Tensile Properties of Mechanically-Defibrated Cellulose Nanofiber-Reinforced Polylactic Acid Matrix Composites Fabricated by Fused Deposition Modeling

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Abstract: Biodegradable polymers are highly attractive as potential alternatives to petroleum-based polymers in an attempt to achieve carbon neutrality whilst maintaining the mechanical properties of the structures. Among these polymers, polylactic acid (PLA) is particularly promising due to its good mechanical properties, biocompatibility and thermoplasticity. In this work, we aim to enhance the mechanical properties of PLA using mechanically-defibrated cellulose nanofibers (CNFs) that exhibit remarkable mechanical properties and biodegradability. We also employ fused deposition modeling (FDM), one of the three-dimensional printing methods for thermoplastic polymers, for the low-cost fabrication of the products. Mechanically-defibrated CNF-reinforced PLA matrix composites are fabricated by FDM. Their tensile properties are investigated in two printing directions (0°/90° and +45°/−45°). The discussion about the relationship between printing direction and tensile behavoir of mechanically-defibrated CNF-reinforced PLA matrix composite is the unique point of this study. We further discuss the microstructure and fracture surface of mechanically-defibrated CNF-reinforced PLA matrix composite by scanning electron microscope.

Key words: cellulose nanofiber (CNF); polylactic acid (PLA); tensile property; fused deposition modeling

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0 Introduction

Polymers are widely used due to their flexibility, low fabrication cost, workability and so on. However, nowadays, polymers have been pointed out for the enormous plastic pollution they generate in oceans and landfill. In addition, their recycling and incineration are often complex and expensive. Therefore, interest in biodegradable polymers, such as polylactic acid (PLA), polybutylene adipate terephthalate and polybutylene succinate[1], has surged as they may be used as replacements for petroleum-based polymers, thereby assisting achieving carbon neutrality. In particular, PLA attracts attention due to its strength, stiffness and biocompatibility, although it also possesses low toughness and biodegradability, and is expensive[2-3].

Cellulose nanofibers (CNFs) are regarded as promising next-generation fibers owing to their sustainability, outstanding mechanical properties, biodegradability and so on[4-5]. CNFs are generally obtained by either chemical treatment or mechanical defibration. 2, 2, 6, 6-tetramethylpiperi-dinyloxy

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(TEMPO) oxidation is one of the most well-known chemical treatments to obtain CNFs[6-7]. However, it has been reported that TEMPO is toxic and pollutes the environment[8]. In contrast, aqueous counter collision (ACC) methods based on mechanical defibration can obtain CNFs by using only water, although CNF bundles (as opposed to single nanofibers) are often produced[9].

Three-dimensional (3D) printing is a promising approach for the fabrication of complex products at low cost. Various methods, such as fused deposition modeling (FDM) and stereolithography for thermoplastic polymers, additive manufacturing for metals and direct ink writing for ceramics, have been studied[10]. In particular, FDM is a widely distributed 3D printing method for thermoplastic polymers, due to its low fabrication costs, capability of printing large-sized products, easy maintenance, and variation of raw filaments. The fabrication and mechanical properties of carbon fiber-reinforced thermoplastics by FDM have been recently reported by Li et al[11].

Xie et al.[12] reported that epoxy resin can be enhanced by the molecular chain cross-linkage of epoxy with extremely low CNF addition. This strengthening mechanism shifts to a rule of mixture (i.e. mechanical enhancement) with higher CNF addition. Moreover, Narita et al.[13] revealed that agglomerated CNFs (i.e. a CNF bundle) can be regarded as single CNF with a small aspect ratio by finite element analysis.

In this study, we fabricate CNF-reinforced PLA matrix composites by FDM. Considering environmental load, we select mechanically-defibrated CNFs by an ACC method. We investigate the tensile properties of the 3D-printed CNF-reinforced PLA matrix (PLA-CNF) composites in two printing directions of 0°/90° and +45°/−45°. Furthermore, we discuss these tensile properties on the basis of scanning electron microscopy (SEM) images.

1 Materials and Methods

As starting materials, we prepared PLA pellets (Terramac® TE-2000, Unitika Ltd., Japan) and mechanically-defibrated dry CNFs (BiNFi-s® WFo-UNDP, Sugino Mashine Ltd., Japan). The PLA pellets and CNF were mixed at 12 000 r/min using a mixer (TM-8100, TESCOM Denki Co., Ltd., Japan) and the CNF volume fraction was controlled between 0 and 0.5 % (volume fraction). After mixing, PLA-CNF filaments were prepared from the mixed powder at 168 ℃ by an extruder (Filabot Ex2, Filabot, USA).

Tensile testing was performed in compliance with JIS K 7161 1BA[14]. Tensile specimens (Fig.1) were printed by a 3D printer (L-DEVO M2030TP, Fusion technology Co., Ltd., Japan) with a printing speed of 30 mm/s, a filling density of 100%, a lamination pitch of 0.2 mm, a nozzle temperature of 200 ℃ and a nozzle hole diameter of 0.4 mm in two printing directions of 0°/90° and +45°/−45° (Fig.1). Fig.2 shows the dimension of the tensile specimens. The stage temperature was controlled between 40 ℃ and 70 ℃. Tensile testing was carried out by using a universal testing machine (Autograph™ AG-Xplus, Shimadzu Corporation, Japan) with a crosshead speed of 1 mm/min. We assumed that the volume is constant (i.e. the cross-sectional area proportionally decreases by applying the load) and that the true strain (ε_T) and true stress (σ_T) were estimated as

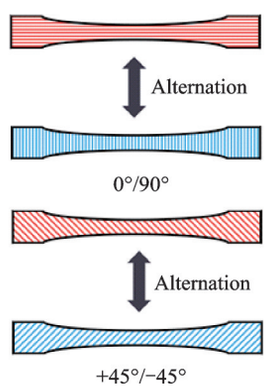

Fig.1 3D-printed specimens using the fused deposition modeling in the 0°/90° and +45°/−45° directions

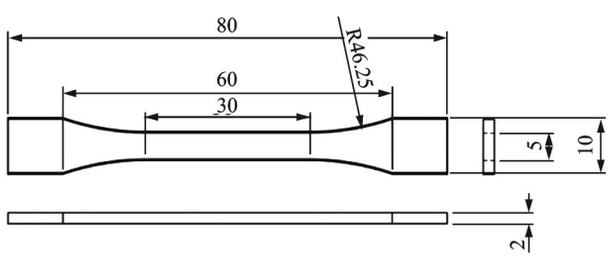

Fig.2 Dimension of tensile specimens (JIS K 7161 1BA [14])

$$\varepsilon_T = \ln(1+\varepsilon_N) \quad (1)$$

$$\sigma_T = \sigma_N(1+\varepsilon_N) \quad (2)$$

where ε_N and σ_N are the nominal strain and the nominal stress, respectively.

After testing, the fracture surface of the PLA-CNF composite was analyzed by SEM (JSM-7800F, JEOL Ltd., Japan). The preparation of the specimens consisted of the following steps: (1) Embedding 3D-printed PLA-CNF composites in acrylic resin; (2) polishing them with waterproof SiC paper of #600, #1000, #1500, #2400 and diamond slurries of 6 and 1 mm; (3) polishing the specimen surface by argon-ion spattering, before (4) coating with platinum. The microstructure and fracture surface of the 3D-printed PLA-CNF composites were observed by SEM with an accelerating voltage of 5 kV.

2 Results and Discussion

The CNFs were not burned during extrusion and white PLA-CNF filaments were obtained. The apparent CNF agglomeration was not visually observed. Fig.3 shows the relationship between specimen shape and stage temperature. The specimens were deformed because of thermal shrinkage when the stage temperature was high. Therefore, we determined 50 ℃ as the stage temperature in this study. Fig.4 shows the printed PLA-CNF 0.5 % (volume fraction)tensile specimen in the 0°/90° direction. It is well known that voids are formed along the printing direction inside the fabricated products by FDM and the printing direction inside the tensile specimens was also visible[15]. Fig.5 shows the SEM images of CNFs inside the PLA-CNF specimen. The CNFs were agglomerated in PLA at any CNF volume fraction and the number of agglomerated CNF clusters was proportionally increased with the CNF volume

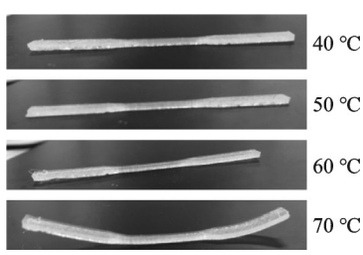

Fig.3 Relationship between specimen shape and stage temperature

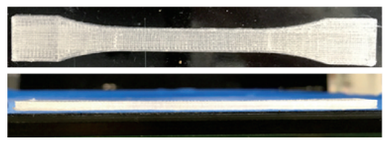

Fig.4 Printed PLA-CNF 0.5% (volume fraction) tensile specimen in the 0°/90° direction

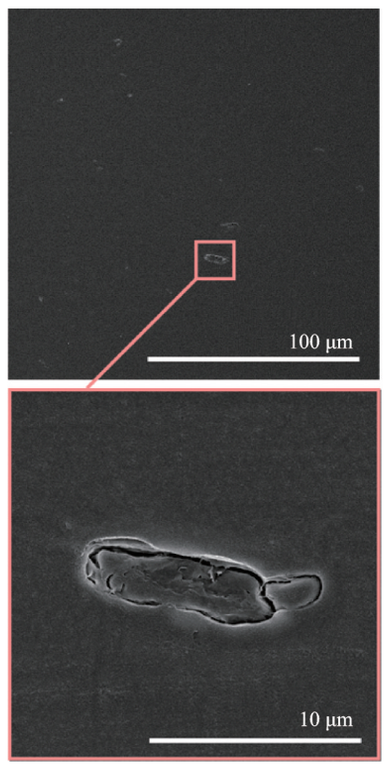

Fig.5 CNF agglomeration in PLA-CNF 0.1% (volume fraction) tensile specimen

fraction. The PLA/CNF interface was not intimate, possibly because PLA is hydrophobic while CNF has hydrophilic groups on its surface[16-17]. This result implies that the load transfer efficiency at the PLA/CNF interface is low. Furthermore, the CNF orientation along the fiber direction was not observed.

Fig.6 shows typical stress-strain curves of the PLA-CNF composites printed in the 0°/90° and +45°/− 45° directions. The PLA-CNF composites printed in +45°/− 45° showed an apparent plastic deformation, while the PLA-CNF composites printed in 0°/90° showed a proportional relationship between tensile stress and strain, thus being looked like to exhibit a brittle behavior. Fig.7 shows the CNF volume fraction versus ultimate tensile strength (UTS) and fracture elongation of the PLA-CNF composites. The UTS and fracture elongation of the PLA-CNF composites printed in +45°/− 45°

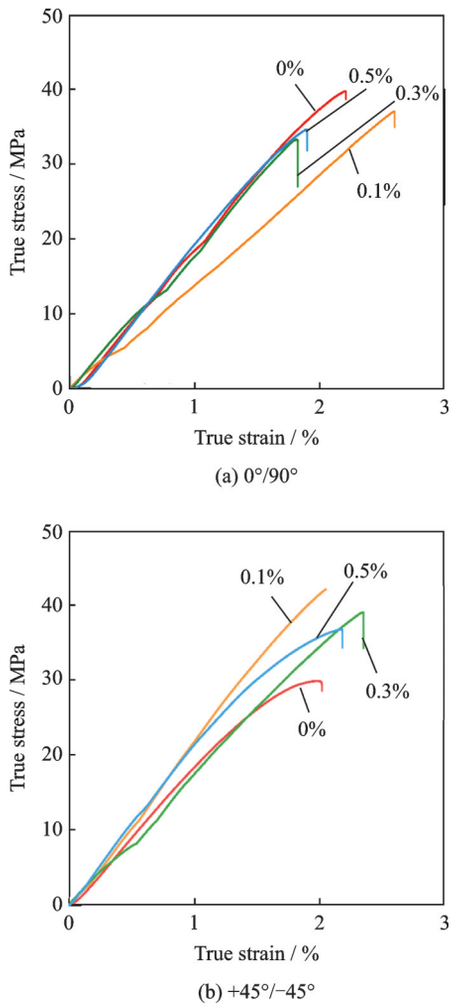

Fig.6 Typical stress-strain curves of PLA-CNF composites printed at 0°/90° and +45°/−45°

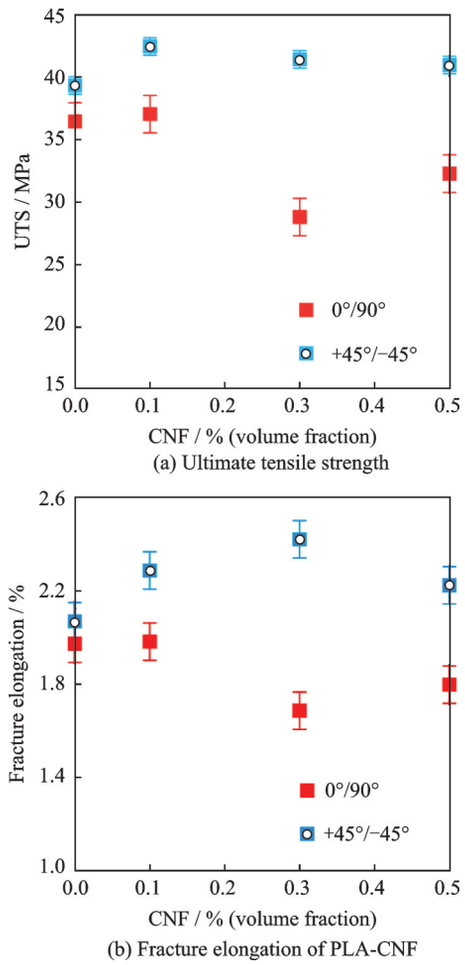

Fig.7 CNF volume fraction versus ultimate tensile strength and fracture elongation of PLA-CNF composites printed in 0°/90° and +45°/−45°

were higher than the ones of the PLA-CNF composites printed in 0°/90°. The reason lies in the fact (Fig.8) that in the PLA-CNF composites printed at 0°/90°, the filament in the direction perpendicular to the loading direction does not contribute to bearing the applied tensile load; thus, the stress concentrates in the void at the intersection between the two directions. In contrast, for PLA-CNF composites printed at +45°/ −45°, the filaments in both directions bear the applied tensile load. Moreover, it seems that the stretching of filaments to loading directions provides the apparent plastic deformation and higher fracture elongation. A CNF addition of only 0.1% (volume fraction) increased the UTS and fracture elongation of PLA printed at +45°/−45° by 8% and 11%. However, it was inclined that a CNF addition higher than 0.3% (volume fraction) decreased the UTS and fracture elongation of PLA.

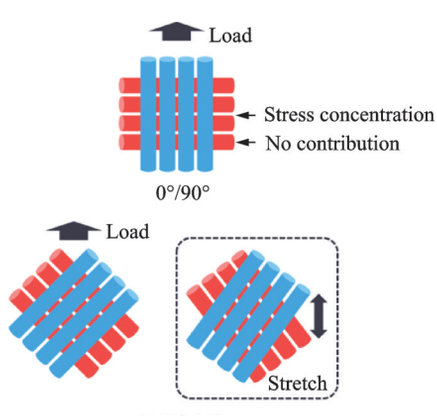

Fig.8 Mechanical behavior of PLA-CNF composites printed a 0°/90° and +45°/−45° under tensile load

Fig.9 shows the SEM fractographs of the printed PLA-CNF composites. Many pores were observed between the printed filaments and the fracture surface appears flat (i.e. a typical fracture surface of brittle materials) (the image in the first row

in Fig.9). Therefore, these fractographs support the stress-strain curves of the PLA-CNF composites. Few distributed CNFs were observed on the fracture surface (the three images in the second row in Fig.9). These distributed CNFs were exposed without breaking. This result implies that the distributed CNFs were pulled out after bearing the applied tensile load. However, the agglomerated CNF clusters were broken and large pores were observed around them (Fig.10). The number of agglomerated CNF clusters increased with the CNF volume fraction. It seems that the agglomerated CNF clusters decrease the tensile properties of PLA rather than increase them. Therefore, it is likely that homogeneously dispersed CNFs significantly increase the tensile properties of PLA.

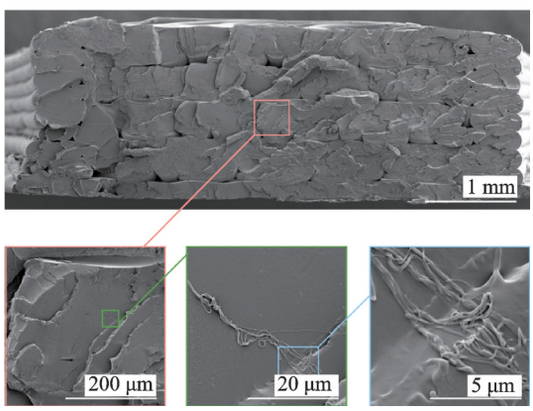

Fig.9 SEM fractographs of PLA-CNF 0.1 % (volume fraction) composite printed in the 0°/90° direction.

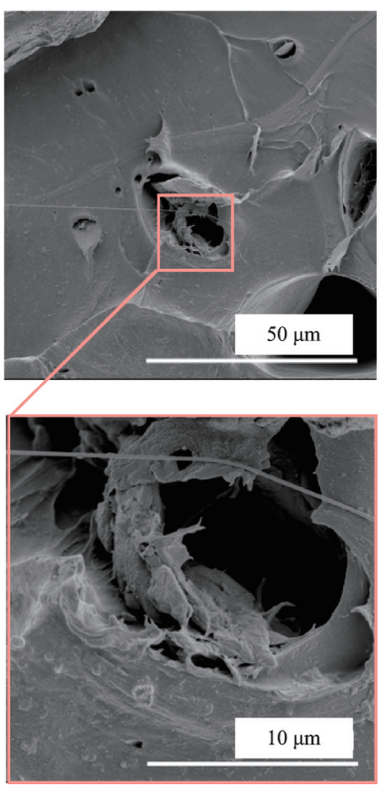

Fig.10 CNF agglomeration on fracture surface of PLA-CNF 0.3 % (volume fraction) composite printed in the 0°/90° direction.

3 Conclusions

Mechanically-defibrated CNF-reinforced PLA matrix composites were fabricated by FDM. The tensile properties of the 3D-printed CNF-reinforced PLA matrix (PLA-CNF) composites were investigated in two printing directions: 0°/90° and +45°/−45°. The microstructure and fracture surface were also analyzed by SEM.

Several voids were observed inside the printed specimens along the printing direction, as reported in previous studies. CNFs were agglomerated in PLA and a number of agglomerated CNF clusters was proportionally increased with the CNF volume fraction. The delaminated PLA/CNF interface attributed to the mismatch of hydrophilicity implies that the load is not effectually transferred from PLA to CNFs at the PLA/CNF interface. The CNF orientation along the printing direction was not observed.

The UTS and fracture elongation of the PLA-CNF composites printed at +45°/−45° were higher than the ones of the PLA-CNF composites printed at 0°/90°. In the PLA-CNF composites printed at 0°/90°, the filament in the direction perpendicular to the loading direction does not likely contribute to bearing the applied tensile load and the stress concentrates to the void between the filament. In contrast, in PLA-CNF composites printed at +45°/−45°, the load is beared by the filaments printed in both directions. The stretching of the filaments and their re-orientation in the loading direction induce apparent plastic deformation and higher fracture elongation.

The exposition of distributed CNFs without breaking, the failure of CNF clusters and large pores around CNF clusters were observed on the fracture surface. Hence, the agglomerated CNF

clusters decrease the tensile properties of PLA rather than increase them. Consequently, it was revealed that homogeneously dispersed CNF significantly increase the tensile properties of PLA.

Consequently, the mechanically-defibrated CNF reinforced PLA composite, which can be fabricated eco-friendly and in low-cost, has a potential to be used as a green composite with further studies to understand its strengthening mechanism and effective enhancement.

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able polymer matrix composites.

Author contributions Dr. **KURITA Hiroki** designed the study, interpreted the results and wrote the manuscript. Dr. **BERNARD Chrystelle** and Ms. **LAVROVSKY Agathe** contributed to the analysis, the discussion and background of the study. Prof. **NARITA Fumio** contributed to the discussion and to the project administration. All authors commented on the manuscript draft and approved the submission.

Competing interests The authors declare no competing interests.

(Production Editor: ZHANG Bei)

熔融沉积法制备纤维素纳米纤维增强聚乳酸基复合材料的拉伸性能

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摘要:生物可降解聚合物可以在保持结构力学性能的同时可以实现碳中性,是石油基聚合物的潜在替代品。在这些聚合物中,聚乳酸(Polylactic acid, PLA)因其良好的力学性能、生物相容性和热塑性而特别有发展前景。本文利用机械脱脂纤维素纳米纤维(Cellulose nanofiber, CNF)来提高聚乳酸的力学性能,该纤维具有显著的力学性能和生物降解性。熔融沉积建模(Fused deposition modeling, FDM)是热塑性聚合物的三维打印方法之一,可以降低制造成本。本研究采用FDM法制备了机械脱脂CNF增强PLA基复合材料,并在两个打印方向(0°/90°和+45°/−45°)上研究了它们的拉伸性能,梳理了机械制备CNF增强PLA基复合材料的印刷方向与拉伸行为之间的关系。此外,利用扫描电镜研究了机械脱脂CNF增强PLA基复合材料的显微组织和断口。

关键词:纤维素纳米纤维;聚乳酸;拉伸性能;熔融沉积制备