MECHANICAL CHARACTERISTICS OF BACTERIAL CELLULOSE COMPOSITE MATERIALS

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Abstract

Bacterial Cellulose is one of the eco-friendly materials, and is synthesized by the acetic bacterium "Acetobacter xylinum". In this paper, the fabrication method and mechanical properties of Bacterial Cellulose (BC) composites is investigated. The matrix of composites is BC and their reinforcements are powdered paper (PP), $CaCO_3$, and clay. The BC composite specimens are prepared under the test method of JIS K7113. From the experimental results of tension tests for BC composites, the value of Young's modulus E is dependent on the contents of reinforcement, and a maximum value of E could exist by choosing an optimum content of reinforcement. In all the cases of BC composites, the tensile strength takes a smaller value than that of pure BC materials. The effects of material properties and configurations on the properties of BC composites were discussed, and three-dimensional micro structure for strengthening in BC composite was also considered.

1 Introduction

Natural fibers and materials are widely noticed due to the intrinsic properties of light weight, high strength, abundant availability and eco-friendly characteristics[1-5]. Bacterial Cellulose (BC) is one of the eco-friendly materials, and is synthesized by the acetic bacterium *Acetobacter xylinum*. The fibrous structure of BC consists of a three-dimensional network of microfibrils containing glucan chains bound together by hydrogen bond [6]. BC composite materials would effectively be used as the high performance structural components for various applications [7, 8].

In this paper, the mechanical behavior of BC composite materials with various reinforcements is investigated. Tension tests were performed in order to examine mechanical characteristics, and fracture surfaces of BC composite specimens were observed after the tests. The effects of each material property and composite configurations on the mechanical properties of BC composites are discussed, and the method of fabrication is also evaluated in order to have good properties from BC microfibril network of three-dimensional structure.

2 Test specimens and experimental procedure

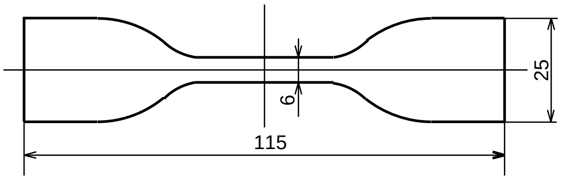
2.1 Bacterial Cellulose composite materials

Three types of eco-friendly composite materials were used in this study[9]. The matrix of composites is Bacterial Cellulose (BC) which was industrial waste provided by Japanese traditional vinegar maker. The reinforcements of BC composites are powdered paper (PP), calcium carbonate ($CaCO_3$), and clay (Montmorillonite).

Using a mixer, the BC slurry was break into fine pieces with a small amount of water. The polymerization is about 3000 and the contents of nitrogen is about 0.2 - 0.4% [6]. Adding reinforcements into it, the slurry was blended well into a source of composite mixture. A large mount of water in BC slurry was removed by percolation method. After drying it by holding in an oven, the BC was pressed with heat plates and a sheet type of BC composite materials was obtained.

2.2 BC Composite sheet specimens and experimental method

BC composite materials were prepared with various contents of reinforcement, that is, 20%, 35%, 60% and 70% by weight in the composites. For the



Thickness: t =1mm

Fig. 1. Geometry of BC composite sheet specimens

experiments, BC composites were cut into tension specimens of coupon type (JIS K7113) 115mm×25mm× 1mm as shown in Figure 1. TGA calorimetry analysis was done before the experiments.

Tension tests for the BC composite specimens were performed under the conditions at 298 K (25˚C) of 55%RH. The specimens were subjected to tensile load in the longitudinal direction, and the relationship between the load P and the loading point displacement δ was recorded. The testing speed was kept at 0.2 mm/min throughout the tests. After the tests, we observe the damage propagation in the BC specimens by an optical microscope and a scanning electron microscope (SEM).

3 Experimental results and considerations

3.1 Experimental Results for BC composites

From the experimental results, Figure 2 shows the stress σ - strain ε curves for $CaCO_3$/BC composite specimens of various contents of reinforcement. The recorded σ-ε curves indicate significant non-linear behavior from the earlier stage of loading over 12 MPa to the maximum load, and no load drop occurs. As can be seen from Fig. 2, the value of Young's modulus E, which corresponds to a slope of each curve, is dependent on the content of reinforcements. A maximum value of E would exist by choosing an optimum content of filler.

Observing the fractured surface of $CaCO_3$/BC composite specimen, $CaCO_3$ is dispersed well in the specimen shown in Figure 3. The fibrous structure of BC consists of a three-dimensional network of microfibrils containing glucan chains bound together by hydrogen bond. In the composites, the interfacial bonding strength between the BC and $CaCO_3$ is found to be good for effective hydrogen bond and physical entanglement, and then $CaCO_3$/BC composite takes high Young's modulus E. The details are not shown in this paper for the brevity's sake.

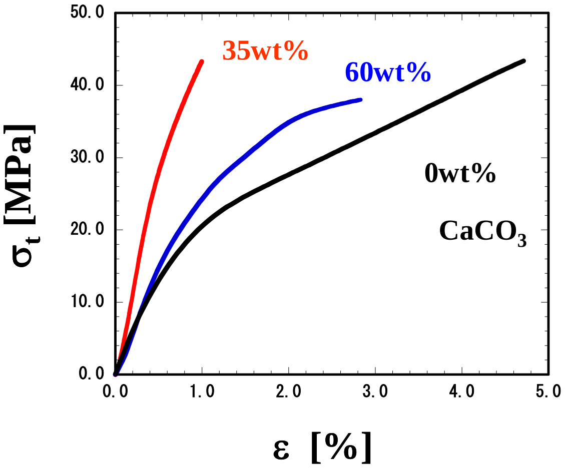


Fig. 2. Stress σ – strain ε curve for $CaCO_3$/BC composite sheet specimen

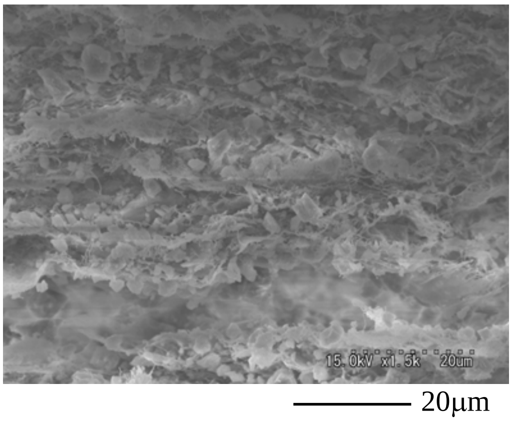


Fig. 3. SEM observation of fractured surface of $CaCO_3$/BC composites sheet specimen

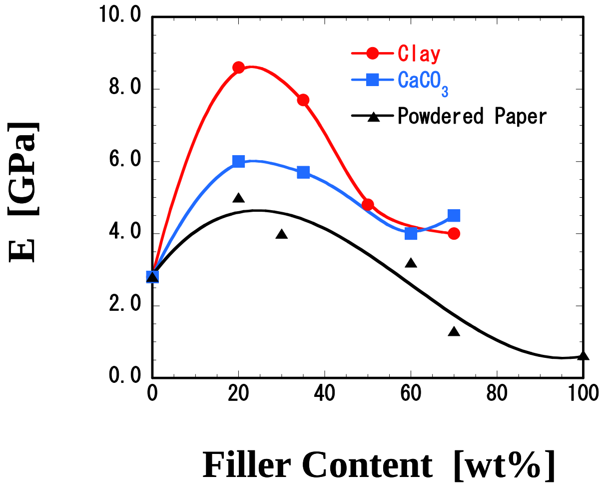


Fig. 4. Young's modulus of BC composite materials versus filler contents

3.2 Considerations

Young's modulus E of BC composites in each case are summarized and shown versus the contents of reinforcements in Figure 4. It can be easily found that an optimum value of reinforcement content could exist in order to take a maximum value of Young's modulus of BC composites. Strengthening effects are clearly observed in the cases of $CaCO_3$/BC and Clay/BC.

Figure 5 shows the comparison of the mechanical properties of BC composites with those of other engineering plastic materials. From this figure, by comparing the results of pure BC material, Young's modulus of $CaCO_3$/BC composites take twice higher value than that of pure BC material while the E of Clay/BC composites take three times higher. However, in the both case, tensile strength and elongation until fracture decrease in adding the reinforcements.

For the BC composites of 20 wt% reinforcement, Young's modulus of Clay/BC composites is higher than that of $CaCO_3$/BC composites and PP/BC composites. The mean value of diameter of clay particle is about 1 μm, and that of $CaCO_3$ particle is about 1.5 μm. In the case of PP/BC composite specimen, the interlaminar debonding was observed in the fracture surface and the maximum load takes a small value. The fiber length of powdered paper is about 1 - 2 mm, and it is much longer than that of BC microfibrils by double-digit number to four-digit number (Figure 6). The dispersion of PP fibres vary in the part of specimen, and the BC microfibril network is not effectively entangled around the fibres of PP.

From these considerations, in the case that the reinforcements have same size of the BC microfibrils, the BC composites have a maximum value of Young's modulus at an optimum value of reinforcement contents. This phenomenon could be caused because the interfacial bonding strength between the BC and reinforcements is high in the good condition for effective hydrogen bond and physical entanglement of BC microfibril network. A model for strengthening is shown in Figure 7.

Figure 7 (a) shows a model of strengthening of BC composites with reinforcement fillers. Solid lines indicate BC micro fibrils and circles show fillers. The other model is BC microfibril networks with no reinforcement fillers as shown in Figure 7(b). As mentioned above, the fibrous structure of BC consists of a three-dimensional network of microfibrils containing glucan chains bound together by hydrogen bond. In order to reinforce composite

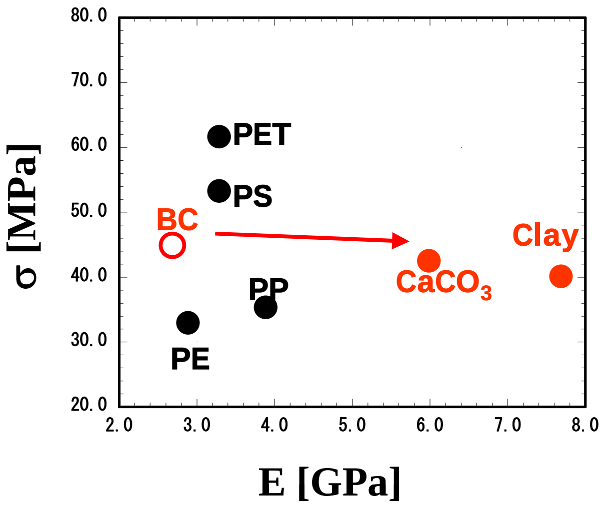
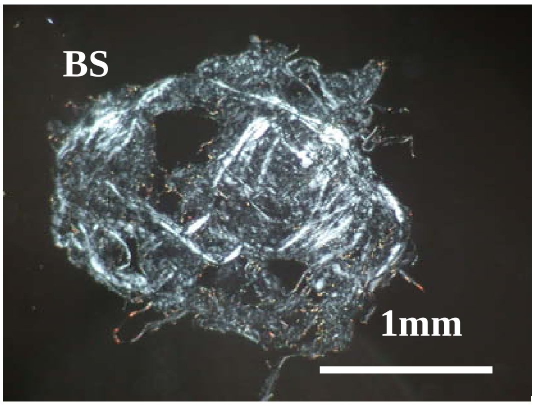
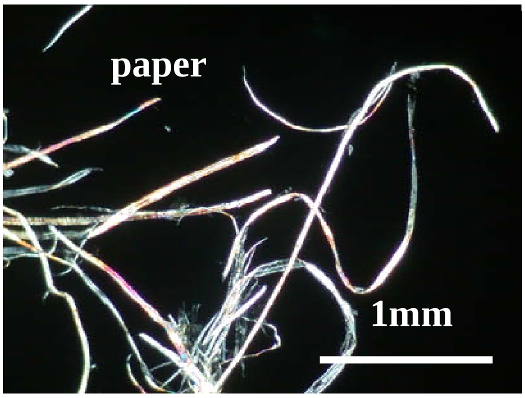


Fig. 5. Comparison of mechanical properties of BC composites and other polymer materials



(a) Micro fibril of Bacterial Cellulose



(b) Cellulose of powdered paper

Fig. 6 Photograph of cellulose by polarized optical microscope

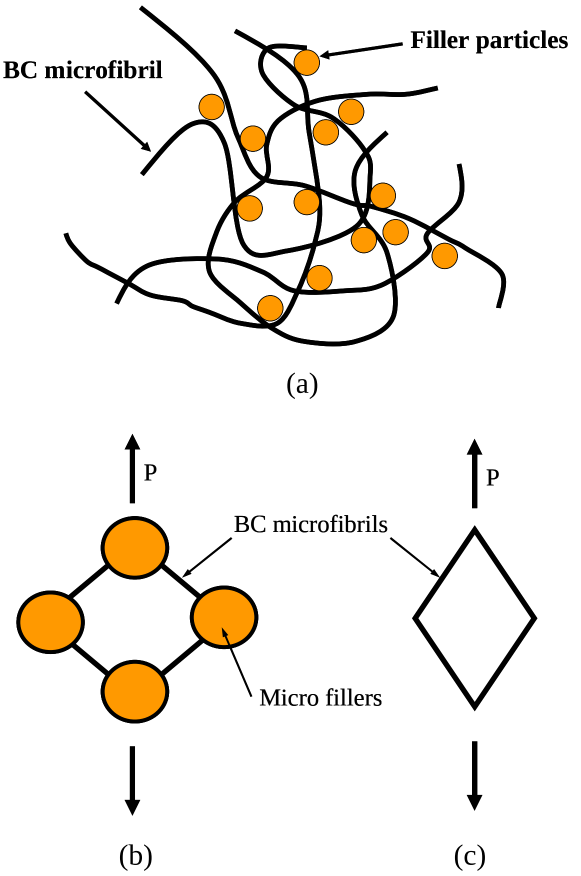


Fig. 7. A model for strengthening mechanism of BC composite

materials with BC, the effective processing method is required for keeping the effective hydrogen bond between the BC and fillers, and physical entanglement of three-dimensionally oriented BC microfibril networks of nano-scale.

It is noted that the residual stresses change the performance of the composite and the interphase characteristic. In order to clarify the mechanical properties of BC composites, it will be necessary to introduce a model for BC microfibril networks and reinforcements in the BC composites, and evaluate the effect of each material property, composite configurations and residual stresses on their mechanical properties with stochastic consideration.

In order to estimate the mechanical properties of BC composites, it will be necessary to introduce a model for BC microfibril networks and interaction of reinforcements in the BC composites by using multiscale analysis method.

4 BC composites form of three-dimensional structure

In using the BC as reinforcements, the water in the BC slurry of gel type badly affects processing of the composites, especially in the case that the polymer resin is used as a matrix of composites. Therefore, we must remove the water from the BC slurry. This is a key technology to process green composites suggested in a study on pulp injection molding [3], and in development of cellulose nano-fiber reinforced nano-composites [4].

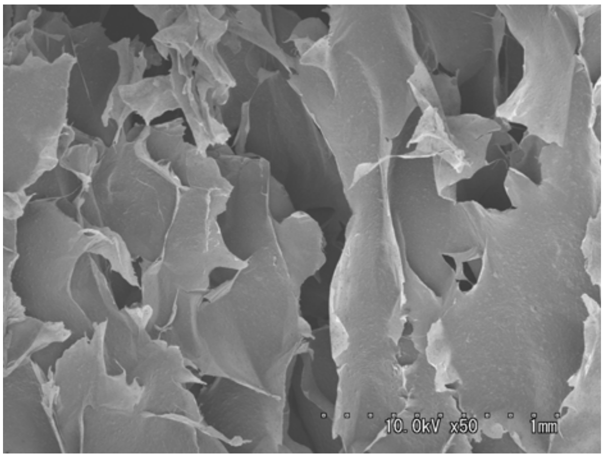
Because the BC takes a three-dimensional network (3D network) of microfibrils, we have very hard solid materials of the BC after drying it in a furnace. This dried BC has strong bond between microfibrils ant does not return to the slurry of gel type in soaking it into the water. It is difficult to impregnate the polymer resin into the dried BC. Some fabrication methods by using the micro-fibrous fillers of finely broken BC[10] and the specially blended resin were proposed in order to improve the process of composites with reinforcing dried BC.

Generally speaking, in using fibres as reinforcements of composite materials, large value of the ratio of length to diameter of reinforcing fibres is required to have good performance of fibre reinforce composite materials. Fibres aligned unidirectionally are better than randomly oriented fibres in order to have better performance of fibre characteristics. In the case of BC composites, it is said that short fibrils of dried and milled BC are NOT good for making composites.

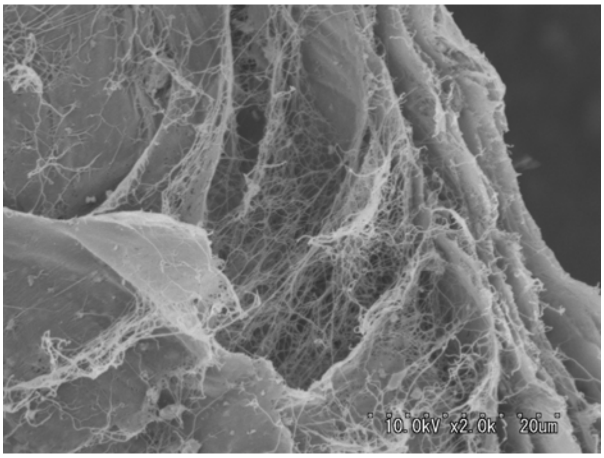
4.1 Fabrication method of 3D form of BC composites

Let us develop a fabrication method of BC form, in which BC microfibril network of three-dimensional structure and their bonding conditions remains, and consider characteristics of BC form and its applicability to impregnation of polymer resin.

Using a mixer, the BC slurry was mixed with a small amount of water. Adding reinforcements into it, the slurry was blended well into a source of composite mixture. After pouring the BC slurry into a container of cup type, it was frozen in a freezer. Frozen samples ware dehydrated in a vacuum chamber, then we had BC forms in which three-dimensional network of BC microfibrils and their bonding conditions remain. Specific volume of 3D-BC forms developed was 100 - 200cm^3/g.



(a) Surface of BC form



(b) Observation at magnification x 2000

Fig. 8. SEM observations for surfaces of BC form

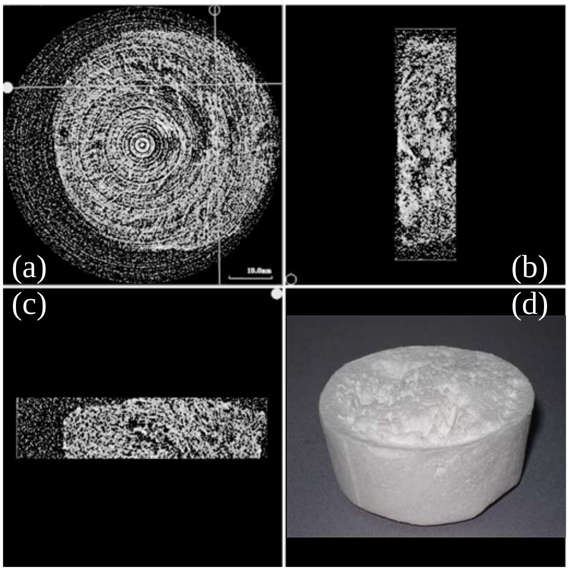


Fig. 9. X-ray CT examination for BC form

Figure 8 shows photographs of a scaning electron microscope (SEM) for observation of BC form with three-dimensional microfibril network and $CaCO_3$ fillers. It is found from the photograph that thin BC sheets of several micrometer thickness are layered and making a unit cell of stacked BC sheets with hundred micrometer order. In observation at high magnification, BC microfibrils of nano-scale are randomly entangled each other, $CaCO_3$ fillers are well dispersed in three-dimensional network of BC microfibrils. This BC network with reinforcement fillers could give the high Young's of BC composite materials.

X-ray CT examination for BC form specimens was performed in order to evaluate the homogeneity of BC form. Figure 9 shows x-ray photographs of $CaCO_3$/BC composite form of 50mm diameter and 30mm thickness. Fig. 9(a) shows a scanning picture of horizontal cross section of BC form, and the photographs of Fig. 9(b) and 9(c) are images of vertical cross section along two lines indicated in Fig. 9(a).

White parts in pictures correspond to BC and black parts are air cavities. Larger cavities are observed in the central part of BC form because it takes long time to freeze the water of BC slurry in the central part due to heat conduction and the low growing speed of ice causes the different size of ice which yields the difference of BC cell size.

This consideration is schematically shown in Figure 10. At the first stage, BC microfibrils dispersed homogeneously in large mount of water. In the next stage of freezing process, BC fibrils ware put out by freezing ice crystals and gathered up with each other around the surface of ice blocks to make BC microfibril network of shell structure. By holding the BC form in a vacuum chamber, the water would be sublimed from the frozen BC slurry, and finally the dried BC form with complicated geometry of microfibril network could be obtained.

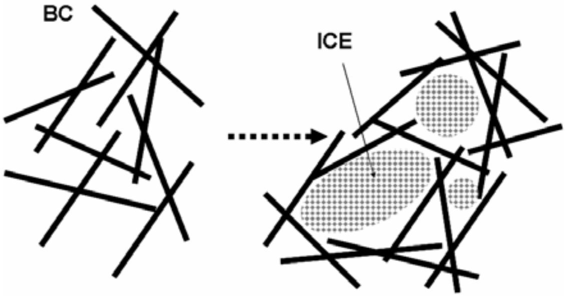


Fig. 10. BC form after fabrication process

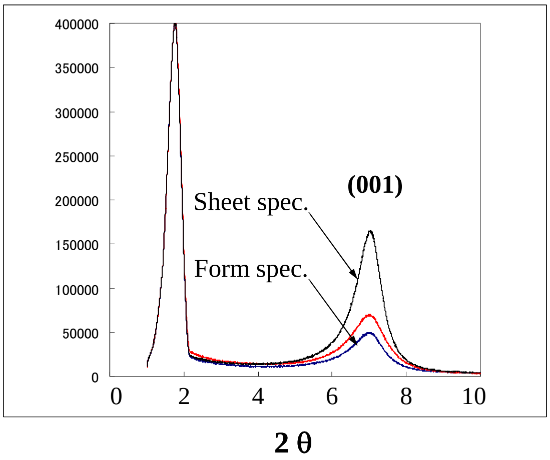


Fig. 11. Patterns of X-ray diffraction for Clay/BC composites of sheet type and of 3D form type

Figure 11 shows the patterns of x-ray diffraction for Clay/BC composites of sheet type and of 3D form type. It is seen that BC microfibrils in the form type specimen are three-dimensionally oriented because a peak of (001) for BC form is much lower than that for BC sheet. The fabrication method of BC form is valid to have a three-dimensional network of BC microfibrils.

4.2 Examination of 3D-BC form/Epoxy composite materials

Further more, let us examine the characteristics of 3D-BC form by processing it with the epoxy resin.

Figure 12 show a microphotograph of [$CaCO_3$/BC-3D form] / Epoxy composite materials by polarized optical microscope. This composite was fabricated by taking the impregnate process of the epoxy resin into the BC form and heating process. The line parts which look like “frills” are the unit cells of BC structure. From the observation of the BC-3D form / Epoxy composite materials, it is seen that there exists no large void and defect.

Figure 13 shows in SEM photographs of fracture surfaces of BC-3D form / Epoxy composite material which was broken in the liquid nitrogen. Fig. 8(a), Fig. 12 and Fig. 13(a) were taken at same magnification power for fracture surface observation. Seeing the photograph of fracture surface of Fig. 13(a), the material consists of BC unit cells in contact with each other. It is found from Fig. 13(b) at high magnification that the epoxy resin was impregnated into complicated structure of BC cell. Some interlaminar debondings between BC cells ware observed in the parts of fracture surface. It

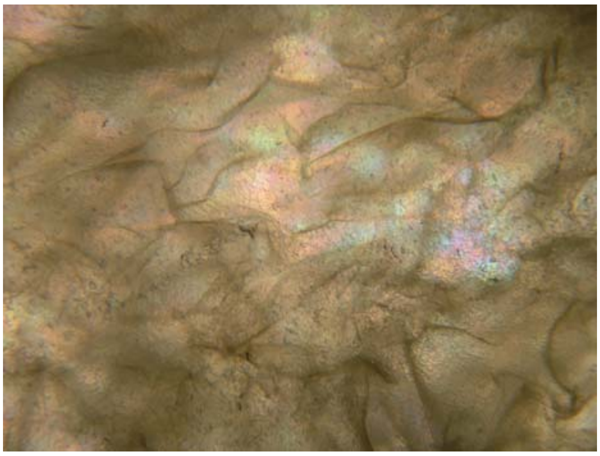
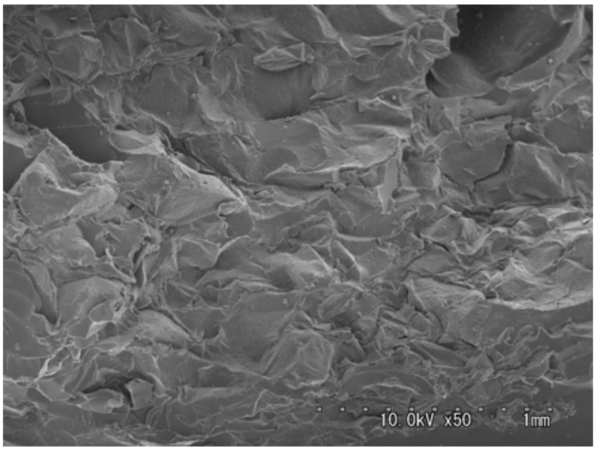
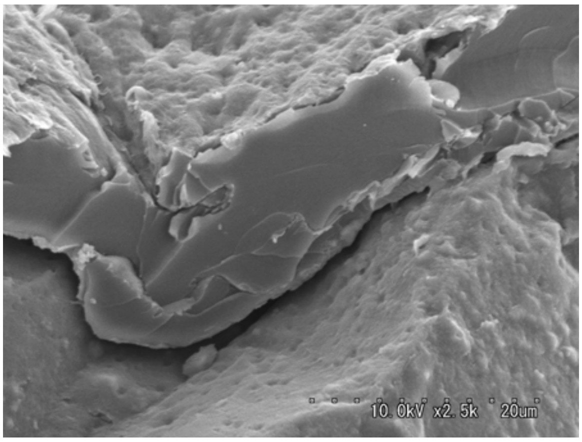


Fig. 12. Microphotograph of BC-3D form/ Epoxy composite materials by polarized optical microscope



(a) Fracture surface at magnification x 50



(b) Fracture surface at magnification x 2500

Fig. 13. SEM photographs of fracture surfaces of BC-3D form/ Epoxy composite material

remains unclear at the present time that the interlaminar debondings occured in impregnation process of epoxy resin or in the fracture process in liquid nitrogen. Further examination for understanding the characteristics of BC form and choice of bio-based matrix polymer, and development of processing method will be needed.

5 Conclusions

In this paper, the mechanical behavior of bacterial cellulose (BC) composites with various reinforcements is investigated. The effects of each material property and composite configurations on the mechanical properties of BC composites are discussed, and the method of fabrication is also evaluated in order to have good properties from BC microfibrils network of three-dimensional structure.

(1) The fabrication method is developed for eco-friendly Bacterial Cellulose (BC) composite materials of sheet type. The reinforcements of BC composite are powdered paper (PP), calcium carbonate ($CaCO_3$), and clay (Montmorillonite).

(2) In the cases of $CaCO_3$/BC composites and Clay/BC composites, it is found that the BC composites have a maximum value of Young's modulus at an optimum value of reinforcement contents. In the case that the reinforcements have same size of the BC microfibrils, the BC composites have a maximum value of Young's modulus at an optimum value of reinforcement contents. This phenomenon could occur because the interfacial bonding strength between the BC and reinforcements is high in the good condition for effective hydrogen bond and physical entanglement of BC microfibril network. A model for strengthening is proposed.

(3) Another fabrication method of BC form, in which BC microfibrils network of three-dimensional structure and their bonding conditions remains, was developed and the characteristics of BC form and its applicability to impregnation of polymer resin were considered.

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