber scaffolding derived from the pyrolysis of BC. The BC was freeze-dried prior to the pyrolysis. The absorption capacity of five types of liquid (water, ethanol, methanol, benzene, palm oil) was studied.

Objective of the study

To study the liquid absorption capacity of the 3D carbon nanofiber scaffolding derived from the pyrolysis of freeze-dried BC.

Materials and Methods

Sample Preparation and Characterization

Bacterial cellulose (BC) was purchased in the form of nata de coco (coconut gel in syrup, Chao Koh brand, Figure 1a). To remove the syrup, the BC was washed with deionized (DI) water for 8 hours with stirring. The DI water was changed every 30 minutes. After that it was soaked in the DI water for 16 hours (Figure 1b). The stirring and soaking processes were alternated for the length of 3 days. At this stage, large amount of water was in the nanostructure of BC. It had a shape of a wet gel, which is called the never-dried BC. After removing the syrup and water, the BC was blended in an electrical blender (Figure 1c). Then, the BC was dried in the freeze-dried (FD) process at the temperature of -60 $^\circ$C for 5 days until all the liquid was removed (Figure 1d). The FD process was chosen because it could preserve the nanofiber structure of the BC. The FD-BC was cut into pieces with the size of $3 \times 3 \times 2$ cm^3 approximately (Figure 1e). To obtain carbon nanofiber, it was pyrolyzed at 700 $^\circ$C under continuous Ar gas flow. Two-step heating rates were employed. From room temperature to 500 $^\circ$C, the heating rate was 2 $^\circ$C/min. From 500 $^\circ$C to 700 $^\circ$C, the rate of 5 $^\circ$C/min was chosen. It was hold at 700 $^\circ$C for 2 h before cooling down to room temperature. Figure 1f shows the image of carbon nanofiber after the pyrolysis process.

The BC and carbon nanofibers were characterized using several techniques. The never-dried BC and FD-BC was subjected to thermogravimetry (TG) and differential thermal analysis (DTA) using Hitachi, STA7200, Japan. The phase and crystal structure of the FD-BC and pyrolyzed FD-BC were analyzed using the X-ray diffraction (XRD) with K-α radiation (PANalytical, Empyrean, USA). The morphology of the nanostructure of both FD-BC and pyrolyzed FD-BC was studied using the scanning electron microscope (SEM: LEO, 1450VP, UK).
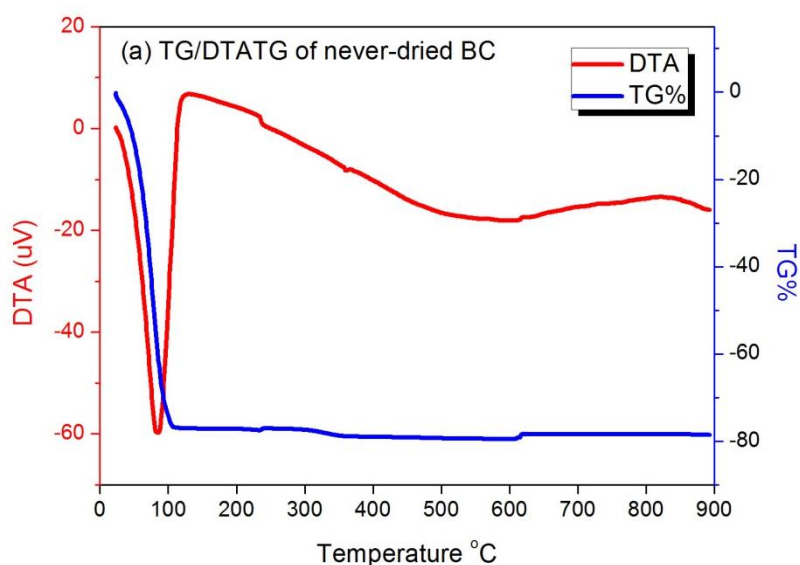
The National and International Graduate Research Conference 2017
March 10, 2017 : Poj Sarasin Building, Khon Kaen University, Thailand

IPMP2-4

Figure 1 Processing of BC: (a) as-purchased BC in the form of Nata de coco (Coconut gel in syrup, Chao Koh), (b) BC soaked in water to remove syrup, (c) BC after blending, (d) BC after freeze-dried, (e) FD-BC cut into pieces, (f) carbon nanofiber obtained from the pyrolysis of FD-BC.

The National and International Graduate Research Conference 2017
March 10, 2017 : Poj Sarasin Building, Khon Kaen University, Thailand

IPMP2-5

Liquid absorption test

Five types of liquid were used to test the absorption capability of the samples: water, ethanol, methanol, benzene, and palm oil. The carbon nanofibers derived from FD-BC after pyrolysis was weighed before soaking in any liquid. It was then soaked in the tested liquid for 2 minutes, and the weight was measured again. To release the liquid, it was baked in the 95 $^{\circ}$C oven for 2 hours (except the palm oil which was burned using a lighter) to ensure that no residual liquid remained. The process was repeated to test the cyclic ability of carbon nanofiber in liquid absorption. The weight before and after liquid absorption for each cycle was analyzed. Since the FD-BC had the hydrophilic nature (Olsson et al. 2010, Zhang et al. 2011), it was tested for water absorption (but not for other liquid).

Results

The thermal behavior of the BC was studied using the TG/DTA technique as shown in Figure 2. Figure 2a shows the TG/DTA curves of the never-dried BC. It is clear that most of the weight was lost (nearly 80%) at the temperature < 100 $^{\circ}$C alongside with the huge endothermic peak. This is attributed to the loss of water molecules because the never-dried BC contains a significant amount of water. Another slight weight loss was found around 300-350 $^{\circ}$C together with a small endothermic peak. It is attributed to the change from the BC molecules to carbon fibers by decomposing the functional (–OH) groups. (Iguchi et al. 2) Figure 2b shows the TG/DTA of the FD-BC. Unlike the never-dried BC, the significant weight loss below 100 $^{\circ}$C was not obviously observed because most water molecules were already extracted in the FD process.The majority weight loss was found at around 300-350 $^{\circ}$C, with the presence of the endothermic peak. This weight loss again was due to the decomposition of the chemical functional groups of BC, and the transformation to carbon nanofibers. (Huang et al. 2014)
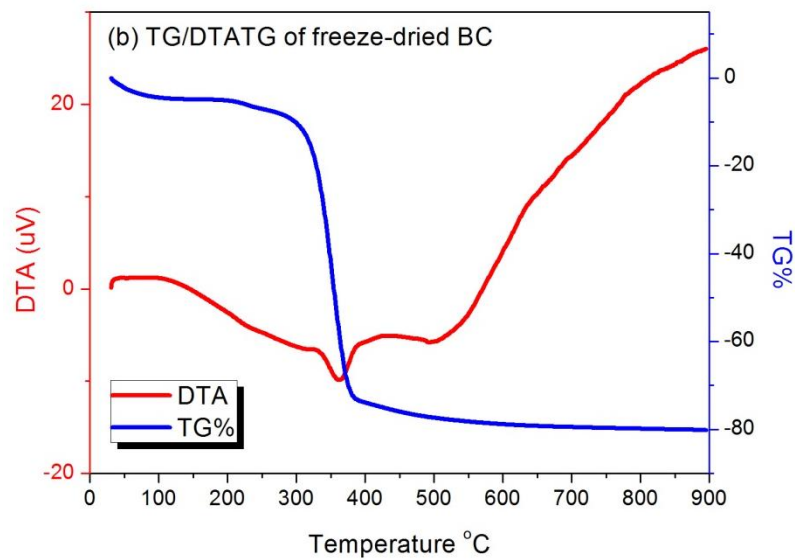
The National and International Graduate Research Conference 2017
March 10, 2017 : Poj Sarasin Building, Khon Kaen University, Thailand

IPMP2-6

Figure 2 TG/DTA graphs of **(a)** never-dried BC, and **(b)** freeze-dried (FD) BC.

The phase and crystal structure of the FD-BC and the pyrolyzed FD-BC were investigated using the XRD technique as shown in Figure 3. It can be clearly seen the diffracted peaks of the FD-BC, with the strong peak at 23 $^{\circ}$. This clearly indicates the crystalline structure of the BC. Our XRD patterns match really well with the previous reports (Zheng et al. 2013). On the other hand, for the pyrolyzed FD-BC, the diffracted peaks were totally disappeared. Only the broad hump was observed. This shows the destruction of the crystallinity and the formation of the amorphous phase. It is thus confirmed that the pyrolysis process promoted the formation of carbon nanofiber which possessed the amorphous structure. (Chen et al. 2010)
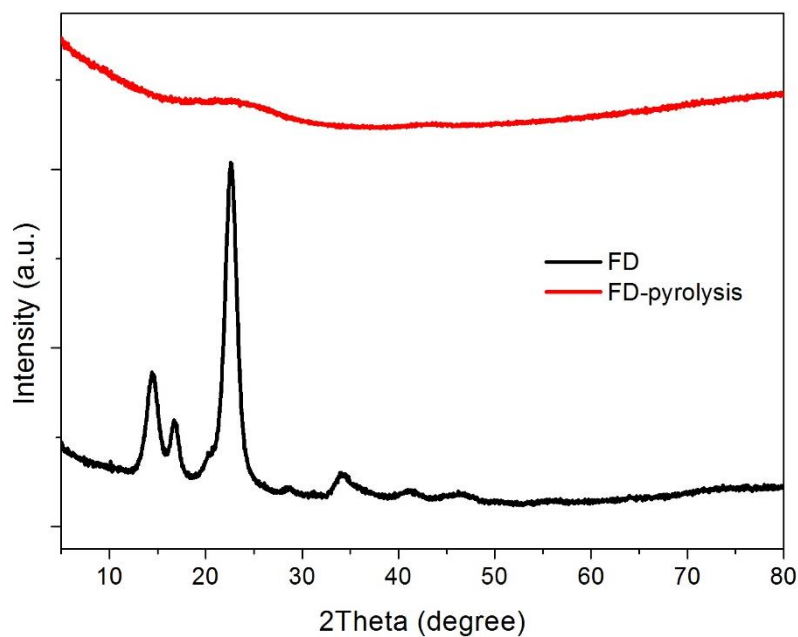

Figure 3 XRD pattern of FD-BC (black) and pyrolyzed FD-BC (red).

The National and International Graduate Research Conference 2017
March 10, 2017 : Poj Sarasin Building, Khon Kaen University, Thailand

IPMP2-7

The SEM images of the FD-BC are shown in Figure 4. It can be seen from the images that the nanofiber structure of BC was preserved from the FD technique. The diameter of each fiber is <100 nm wide. However, the nanofibers were bundled together. The 3D open structure of the BC previously reported (Katepetch and Rujiravanit 2011) was not present in our work. The main reason was probably due to our sample preparation process. The washed BC was blended by an electrical blender prior to the FD process, in order to obtain the larger size of the sample. The original size of the as-purchased nata de coco (Chao Koh) was too small for the liquid absorption test. The blending process might be the reason for the destruction of the 3D nanofiber network. Nevertheless, when the FD-BD had gone through the pyrolysis process to obtain the carbon nanofiber, the 3D open structure could be observed as shown in Figure 5. The size of each carbon nanofiber was less than 100 nm.   The carbon nanofiber scaffolding with high surface area was successfully produced which wasdesirable for high capability of liquid absorption.
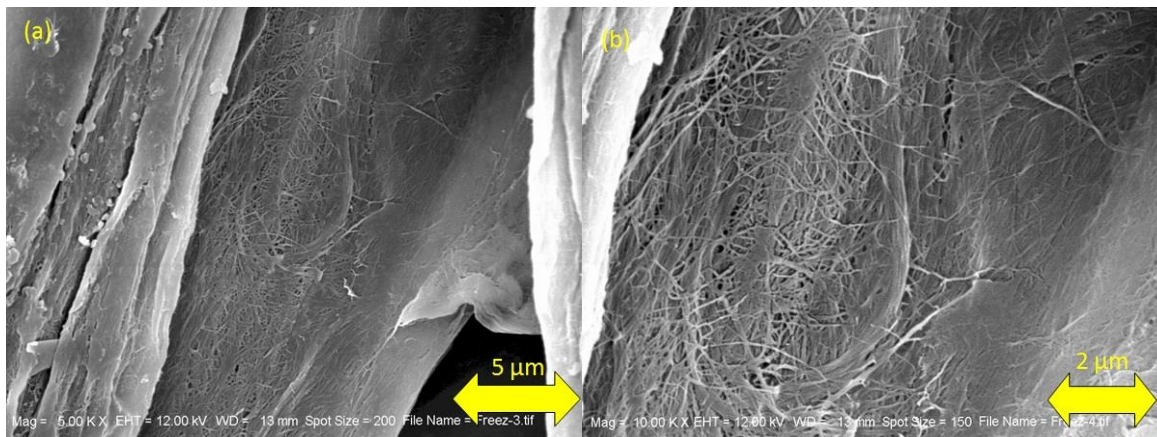

Figure 4   SEM images of the FD-BC showing the 3D network of nanofibers at the magnification of (a) 5 kX, (b) 10 kX.
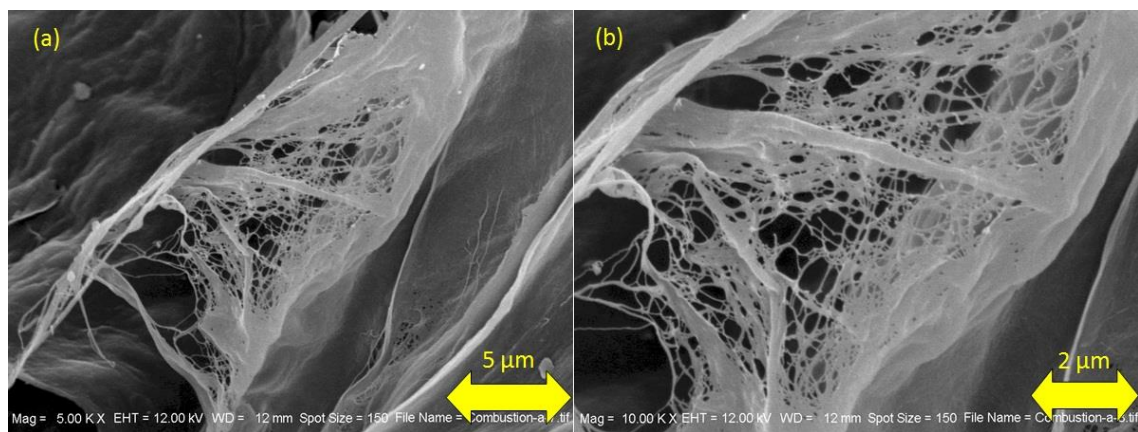

Figure 5   SEM images of the carbon nanofibers from pyrolysis of the FD-BC at the magnification of (a) 5 kX, (b) 10 kX.

The National and International Graduate Research Conference 2017
March 10, 2017 : Poj Sarasin Building, Khon Kaen University, Thailand

IPMP2-8

The FD-BC was tested for water absorption only whereas the carbon nanofibers were examined for the absorption of water, ethanol, methanol, benzene, and palm oil. Figure 6 shows the images of the experiments for the liquid absorption. The weight before and after liquid absorption is illustrated in Figure 7.

Figure 6 Liquid absorption experiment. From left, FD-BC soaked in water, carbon nanofibers from pyrolysis of FD-BC soaked in water, ethanol, methanol, palm oil and benzene (gasoline).

In Figure 7, the absorption experiments showed that the FD-BC and carbon nanofibers can adsorb the liquid for >600% (water) and several thousand % (other solvents) of their own weights. For the FD-BC, the cyclic absorption capability could be extended to 46 cycles (Figure 7a), due to its good mechanical properties (high toughness and ductility). Although the absorption weight% dropped significantly from 860% in the 1st round, the weight% was nearly constant around 200% from the 15th cycle onwards. This indicates the high stability of the FD-BC structure.

For the pyrolyzed carbon fiber, even though absorption weight% was as high as 700% in the 1st round, it decayed rapidly (Figure 7b). After the 9th round, it could not be recycled because of the brittleness of the sample. Furthermore, after the pyrolysis, the water absorption behavior has changed from hydrophilicity (FD-BC) to hydrophobicity (carbon nanofibers)(Zhang et al. 2011, Liu et al. 2015). Thus the carbon nanofibers in fact do not "like" water. In the experiment, we actually had to force it to adsorb water.

On the other hand, when in contact with other organic solvents, the 3D carbon nanofiber scaffolding could uptake large amount of liquid. As obviously seen in Figure 7(c-f), the weight% of the liquid absorption in ethanol, methanol, benzene and palm oil reached several thousands percent. It means the carbon nanofibers could absorb the liquid for several ten times of their own weights. Even though the absorption capability dropped quite rapidly from the 1st round, at 10th cycle, the weight percent were still more than 1000%. The exception was for the palm oil because in this case the palm oil was burned for evaporation instead of oven bake (due to high boiling point of 230°C). Due to the brittleness of the carbon nanofiber scaffolding, the structure could not be tolerated when handling with flame.
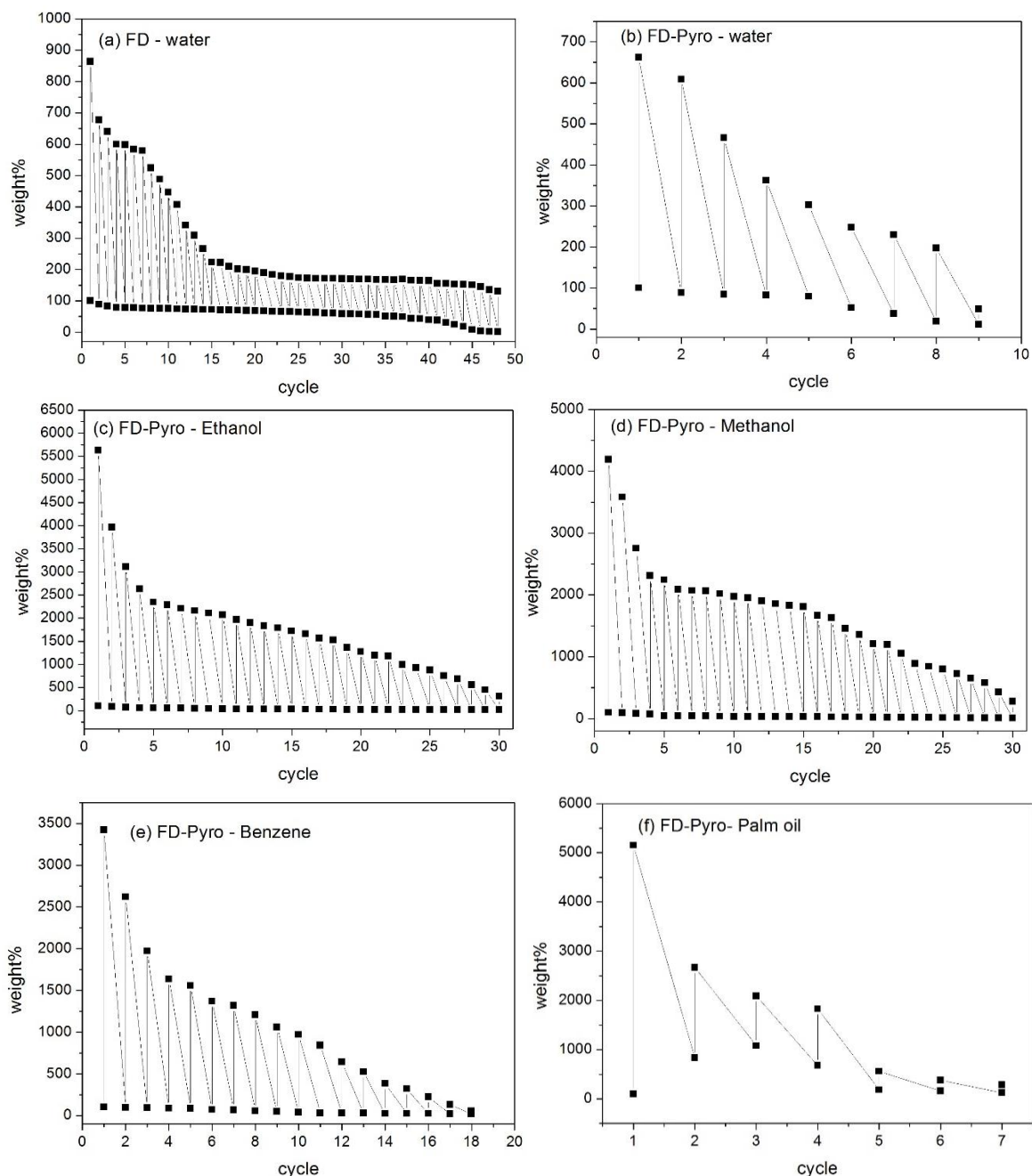
Figure 7 Cyclic measurement of weight before and after liquid absorption for (a) FD-BC in water, (b) – (f) carbon nanofibers in water, ethanol, methanol, benzene, and palm oil.

Figure 8 summarized the liquid absorption capacity in the 1st and 5th cycle. It can be seen that the FD-BC can absorb water better than the carbon nanofibers due to the hydrophilic behavior. On the other hand, the carbon nanofibers can absorb the organic solvent for several thousands percent due to the hydrophobic behavior. The absorption weight% dropped from the 1st to 5th cycles but the capacity was still very high. This implied that these materials could be recycled for at least 5 times.

The National and International Graduate Research Conference 2017
March 10, 2017 : Poj Sarasin Building, Khon Kaen University, Thailand
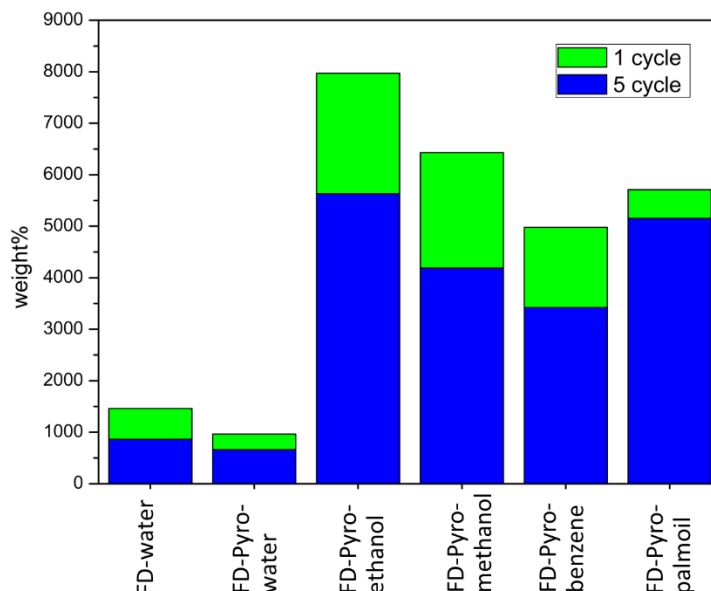
IPMP2-10

Figure 8 Summary of the liquid absorption capacity of FD-BD and carbon nanofibers (pyrolysis of FD-BC) in water, ethanol, methanol, benzene, and palm oil, at the 1st and 5th cycle.

Discussion

The pyrolysis of FD-BC changed the BC nanofiber structures into the carbon nanofiber scaffolding. It also changed the liquid absorption behavior from hydrophilicity to hydrophobicity(Zhang et al. 2011, Liu et al. 2015). The absorption of organic solvent can reach several thousand times of its own weight. However, the uptake of organic solvent of the carbon nanofiber scaffolding in this study was still less than the previous report using the carbon nanofiber aerogels (Wu et al. 2013). The main difference is the weak mechanical property of the carbon nanofibers in this study. It was be attributed to the blending process to obtain a larger size of samples. This process might have destroyed the 3D open structure of the nanofibers which act as a strong scaffold for mechanically supporting the whole structure. Another consequence of the blending process was the reduction of the surface area of the nanofibers. This decreased the contact area with the liquid, resulting in less liquid absorption. Therefore, in the future work, the blending process should be avoided. Instead, the BC should be grown in the lab to the desired size before freeze-drying process. This is the ongoing work in our lab.

Conclusions

In this paper, we have produced the 3D carbon nanofiber scaffolding from the pyrolysis of freeze-dried (FD) bacterial cellulose (BC). The carbon nanofibers scaffolding consisted of tiny fibers with the diameter less than 100 nm. The XRD analysis revealed that the crystallinity changed from the highly crystalline sample for FD-BC to the highly amorphous carbon nanofibers. The liquid absorption behavior was also changed from hydrophilicity before pyrolysis to hydrophobicity after pyrolysis. As a result, the FD-BC can absorb water as high as 10 times of its own weight. For the pyrolyzed carbon fibers, the absorption capacity exceeded several thousand percent, with the stability

for recycling more than 10 times. It is concluded that the carbon nanofibers had a potential in the sewage purification application for separating organic solvents from water.

Acknowledgements

References

Chen SY, Shen W, Yu F, Hu WL, Wang HP. Preparation of Amidoximated Bacterial Cellulose and Its Adsorption Mechanism for Cu2+ and Pb2+. Journal of Applied Polymer Science 2010; 117(1): 8-15.

Gui XC, Wei JQ, Wang KL, Cao AY, Zhu HW, Jia Y, et al. Carbon Nanotube Sponges. Adv Mater 2010; 22(5): 617-+.

Huang Y, Zhu CL, Yang JZ, Nie Y, Chen CT, Sun DP. Recent advances in bacterial cellulose. Cellulose 2014; 21(1): 1-30.

Iguchi M, Yamanaka S, Budhiono A. Bacterial cellulose - a masterpiece of nature's arts. J Mater Sci 2000; 35(2): 261-270.

Katepetch C, Rujiravanit R. Synthesis of magnetic nanoparticle into bacterial cellulose matrix by ammonia gas-enhancing in situ co-precipitation method. Carbohydrate Polymers 2011; 86(1): 162-170.

Klemm D, Heublein B, Fink HP, Bohn A. Cellulose: Fascinating biopolymer and sustainable raw material. Angew Chem Int Edit 2005; 44(22): 3358-3393.

Liu Z, Wan YZ, Xiong GY, Guo RS, Luo HL. Three-dimensional porous nanocomposite of highly dispersed Fe3O4 nanoparticles on carbon nanofibers for high-performance microwave absorbents. Materials Express 2015; 5(2): 113-120.

Olsson RT, Samir MASA, Salazar-Alvarez G, Belova L, Strom V, Berglund LA, et al. Making flexible magnetic aerogels and stiff magnetic nanopaper using cellulose nanofibrils as templates. Nature Nanotechnology 2010; 5(8): 584-588.

Shah J, Brown RM. Towards electronic paper displays made from microbial cellulose. Applied Microbiology and Biotechnology 2005; 66(4): 352-355.

Surma-Slusarska B, Presler S, Danielewicz D. Characteristics of Bacterial Cellulose Obtained from Acetobacter Xylinum Culture for Application in Papermaking. Fibres & Textiles in Eastern Europe 2008; 16(4): 108-111.

Wanichapichart P, Taweepreeda W, Nawae S, Choomgan P, Yasenchak D. Chain scission and anti fungal effect of electron beam on cellulose membrane. Radiation Physics and Chemistry 2012; 81(8): 949-953.

Wu SQ, Li MY, Fang BS, Tong H. Reinforcement of vulnerable historic silk fabrics with bacterial cellulose film and its light aging behavior. Carbohydrate Polymers 2012; 88(2): 496-501.

Wu ZY, Li C, Liang HW, Chen JF, Yu SH. Ultralight, Flexible, and Fire-Resistant Carbon Nanofiber Aerogels from Bacterial Cellulose. Angew Chem Int Edit 2013; 52(10): 2925-2929.

The National and International Graduate Research Conference 2017
March 10, 2017 : Poj Sarasin Building, Khon Kaen University, Thailand

IPMP2-12

Zhang TJ, Wang W, Zhang DY, Zhang XX, Ma YR, Zhou YL, et al. Biotemplated Synthesis of Gold Nanoparticle-Bacteria Cellulose Nanofiber Nanocomposites and Their Application in Biosensing. Advanced Functional Materials 2010; 20(7): 1152-1160.

Zhang W, Chen SY, Hu WL, Zhou BH, Yang ZH, Yin N, et al. Facile fabrication of flexible magnetic nanohybrid membrane with amphiphobic surface based on bacterial cellulose. Carbohydrate Polymers 2011; 86(4): 1760-1767.

Zhang XJ, Chen WB, Lin ZD, Shen JC. Photocatalytic Degradation of a Methyl Orange Wastewater Solution Using Titanium Dioxide Loaded on Bacterial Cellulose. Synthesis and Reactivity in Inorganic Metal-Organic and Nano-Metal Chemistry 2011; 41(9): 1141-1147.

Zhao Y, Hu CG, Hu Y, Cheng HH, Shi GQ, Qu LT. A Versatile, Ultralight, Nitrogen-Doped Graphene Framework. Angew Chem Int Edit 2012; 51(45): 11371-11375.

Zheng Y, Yang JX, Zheng WL, Wang X, Xiang C, Tang L, et al. Synthesis of flexible magnetic nanohybrid based on bacterial cellulose under ultrasonic irradiation. Materials Science & Engineering C-Materials for Biological Applications 2013; 33(4): 2407-2412.