Bio-based resin/cellulose composites for UV-assisted 3D printed orthopedic casts

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Abstract. An orthopedic cast is a device used for stabilizing bone fracture. To date, the conventional plaster casts do not have reasonable control over the functional characteristics of comfort, lightweight, and return in patients' everyday life during the healing process. Three-dimensional (3D) printing is a rapidly growing and impressive technology with plentiful possibilities for customized rehabilitation tools, particularly the orthopedic cast. However, the 3D-printing materials are still limited, especially in terms of their printability and mechanical strength. In this work, bio-based resin/cellulose composites are developed as alternative materials to enhance mechanical performance for DLP (Digital Light Processing) 3D printing, which could further potentially fabricate 3D-printed cast. Triacetin, polypropylene glycol (PPG) and PEGDA are used to improve the distribution and dispersion of cellulose in bio-based resin. The results indicated that the mechanical properties improved with appropriate printed direction. The 90° printing direction gave the higher flexural strength than that of the 46.62° printing direction, which are 2650 MPa and 2487 MPa, respectively. Also, more printing accuracy was found for the 90° printing direction. SEM images revealed well dispersion of cellulose in bio-based PLA resin composite with PEGDA. However, the interfacial adhesion needs to be further improved to enhance the mechanical performance.

1. Introduction

An orthopedic cast is a medical device frequently made from plaster or fiberglass, that used for stabilizing and holding bone fracture in place until healing is confirmed. Plaster casting is a conventional method for producing orthopedic cast. However, such classical plaster casts do not have reasonable control over the functional characteristics of comfort, lightweight, and return in patients' everyday life during the healing process. Three-dimensional (3D) printing is a rapidly growing and impressive technology with plentiful possibilities for customized rehabilitation tools, particularly the orthopedic cast. For non-surgical treatment of fractures, 3D printing technology could benefit in making personalized cast with an appropriate fit and a ventilated structure for patients [1]. 3D printing has many advantages, including high-quality detail products and easy custom product design. It can be applied in many fields such as education, industrial design, automotive, engineering, architecture, medical, dental, accessories, food, astronautics and more [2,3].
Digital Light Processing (DLP) 3D printing is the most common UV-assisted 3D printing technique. The materials used in DLP 3D printing are resin or pre-polymer that can be cured under light. DLP uses a projection of ultraviolet (UV) light or visible light from a digital projector to flash a single image of the layer across the entire resin at once. The print bed will move up to project the next layer until the model is complete. DLP technique gives a high-resolution printing; however, materials used for DLP 3D printing process are still limited, especially in terms of their printability, mechanical properties and cost-efficiency [4,5,6].

Cellulose is a biopolymer with a straight-chain structure with many D-glucose structures, connected by a Beta -1,4 glycosidic bond. Its unique properties are high crystallinity, good mechanical properties, ductility, and biodegradability [7]. Cellulose is hydrophilic material from glucopyranose molecule of each repeating unit which consists of three hydroxyl groups. For polymer composites, cellulose is often used as a filler to reduce cost by replaces the proportion of the polymer matrix. Also, cellulose can be used as a reinforcement to enhance the mechanical properties of the composites. However, the hydrophilic cellulose is poorly compatible and dispersible in hydrophobic polymer matrix. This directly affects the mechanical properties and also the printability of the composite material. V.P. Anju and S.K. Narayanan Kuttty [8] studied the effect of the coupling agent on the dynamic mechanical properties of poly(methyl methacrylate) (PMMA)/cellulose micro composites. The results indicated that bis-(3-triethoxysilylpropyl) tetrasulphide (Si69) enhanced the mechanical properties of the micro composite by forming chemical bonds with both PMMA and cellulose. Besides, SEM images showed well dispersion of cellulose in PMMA matrix in presence of Si69. This is in good evidence with the improved strength of the composite. Also, Vincent Chi-Fung Li et al. [9], improved the compatibility of cellulose nanocrystal (CNCs) and poly(ethylene glycol) diacrylate (PEGDA) by adding other substances. The results indicated that using glycerol 1,3-diglycerolate diacrylate (DiGlyDA) as a secondary polymer, the compatibility of CNCs and PEGDA was improved by creating a hydrogen bond.

This work aims to develop bio-based PLA resin/cellulose composites as alternative materials to enhance mechanical properties for DLP 3D printing, which could further potentially fabricate 3D-printed cast. Triacetin, polypropylene glycol (PPG) and PEGDA are used to improve the distribution and dispersion of cellulose in bio-based resin. In terms of printability, the suitable printing angle and the sedimentation of cellulose in bio-based PLA resin are elucidated. Furthermore, the mechanical properties and morphology of the 3D printed parts are investigated.

2. Materials and Methods

2.1 Materials
Bio-based PLA resin (eSUN) was used as received. Microcrystalline cellulose (20 μm) from Sigma-Aldrich Chemistry was used as the filler to reinforce polymer matrix. Triacetin (Sigma-Aldrich Chemistry), polypropylene glycol (PPG) (SyncoPol DL1000, IRPC POLYOL), and polyethylene glycol dimethacrylate (PEGDA) (Mw 550, Sigma-Aldrich Chemistry) were used as dispersing agent. Also, isopropyl alcohol (IPA) was used to clean the specimen obtained from 3D printing process.

2.2 Bio-based PLA resin/cellulose composite preparation
Microcrystalline cellulose at different concentrations (1, 10 and 20 phr) were mixed with bio-based PLA resin under magnetic stirring for 60 minutes. The mixtures were then sonicated for 1 hour to ensure that they were homogenous. To improve cellulose dispersity, Triacetin, PPG and PEGDA were added into the bio-based PLA resin/cellulose composites with fixed concentration at 10 phr. The composites without dispersing agent were named as RC series (RC001, RC010 and RC020). The composites with Triacetin, PPG and PEGDA were named RCT, RCP and RCA series, respectively. The material compositions for all composites were presented in Table 1.
Table 1. Summary of the compositions of the bio-based PLA resin/cellulose composites.

| Resin (ml) | Dispersing Agents (10 phr) | Cellulose (phr) |
|------------|----------------------------|-----------------|
| 100 -      | RC001                      | RC010           |
| 100 Triacetin | RCT001                     | RCT010          |
| 100 PPG    | RCP001                      | RCP010          |
| 100 PEGDA  | RCA001                      | RCA010          |

2.3 Printing Direction Optimization
The flexural testing specimens (according to the ASTM D790) were 3D printed using the Digital Light Process (DLP) 3D printer, Elegoo Mars Pro, using the printing angle of 46.62° and 90.00°, respectively. In this section, only pure bio-based PLA resin was used as a representative material for analyzing. The 3D printing parameters were listed in Table 2. The printed specimens were then washed with IPA and post-cured for 15 minutes under 405 nm light box.

Table 2. Digital Light Process (DLP) 3D printing parameters

| Parameter                  | Value |
|----------------------------|-------|
| Light source wavelength (nm) | 405   |
| Layer height (mm)          | 0.05  |
| Exposure Time (s)          | 8     |
| Bottom Exposure Time (s)   | 45    |
| Bottom layer count         | 5     |
| Support                    | Enable|
| Anti-aliasing              | Enable|

2.4 3D printing of bio-based PLA resin/cellulose composites
All bio-based PLA/cellulose composites were prepared as the flexural testing specimens using the same printing parameters listed in Table 2. The printed specimens were then washed with IPA and post-cured for 15 minutes under 405 nm light box.

2.5 Flexural Test
The flexural properties of all 3D printed specimens were measured according to ASTM D790 standard, using a Universal Testing Machine (Tinius Olsen Model 1 ST) equipped with a 5 kN load cell at a crosshead speed of 5 mm/min.

2.6 Morphology
The fractured specimens obtained from the flexural test were then analyzed by Scanning Electron Microscope (Hitachi SU3500 SEM) with an accelerating voltage of 5.00 kV to investigate cellulose dispersion in the bio-based PLA resin/cellulose composites. Before observation, the fractured surfaces of the samples were sputter-coated with a thin conductive gold layer to make the surfaces conductive.
3. Results and Discussion

3.1 Printing Direction Optimization

Figure 1 shows the flexural properties of bio-based resin printed with 46.62° and 90.0° printing directions. With a 90.0° printing direction, the flexural strength was higher than that of the 46.62° printing direction. The flexural strengths of printed specimens of 90.0° and 46.62° printing directions were 2,237 MPa and 2,006 MPa, respectively. Contrastingly, the 46.62° printing direction gave a more flexural modulus than that of the 90.0° printing direction, which was 81 MPa and 76 MPa, respectively. However, the 90.0° printing direction gave more accurate dimensions than those of the 46.62° printing direction by measuring the 3D printed sample dimension (width, length, and thickness) with a vernier caliper, compared to the dimension specified in 3D model file. Therefore, the 90.0° printing direction was then used to 3D print the resin composites.

![Figure 1. Flexural properties of printed specimens at 46.62° and 90.0° printing directions: (a) Flexural strength and (b) Flexural modulus.](image)

3.2 3D printing of bio-based PLA resin/cellulose composites

Figure 2 (a) shows the 3D printed specimens of pure bio-based PLA resin and its composites, RC with 1, 10, and 20 phr of cellulose. The scale on the left represented the printing time scale, while the scale on the right represented the length of the sample printed at that time. As expected, RC001, the composite with 1 phr cellulose, exhibited an almost similar physical appearance to the pure bio-based PLA resin. However, with increased the cellulose contents of 10 and 20 phr, the layer separation between cellulose and bio-based PLA resin matrix appeared at a shorter time scale. The boundary layer between dense cellulose area (white-area) and light cellulose area (clear-area) is evidenced at almost 3 hours and 2.5 hours for RC010 and RC020. The results showed that cellulose concentration directly influenced the distribution and dispersion of the cellulose, which is consistent with the cellulose precipitation time in the composite resin. It could be concluded that the higher the cellulose loading, the shorter time for printing, or the decrease in the length of the printed part.
Figure 2. Cellulose dispersion in the printed specimens from (a) bio-based PLA resin, RC001, RC010 and RC020 and (b) RC020, RCT020, RCP020 and RCA020.

In this study, the three dispersing agents were added, aiming to enhance the distribution and dispersion of cellulose in bio-based PLA resin polymer matrix. Figure 2(b) shows printed specimens from the bio-based PLA resin and its 20 phr cellulose composites with different dispersing agents, RCT 20, RCP20 and RCA20, respectively. It is clearly seen that RCA020 or the composite with PEGDA improved the cellulose dispersion in the composites than others. It is believed that the improvement in cellulose dispersion resulted from the hydrogen bonding between cellulose and PEGDA [10,11].

3.3 Mechanical Property
Figure 3 shows the flexural strength of the bio-based PLA resin and bio-based PLA resin/cellulose composites (20 phr cellulose) with different dispersing agents. The flexural strength of RCT020, RCP020 and RCA020 were 1,179.6 MPa, 1,369.4 MPa and 2,137.3 MPa, respectively. As expected, the composite with Triacetin, RCT020, showed the lowest flexural strength due to the poor dispersion of cellulose. The flexural strength was improved for RCP020, which is again consistent with the homogeneity of cellulose dispersion in the bio-based PLA resin matrix. RCA020, which showed the most homogeneous cellulose dispersion, gave a good mechanical property at a comparable level to the bio-based PLA resin. In summary, using PEGDA as dispersing agent led to an enhancement in the cellulose dispersion in the bio-based PLA resin matrix.

Figure 3. Flexural properties of printed specimens from Bio-based PLA resin, RCT020, RCP020 and RCA020.
3.4 Morphology
Figure 4 shows the morphology of the fracture specimens of pure bio-based PLA resin, RC020 and RCA020. From RC020, the large sizes of cellulose clusters were observed, which indicated the poor dispersion and agglomeration of cellulose in the composite resin. The addition of PEGDA resulted in the better distribution and dispersion of cellulose as evident by the smaller size and better dispersion of cellulose in RCA020.

![Figure 4. The SEM images from the fracture surface of (a) pure bio-based PLA resin, (b) RC020 and (c) RCA020 at the magnification of 500x.](image)

4. Conclusions
PEGDA successfully improved the dispersion of cellulose fiber in bio-based PLA resin used for DLP 3D printing. 3D printing of cellulose-based composites is currently gaining more attention regarding environmental concerns. With high cellulose loading, successfully 3D printing is a significant challenge since the cellulose tend to agglomerate and precipitate before the printing is finished. The advantage of incorporating PEGDA is to improve the dispersion and distribution of cellulose fiber during 3D printing process, lasting about 6 hours in this study. SEM images revealed well dispersion of cellulose in bio-based PLA resin composite with PEGDA. However, the interfacial adhesion needs to be further improved to enhance the mechanical performance. Besides, the 90.00° printing direction allowed higher flexural strength and more dimensional accuracy than those of the 46.62° printing direction. As a result, the high precision DLP 3D printing of bio-based PLA resin/cellulose composites could expand the opportunity to accurately reproduced the orthopedic cast which matches the patient's unique anatomy.

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