FABRICATION METHOD AND MECHANICAL PROPERTIES OF CARBON/CARBON COMPOSITES WITH BACTERIAL CELLULOSE

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Abstract

The fabrication method of Carbon/Carbon composites made from Bacterial Cellulose (BC) wad / Polymer composites and their mechanical and wear properties of the composites were investigated in this paper. Three dimensional BC microfibrils network of nano-scale and their bonding conditions remains in BC wad. The experimental results of wear characteristics were shown for nano-C/C composites. Wear tests were conducted under dry sliding condition. The coefficient of friction took the low values of 0.02-0.05 during the tests and specific factors of wear element loss were 5.17-6.86×10^{-10}mm^2/N. It revealed that the composites have excellent wear properties in comparison with silicon nitride ceramics and the diamond-like carbon (DLC) coating, and the effects of temperature condition of fabrication on the properties are clarified.

1 Introduction

The fibrous structure of Bacterial Cellulose (BC) consists of three-dimensional network of microfibrils containing glucan chains bound together by hydrogen bond [1]. Therefore, BC composite materials could be effectively used as the high performance structural components for various applications [2, 3].

We have already investigated the mechanical behavior of BC composites with various reinforcements in order to establish the fabrication methods of two different types of BC composites; BC composite materials of sheet type and that with BC wad [4]. In the case that the reinforcements of calcium carbonate ($CaCO_3$) and clay have same size as the BC microfibril, the BC composites of sheet type have a maximum value of Young's modulus at an optimum value of reinforcement contents.

The new method is developed by two of the authors, and it is called "the Direct Impregnation Method (DIM)". Using the DIM, BC microfibrils network of three dimensional nano-structure and their bonding conditions remains in the composites. In this study, the mechanical and wear characteristics of Carbon/Carbon composites made from BC wad/Polymer composite are investigated. Wear tests for carbonized BC/polymer composites (nano-C/C composites) are conducted under room condition and dry sliding condition. The effects of temperature condition of fabrication on the properties of nono-C/C composites are clarified, and three dimensional structure of nano-scale for strengthening is also considered.

2 Fabrication of C/C composites with BC

2.1 Bacterial Cellulose

The material used in this study is Bacterial Cellulose (BC, Fig. 1) which is synthesized by the acetic bacterium *Acetobacter xylinum*. Our BC is from industrial waste provided by Japanese traditional vinegar maker. The polymerization of BC is about 3000 and its contents of nitrogen is about 0.2 - 0.4% [1].

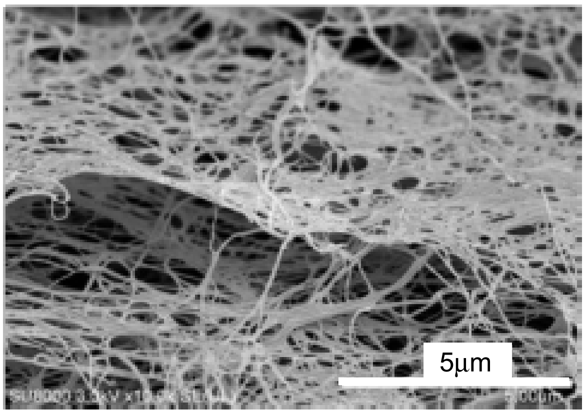


Figure 1. SEM observations for surfaces of BC wad

From the results of density measurement, BC has low density of 0.25-0.49g/cm^3. According to the results of bending test for BC/epoxy composites with the BC content of 1%V_f, Young's modulus of BC/epoxy composites is 3.43GPa and it is improved 4% higher compared with that of pure epoxy resin specimens. Using the mixture law, Young modulus of BC is found to be 17.3GPa.

2.2 C/C composites from BC and fabrication by DIM

By adding the alcohol of 50%V_f into the BC slurry with water, and mixing the phenolic resol resin, the water of BC slurry is replaced by the resin in the drying process. It means that the penetration of phenolic resin into three dimensional BC microfibrils network of nano-scale is taken at the same time when the water is evaporated. The method developed by two of the authors is called "the Direct Impregnation Method (DIM) [5]". After taking this procedure, the mixture was dried and hardened in order to get the BC FRP pre-impregnation (BC FRP p/p) of desired shape. In the next stage, BC FRP p/p was processed into the B stage, pressed at 433K (160˚C) and with 1MPa, and then we had transparent BC FRP plates of brown color. Fig. 2 shows the photographs of BC/phenolic resin composites in each stage. In the figure, it is found that the composite has the characteristic of transparency before carbonizing process.

Figure 2. BC/phenolic resin composites in each stage

The BC FRP plates were burned out in the inactive gas environment at various temperature 923-1273K (700-1100˚C) and the heating rate 5K/hr, and finally we had a carbonized BC wad/phenolic resin composite materials, that is, “nano-C/C composites”. By baking BC FRP plates at high temperature, BC microfibrils were changed into the carbon fibres of nano-scale, and the phenolic resin of the matrix became the glassy carbon. The diameter of carbonized BC microfibrils is about 10nm. The processing method is summarized in Fig. 3.

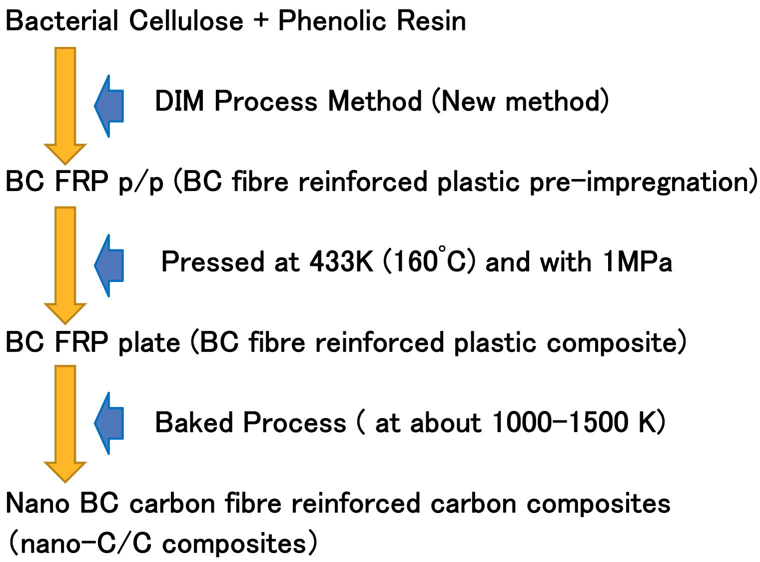


Figure 3. Fabrication method of C/C composites

3 Experimental results of C/C composites

3.1 Wear tests and specimens

To examine the wear properties of nano-C/C composites, wear tests were conducted by using the pin-on-drum type tribology tester shown Fig. 4. The specimens were cut out from the composites and their dimension is 3.5mm× 3.5mm square and 2mm thickness. The test specimen was sliding on surface of SUS304 drum of the surface roughness R_a 0.3 - 0.5. The sliding conditions were as follows; sliding speed 1.5m/sec, sliding distance 130km, and contact pressure 1MPa.

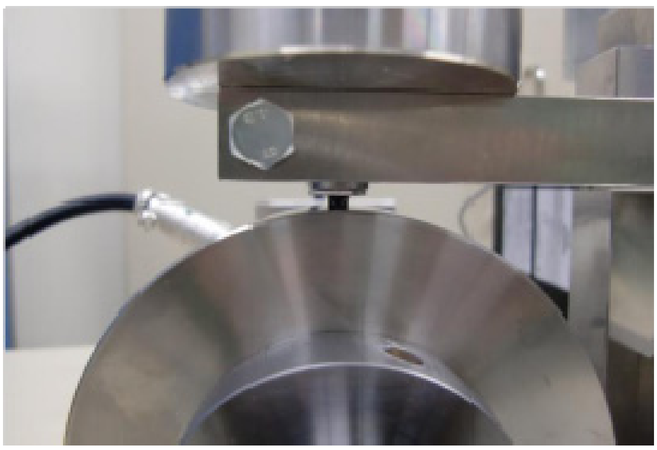


Figure 4. Pin-on-drum type tribology tester

The factor is given by the following equation;

$$\text{Speciffic factor of wear element loss}\,[mm^2/N] = \frac{\text{Volume of wear}[mm^3]}{\text{Load}[N]\times\text{Sliding distance}[mm]} \tag{1}$$

The coefficient of friction μ_c for the specimen were calculated by the values of contact pressure and torque change of drive which is monitored by torque sensor.

According to wear tests, the C/C composites have low coefficient of friction μ_c and take significant low values of the specific factor of wear element loss f_w. The coefficient of friction μ_c for the specimens baked at 1000℃ took the low values of 0.02-0.05 during the tests. The specific factor of wear element loss f_w is 6.11×10^{-10} mm^2/N. In the case of the specimens at 900℃ and 700℃, μ_c =0.02 and $f_w = 6.86\times10^{-10}$ mm^2/N, and μ_c =0.02-0.05 and $f_w = 5.17\times10^{-10}$ mm^2/N, respectively. These experimental results were summarized and shown in Table 1.

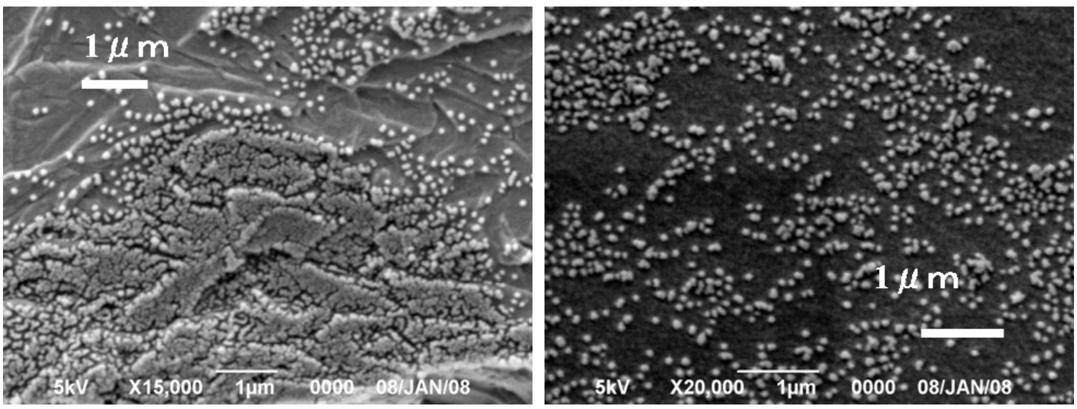
In the comparison with the value of 5×10^{-6} mm^2/N for silicon nitride (Si_3N_4) ceramics and 4×10^{-8} mm^2/N for Diamond-Like Carbon, it reveals that the C/C composites have more excellent wear property than Si_3N_4 ceramics and the DLC.

Test temperature	**700℃**	**900℃**	**1000℃**
Wear element loss [mm^2/N]	5.17×10^{-10}	6.86×10^{-10}	6.11×10^{-10}
Coef. friction	0.02-0.05	0.02	0.02-0.05

Table 1. Wear properties of nano-C/C composites.

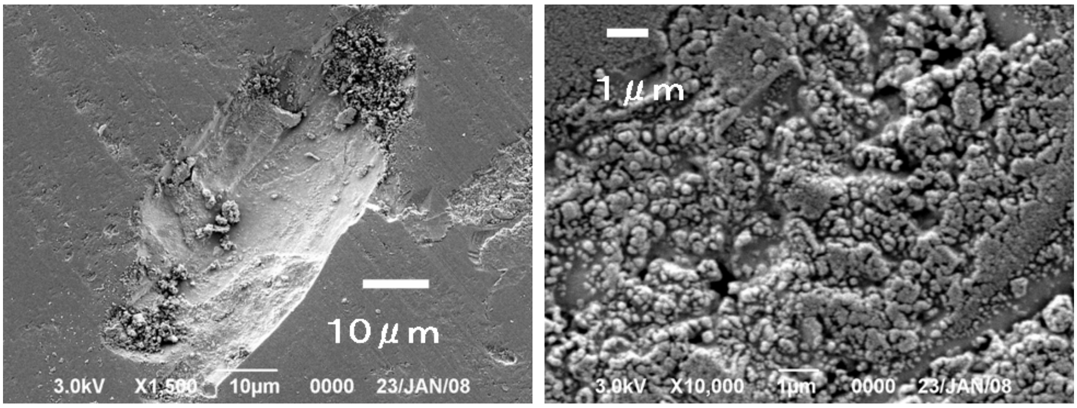
3.2 Results and considerations

To examine the wear properties for C/C composites, Fig. 5 shows the SEM photographs for observing the surface of the carbonized BC FRP composites before wear tests. It can be seen that many BC microfibrils of nano-scale are dispersed over the cross section of the composites, aligned along the vertical to the surface or the parallel to it. Some BC bundles of micrometer are observed in the photograph after wear tests, we examined the sliding surface



(a) (b)

Figure 5. SEM observation for cross section of nano-C/C composites before wear tests



(a) (b)

Figure 6. SEM observation for sliding surfaces of C/C composites

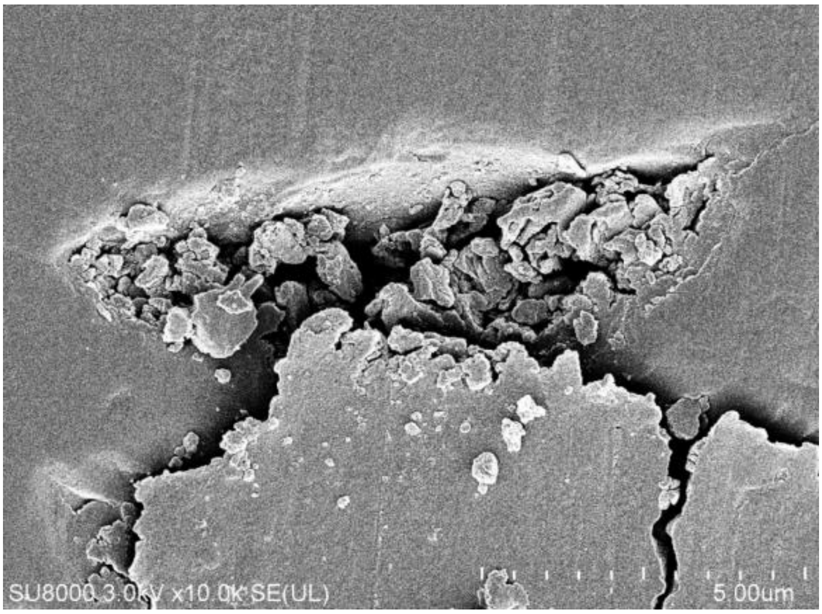


Figure 7. SEM observations for sliding surfaces of C/C composites in high magnification

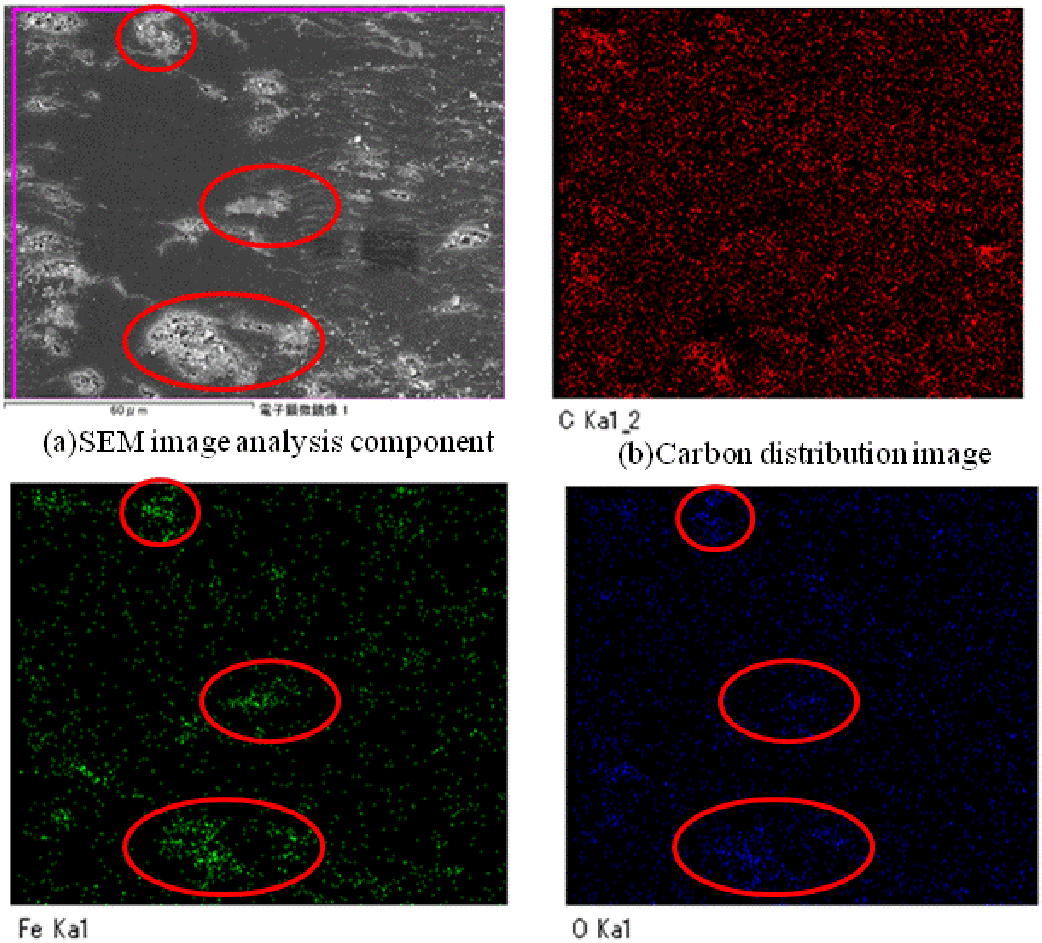
of the carbonized BC FRP composites. SEM observation for the sliding surfaces of nano-C/C composites is shown in Fig. 7. From the Fig. 7, a crack of some hundred nm length occurred at the sliding surface, propagating into the inside and then a small piece of the material was dropped off.

From the experimental results of wear tests for specimens at different temperature condition, we find small deviation of the values of f_w due to the natural difference of density for BC microfibrils network, but could not find large difference between that of f_w for the specimens at different temperature. Then, it can be said that no dependence of wear properties on temperature condition is observed for these temperature range. It should be noted that we could not fabricate C/C composites at 723K(500℃) because the brittle behavior appeared in the composite.

The SEM photographs of for the specimens of C/C composites after sliding is shown in Fig. 7 and the results of SEM image analysis component observations for sliding surface is indicated in Fig. 8. Observing Fig. 7, a crack of some hundred nm were observed, appearing some small cracks from the large crack, and small element of 3μm×10μm was drop off. In nano-C/C composites, many carbonized BC microfibrils of nano-scale were dispersed in glassy carbon which was made from the matrix of phenolic resin. When a small element loses by sliding force in tests, the fracture pass was affected by fibre bridging of BC microfibrils, and large energy was absorbed during micro crack propagation. The C/C composites have high local fracture toughness and good wear characteristic, and this constituent contributes to very low value of the specific factor of wear element loss and the coefficient of wear.

From the SEM image analysis component observations for the surface of the sliding surface of the specimens, the surface is found to consist of the components of C, O, Fe, Cr and Pt. From Fig. 8(b), the C is observed on the whole surface of sliding surface. It is found to be that the components of Fe and Cr stick to the surface of sliding surface because the drum rotor is the stainless steel SUS304. From Fig. 8(c) and (d), the components Fe and O were observed in the position of surface at the fracture initiation points. It means that the oxidization might occur at the heating position and these components must stick onto it when the contacting pressure between the specimen and the rotating drum increased on the sliding surface. It revealed that the C/C composite consists of the material component of C only and has the three dimensional carbonized BC microfibrils network of nano-scale which is reduced from micro-scale.

It is found that the BC nano-fibres their selves and the interface bonding condition between nano-fibres and the matrix play an important role for wear characteristic of materials, and many applications of the nano-C/C composites with BC could be expected for the mechanical elements of machines.



(a)SEM image analysis component

(b)Carbon distribution image

(c) Fe distribution image

(d) Oxide distribution image

Figure 8. SEM image analysis component observations for surface of C/C composites

4 Conclusions

In this study, the fabrication method and mechanical and wear properties of carbonized Bacterial Cellulose wad/polymer composites (nano-C/C composites) were investigated.

(1) A new fabrication method of BC wad/polymer composites, in which three dimensional BC microfibril network of nano-structure and their bonding conditions remain, was developed in order to apply to the high performance structural components.

(2) From the results of density measurement, BC has very low density of 0.25 - 0.49g/cm^3. According to the results of bending test for BC/epoxy specimens with the BC content of 1%V_f, Young's modulus of BC/epoxy composites is 3.43GPa and it is improved 4% higher compared with one of pure epoxy resin specimens. By using the mixture law, it is found that Young's modulus of BC is 17.3GPa.

(3) The experimental results of wear characteristics were shown for the nano-C/C composites made from BC wad/phenol resin composites. The coefficient of friction took the low values of 0.02-0.05 during the tests. The specific factor of wear element loss for the carbonized BC composites was 5.17-6.86×10^{-10} mm^2/N. It reveals that the nano-C/C composites with BC have excellent wear property in comparison with silicon nitride ceramics and the diamond-like carbon.

The carbonized BC microfibrils of nano-C/C composites, which were combined together with the glassy carbon of polymer matrix, worked and had some effect on the higher value of the fracture toughness of composites, and then the specific factor of wear element loss becomes higher in wear tests. The nano-C/C composites with BC could be expected for the structural elements of machines.

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