MECHANICAL PROPERTIES CHARACTERIZATIONS OF GREEN COMPOSITES MADE FROM POLY (LACTIC ACID) AND VARIOUS MILLED FIBERS WITH A MELT MIXING EXTRUDER FOR ADDITIVE MANUFACTURING APPLICATIONS

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ABSTRACT

In the present study, as a preliminary report of the present authors on "On Additive Manufacturing of Green Composites", poly(lactic acid), PLA, composites, which is reinforced with two different kinds of reinforcing fibers in the form of milled filler, i.e., kenaf and carbon fibers, were molded by melt mixing and then filament extruding processes to make green composite filaments for 3D printing additive manufacturing purposes. From tensile test results of single monofilaments extruded from a FDM (Fused Deposition Modeling) 3D printer with a nozzle of 1mm diameter, it was found that the milled carbon fibers were able to reinforce PLA, while milled kenaf fibers and, for comparison purpose, cellulose-base nano-fillers were found to make little contribution for improvement in terms of strength and modulus of the present additive manufactured green composites. From the scanning electron microscope (SEM) fractography of the fracture surfaces in the present green composites, interface imperfections between PLA matrix and reinforcing fibers except carbon fibers, unevenness of reinforcing fiber distribution as well as existence of resin rich portions in the composites may have affected the present poor results obtained in this preliminary study.

1 INTRODUCTION

So-called green composites, which are made up of environmentally-friendly matrices such as poly(lactic acid), PLA, and natural or non-natural reinforcing fibers such kenaf (*Hibiscus Cannabinus* L.) and carbon fibers, have recently been attracting more and more attentions [1-5]. Akil *et al.* reviewed physical and chemical properties of the base materials, the existing processing techniques and the mechanical properties for kenaf fiber reinforced composites up to the year of 2010 [1]. On the other hand, Mukherjee and Kao reviewed PLA-based composites reinforced with various natural plant fibers [2]. However, these types of composite materials are quite new and hence better manufacturing methods suitable for the green composite products should be developed. For example, Tharazi *et al.* investigated optimum conditions for the hot press composite processing of unidirectional long kenaf fiber reinforced PLA composites [3]. On the other hand, Suzuki investigated composite processing and mechanical properties of short-kenaf fiber reinforced PLA composites by his hot-press method [4]. Chen *et al.* conducted preparation and characterization of kenaf fiber/multi-walled carbon nanotube/PLA green composites [5].

By the way, so-called additive manufacturing (AM), commonly known as 3D printing, can be defined as the layerwise process of joining materials to make parts from 3D data as opposed to subtractive manufacturing and formative manufacturing methodologies [6, 7]. Lee *et al.* reviewed fundamentals and applications of 3D printing for novel materials [6]. On the other hand, Tian *et al*. studied on recycling and remanufacturing of 3D printed continuous carbon fiber reinforced PLA composites [7]. In this context, combinations of the green composites and 3D printing additive manufacturing processing will promise quite a few benefits such as making the molded products lighter and more rational in terms of structural optimization.

In this preliminary report of the present authors on 3D printing additive manufacturing of green composites, trial composite filaments for fused deposition modeling (FDM) 3D printers will be molded from poly(lactic acid), PLA, and fibers of kenaf and carbon. Another trial of putting modified cellulose-related fibrous powders into PLA to make 3D printer filaments will also be carried out as well for comparison purpose. Monofilament tensile tests and fracture surface fractography will be conducted to see if effects of reinforcing fiber loading to PLA matrix on mechanical properties improvement of the present green composites.

2 MATERIALS, FILAMENT PROCESSING AND TENSILE TEST

2.1 Base Materials

Base materials used in this study are powdered poly(lactic acid) (PLA, REDOVE101, Zhejiang Hisun Biomaterials Co., Ltd., shown in Fig.1(a)) for the thermoplastic matrix and kenaf (*Hibiscus Cannabinus* L.) bast fibers in Fig.1(b) and milled carbon fibers in Fig.1(c) for the reinforcing fillers. The average length of kenaf fibers was approximately 3-5mm, while that of milled fibers was approximately 15μm. In Fig.1(d), typical mixture of PLA powder and milled carbon fibers are shown. In addition, another samples of putting modified cellulose-related micro-fibrous powders into PLA/CF mixtures were also made for comparison purpose.

(a) PLA powder (REVODE101)

(b) Kenaf fibers (milled, 3-5mm length)

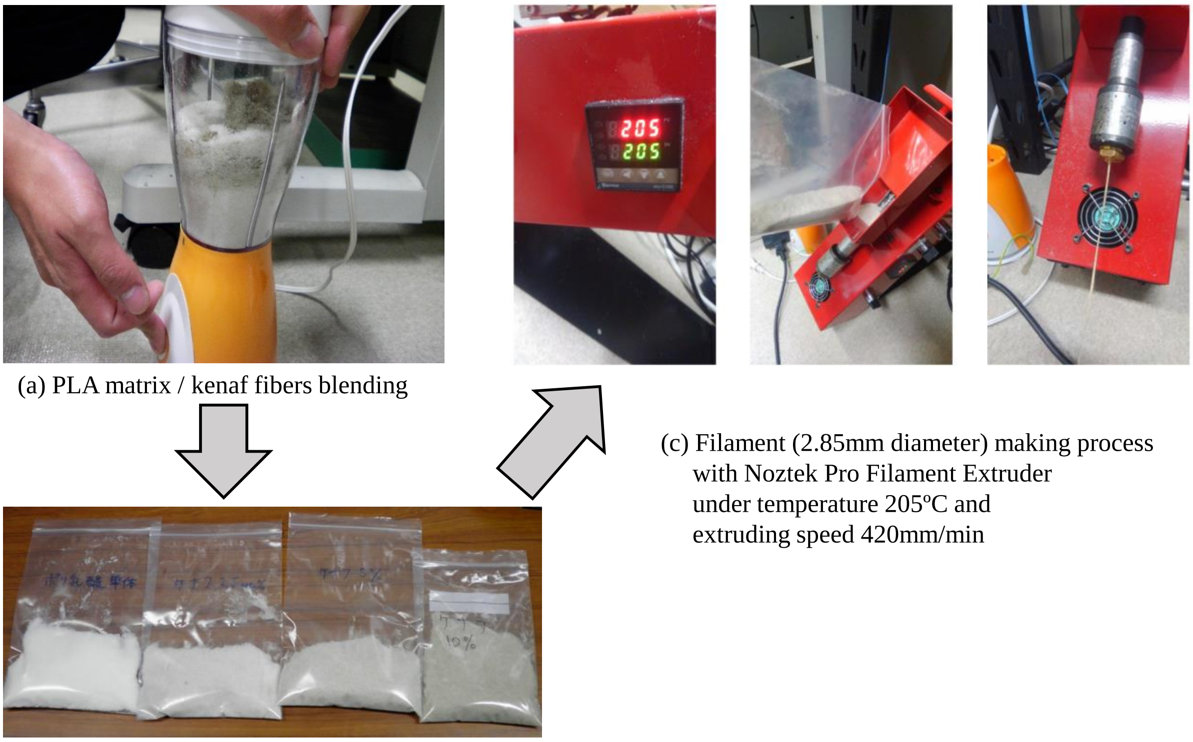
(c) Carbon fibers (milled, about 15μm length)

(d) Mixture of PLA powder and milled carbon fibers

Figure 1: Base materials used for the green composite filaments for additive manufacturing.

2.2 Filament Processing

The typical melt-mixing/extruding process flow of green composite filaments for FDM-type 3D printers conducted in this study is shown in Fig.2 for the cases of neat PLA and PLA/kenaf composites. The powders of neat PLA or PLA with modified cellulose-based fillers and the milled kenaf or carbon fibers were blended with a general-purpose food mixer in dry condition into composite mixtures of four different fiber content weight ratios, that is, for the cases of kenaf fibers, 0wt% (neat PLA), 2wt%, 5wt% and 10wt%. The dry mixtures of PLA and kenaf were loaded into the 3D printing filament extruder (Noztek Pro). Nozzle diameter of the extruder was 2.85mm. The temperature in the hot melting part was set to 205ºC, and filament extruding speed was 420mm/min. In Table 1, all the patterns of kinds of matrix (PLA or PLA with modified cellulose-base filler) and reinforcing fiber (kenaf or carbon), and weight fractions of the base materials, which were considered in this study, are shown.



(a) PLA matrix / kenaf fibers blending

(c) Filament (2.85mm diameter) making process with Noztek Pro Filament Extruder under temperature 205ºC and extruding speed 420mm/min

(b) 0wt% (neat PLA) / kenaf 2wt% / kenaf 5wt% / kenaf 10wt%

Figure 2: FDM 3D printer filament processing in the cases of PLA and kenaf fiber composites.

Table 1: all the combinations of matrix and fibers considered in this study.

2.3 Monofilament specimens

In Fig.3, the FDM 3D printing nozzle part is shown. Each green composite filament described in the previous section was loaded into the hot-end (the nozzle heater section) and then melted and pushed to be extruded from the opposite side of nozzle outlet as a single monofilament.

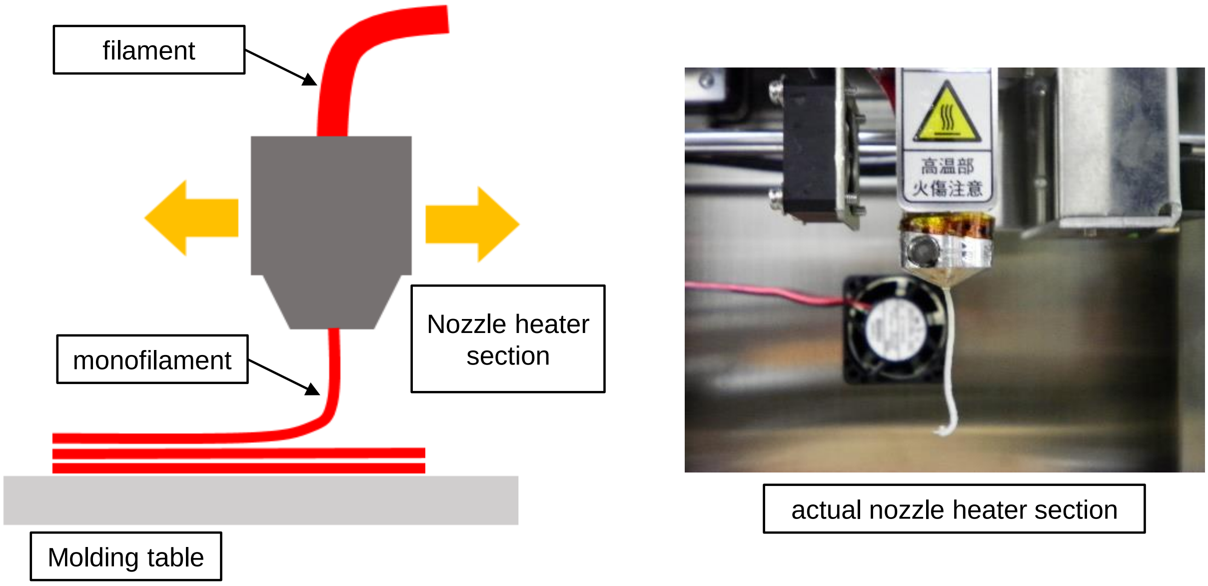


Figure 3: Monofilament 3D printing procedure.

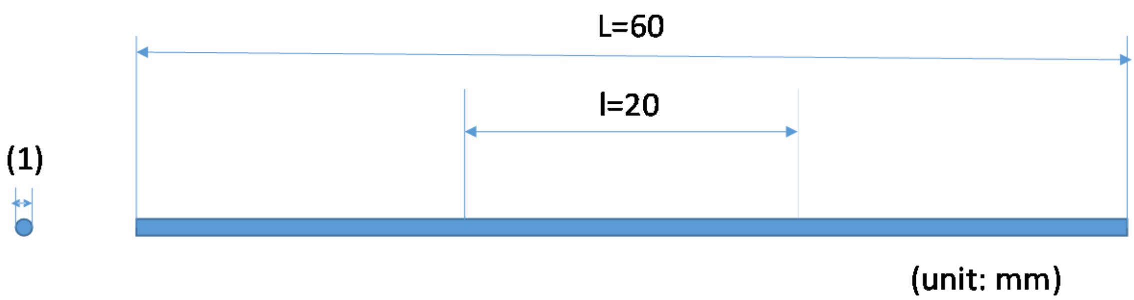


Figure 4: Monofilament tensile test specimen.

In Fig.4, the monofilament tensile test specimen is shown. The whole length was set to L = 60mm and each sample was placed in a vacuum vessel for 3 hours to get rid of moisture from the specimen. After that the weight of each specimen, G [g], was measured with an electric weighing scale, and then the average linear density, D, for each specimen was obtained.

$$D = G / L \tag{1}$$

2.4 Monofilament tensile test and fractography

Quasi-static tensile tests were carried out to the present monofilament specimens of all the different combination of matrix and fibres. The screw-driven universal tester (100N load cell capacity, Shimazu Ez-Test) was used with cross-head speed of 1mm/minute for gauge length, l = 20mm. The distance between the two pin vices fixing the specimen by 20mm deep was used as the gauge length, l, and strain was nominally evaluated based on the cross-head movement divided by the gauge length. On the other hand, as a kind of stress quantity, tenacity, σ [tex], was evaluated as follows;

$$\sigma = F / D \tag{2}$$

The sample size of each combination of matrix and fiber was set to 5. The fractured surface of monofilament tensile specimens were examined using a scanning electron microscope (SEM) (Hitachi Corp., TM1000).

3 RESULTS AND DISCUSSION

3.1 Tensile test results

In Fig.5, the tenacity at break for all the different patterns of matrix and fiber combinations are shown. In general, putting milled kenaf fibers into PLA doesn't improve its strength, while putting milled carbon fibers into it certainly shows a positive effect for strength increase. On the other hand, PLA matrix with modified cellulose-related micro-fibrous powders tends to decrease its strength in proportion as weight ratio of the powder. These results implies the following facts. Firstly, little benefit might not be given when the milled kenaf fibers are used for PLA reinforcement probably because the fiber length is too short as compared to its critical length and also the interfacial adhesion between PLA and kenaf fibers is not enough for effectively utilizing the strength of the kenaf fibers. Secondly, nano-fillers of modified cellulose seem to provide considerably negative impacts on PLA's strength improvement, reasons of which have not yet to be investigated, but it can be doubted that some molecular-level weakening mechanisms might have triggered by loading such nano-fillers into PLA matrix. Only milled carbon fibers are able to give positive effects on PLA's strength impovement.

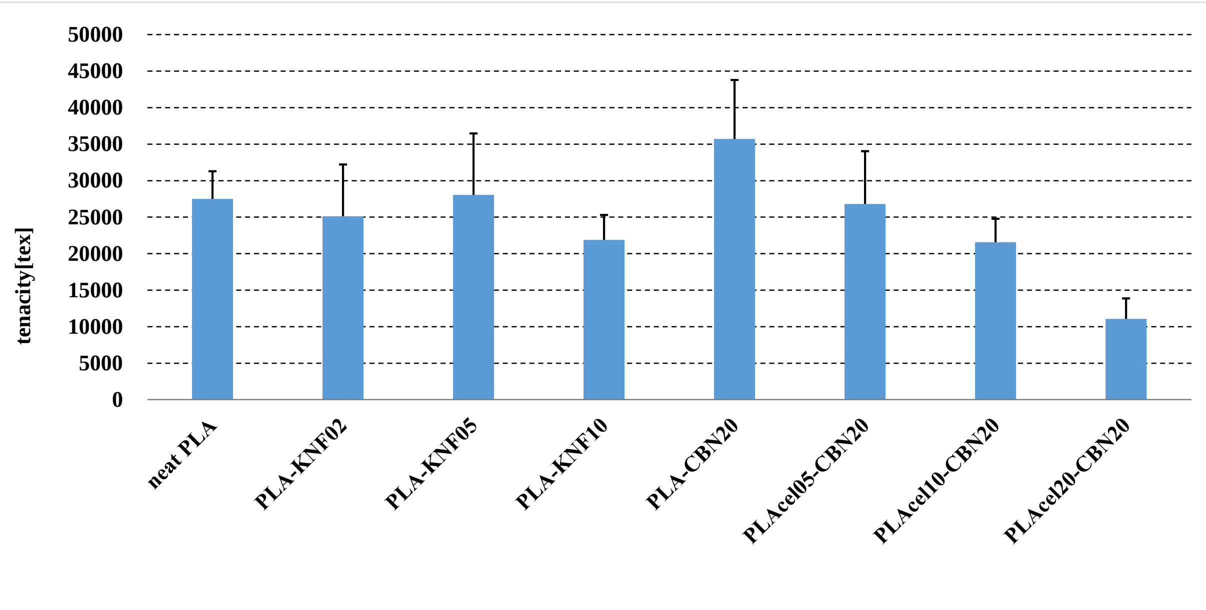


Figure 5: Tensile tenacity at break, σ.

In Fig.6, the tenacity per nominal strain, that is, the rigidity, at the initial loading level for all the different patterns of matrix and fiber combinations are shown. It can be seen that almost the same trends as strength were observed in terms of stiffness. The milled kenaf fibers give little benefit to stiffness improvement of PLA, while certainly carbon fibers can contribute stiffness improvement of the composites. On the other hand, modified cellulose-related micro-fibrous powders tends to decrease its stiffness in proportion as weight ratio of the powder as well as its strength. These result shows that the imperfections of matrix/fiber adhesion were considerably poor in the case of the green composites.

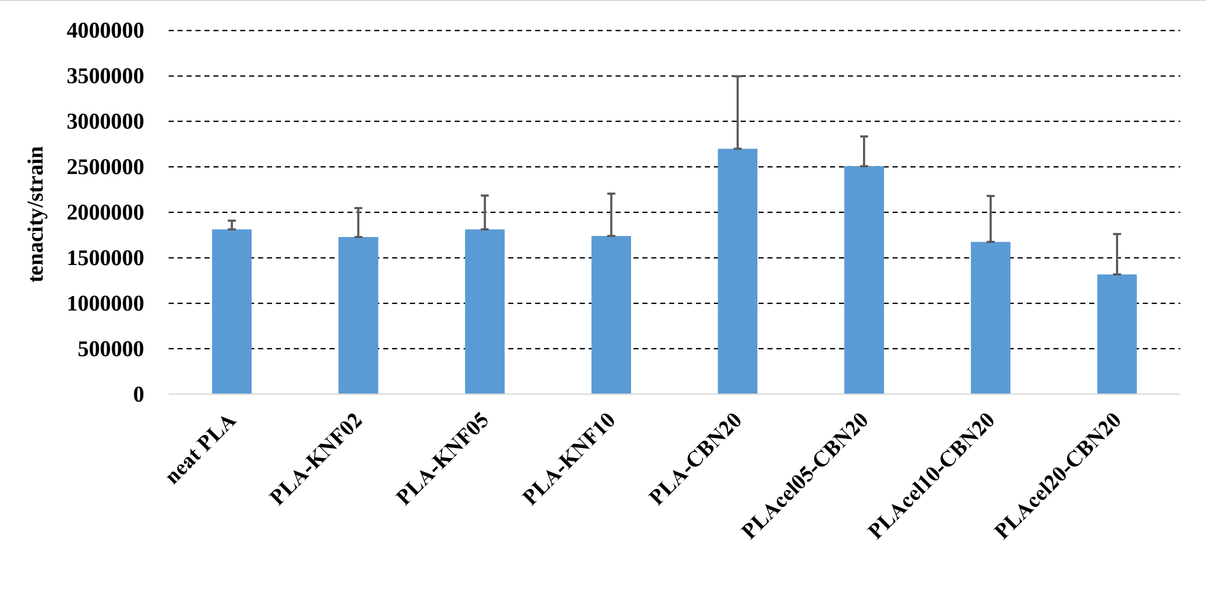
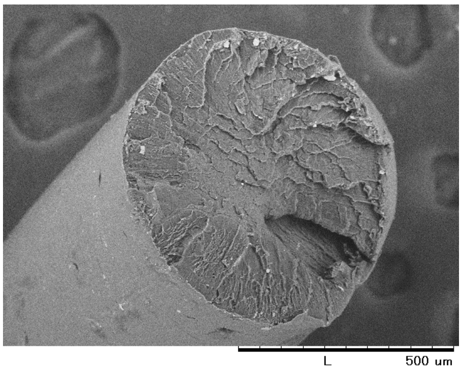


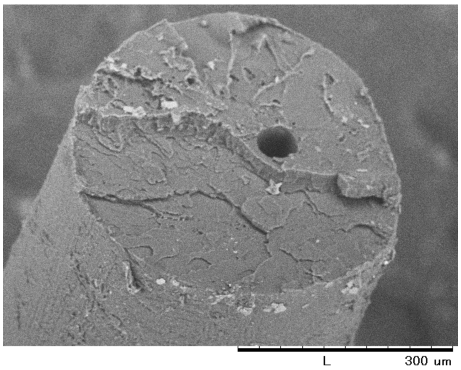
Figure 6: Initial tenacity /strain.

3.2 SEM fractography

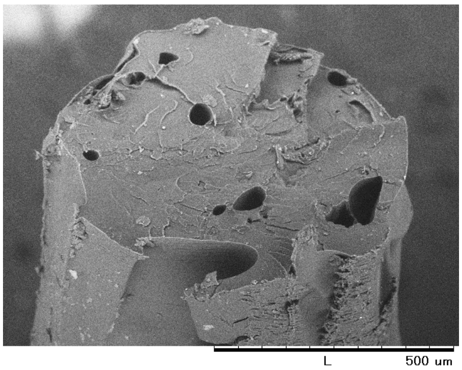
In Fig. 7, scanning electron microscope (SEM) images of the typical fractured surfaces of the monofilament tensile specimens are shown. The neat PLA in Fig.7(a) and the PLA-KNF specimens exhibit nearly similar brittle fracture surfaces. Oddly enough, there were not any kenaf fibers observed on the fracture surfaces of the PLA-KNF specimens with three different fiber content ratios. Probably the fractures had occurred exclusively or selectively in their resin rich portions initiated by a brittle crack somewhere in the specimens. It should also be noted that several voids inside the PLA-KNF specimens can be seen. Quasi-static tensile tests were carried out to the present monofilament specimens of all the different combination of matrix and fibres. The screw-driven unive



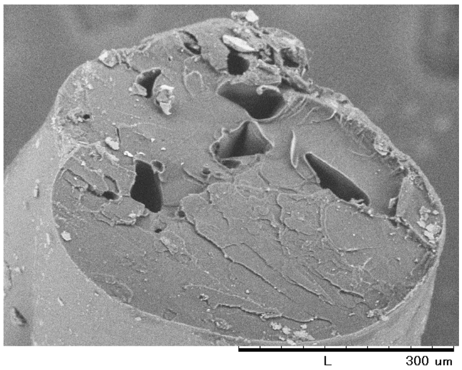
(a) PLA



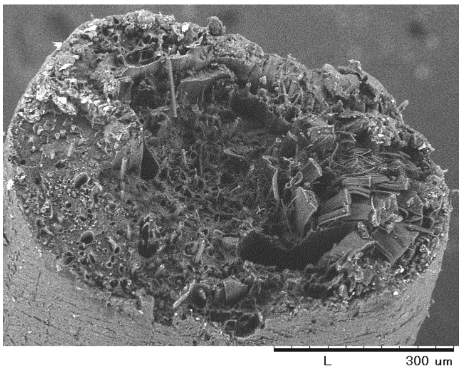
(b) PLA – KNF02



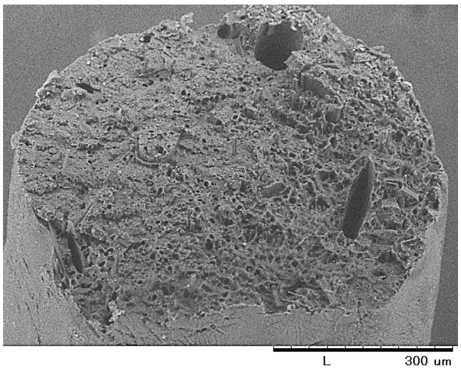
(c) PLA – KNF05



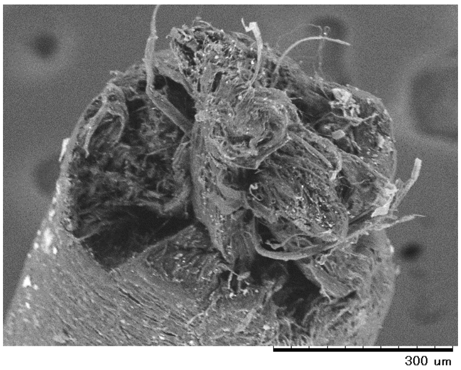
(d) PLA – KNF10



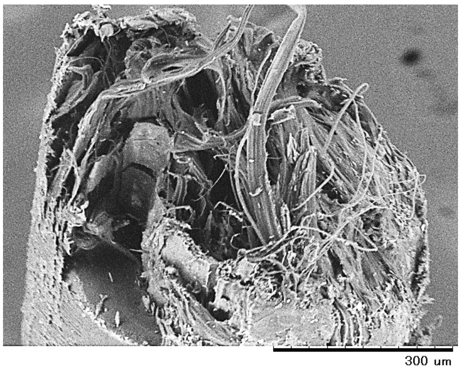
(e) PLA–CBN20



(f) PLAcel05–CBN20



(g) PLAcel10–CBN20



(h) PLAcel20–CBN20

Figure 7 : SEM fractography for monofilament tensile tests.

4 CONCLUSIONS

In this preliminary report of the present author on 3D printing additive manufacturing of green composites, trial composite filaments for fused deposition modeling (FDM) 3D printers was successfully molded from poly(lactic acid), PLA, and kenaf fibers. their quality and 3D printability were discussed. Another trial of putting cellulose-related fibrous powders (CNF) into PLA to make 3D printer filaments was also carried out and used SEM Inspection Examination piece Internal structure

Throughout the filament molding, three kinds of filaments were molded, but the modified cellulose was not uniformly mixed in PLA, the diameter of the filament was unstable by filament molding, a large number of voids were generated in the filament, a large number Voids occurred, many problems occurred, such as the diameters of the single fibers being different depending on the contents although they were discharged from the same nozzle. From this fact, it was thought that it was not possible to uniformly mix only by mixing the modified cellulose, and it was necessary to apply some fiber modification treatment to the modified cellulose. Since the number of voids for each content ratio is different for each content rate, we considered that it is necessary to improve the filament manufacturing machine to change the molding temperature for each content, so that the voids do not occur in the filament manufacturing machine. Just as with filament molding, it is thought that it is necessary to change the temperature for each content rate for single fiber discharge.

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