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BIOPOLYMER COMPOSITES WITH DAIRY PROTEIN FOR USE IN ADDITIVE MANUFACTURING

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Abstract

As the popularity and versatility of additive manufacturing grows, so does interest in developing new materials, including biopolymers. Casein is a protein found in dairy and historically, has been used in food applications, but its use as a biomaterial for engineering structures is less common. This study investigates the development of composite materials for additive manufacturing with casein as a biomaterial filler. To observe the effects of casein on material properties, vat photopolymerization-based and fused filament fabrication-based matrix materials were combined with different weight fractions of casein. Test samples were fabricated to evaluate tensile properties. Test results show a maximum increase of 4% for FFF and 34% for SLA in the stiffness of the materials with casein compared to the neat matrix materials. However, the composite materials showed between 12% and 54% reductions in ductility, and marginal decreases in tensile strengths. The preliminary results indicate viability and prompt further investigation into casein-polymer composites for additive manufacturing.

Keywords: Additive Manufacturing, Biopolymer, Dairy, Casein, Polymers

Introduction

The applications of additive manufacturing (AM) technologies are broad, ranging from prototyping to small batch manufacturing, medical implants and construction, and more uses continue to develop [1]. With technological developments and research initiatives, manufacturing materials continue to evolve as well. Traditionally, polymer AM utilizes petroleum-based materials which carry associated hazards to human health and the environment [2]. Examples of these materials include Acrylonitrile Butadiene Styrene (ABS), Polycarbonate (PC), Nylon, or UV-Curing Resins [2-4]. A few biobased AM materials like polylactic acid (PLA) [2], Polyhydroxyalkanoates (PHAs) [5], and epoxidized sucrose soyate (ESS) resins [6] exist but further development of affordable materials sourced from sustainable resources is important to the future of additive manufacturing [2, 4].

Many composite polymers for AM based on renewable resources have been developed in recent past. Some use biomaterials as fillers in petroleum-based polymers and resins [1,7-9], and others as fillers in biopolymer matrices, such as PLA [10-15]. Lignin, a natural polymer sourced from wood, is a common additive in composite materials and has been recently studied as a filler in materials for fabrication using various AM technologies. [7-9, 13-14]. Cellulose nanofibers have also been incorporated into biobased polymers such as PLA as a beneficial reinforcer [11, 15]. Another study demonstrated that kenaf fibers, a natural plant fiber, in a PLA matrix improved both mechanical and thermo-mechanical properties of the material [12]. A study examining casein-functionalized cellulose fibers in PLA found whole milk casein protein to be an effective dispersant and binder in the composite [15].

This research is an exploratory study on the viability of incorporating casein protein filler into different material matrices for fabricating engineering structures using AM processes. Casein is a protein that is abundant in dairy; it makes up about 80% of the protein found in cow's milk [16]. Its applications are primarily food or pharmaceutical based, but it has historically been used for polymer production as well [17]. Casein molecules consist of hydrophobic and hydrophilic blocks which are able to interact with other molecules [15]. These blocks participate in the crosslinking of casein during the manufacturing processes [17]. In the early 20th century, casein was combined with plasticizer, formaldehyde, or other chemicals to create formable bioplastics [18]. However, the procedure was very time consuming, and the products fabricated from the casein plastic were predominantly small items such as buttons and buckles [18]. More recent products developed using casein include adhesives, foams, gels, and some bioplastics [16].

The source of the casein filler is of long-term interest as well. Significant volumes of wastewater are generated in the dairy industry, with cheese production, whey manufacturing, and milk processing being major contributors [19]. These wastewaters, from washing equipment or whey by-products, have casein contents that can be valorized [19]. Another source of casein that can be valorized is discarded milk from deliberate dumping of milk shipments by farmers or cooperatives [20-22] It is routine for small amounts of milk to be dumped due to seasonal overproduction and other factors such as weather or batch contamination [22]. However, large-scale dumping occurs when there is a major disruption to the dairy industry such as supply-chain issues or a dramatic decrease in market demand [20-21]. All cases of dumping result in economic losses to farmers and the nutrient-rich milk can produce negative effects on the environment [16, 21]. Casein protein can be extracted from the wastewater or discarded milk using precipitation or microfiltration and dried into powder [23]. Casein is used for some medical applications and human or animal consumption but often the wastewater contains contaminants and would require purification to reach medical or food-grade industry standards; however, for engineering-grade applications, the purity of the casein is less relevant [16]. Extracting the casein and producing bioplastics for AM would valorize the dairy industry wastewater, and create an alternate market for discarded milk, reducing financial loss and environmental impact. The materials generated would be sustainable, and, by sourcing the casein from waste, would also be affordable and not compete with the demands of the food industry.

In this work, two different AM technologies are examined: stereolithography (SLA) and fused filament fabrication (FFF). SLA printing fabricates parts using a UV-photocurable resins. Ultraviolet light is employed to locally cure the resin in thin layers to build three-dimensional solid objects. Post-processing or cleaning is often required following SLA printing to finish the parts.

The material for FFF is a solid filament made of thermoplastic polymer. The filament is fed into the print head and heated while being extruded through a nozzle and deposited in layers onto the build platform to form a part.

The purpose of this research is to develop sustainable materials for AM and to reduce economic loss within the dairy industry by determining whether casein protein is a viable filler in composites development for AM. Casein powder will be added to neat polymer materials and test specimens printed. The mechanical properties of the composites will be compared to the neat polymer to observe the effects of the casein filler.

Methodology

For both SLA and FFF printing methods, the casein powder was blended with the neat matrix material in different weight fractions. Five dog-bone tensile test specimens were produced for each treatment to evaluate the mechanical properties. Specimens were dried in a vacuum oven and stored in a desiccator prior to testing to prevent inconsistency in material behavior due to moisture absorption from the air. Tensile testing parameters followed ASTM D638 standards for plastics. A 50 kN MTS tensile testing machine was used for testing all specimens. After testing, the fractured surfaces of the FFF specimens were examined under a scanning electron microscope (SEM). Backscattered-Electron (BSE) imaging was used with variable pressure settings to examine the morphology of the fractured surfaces.

SLA Printing

For SLA printing, Formlabs Clear Resin was used as a matrix for composites containing 5 wt% and 10 wt% casein filler material. Tensile test specimens were printed on a Form 3 printer from Formlabs using the two resin-casein composites. The specimens were angled off the bed of the printer as shown in Fig. 1 for ease of removal after print.

Figure 1: SLA tensile specimens before removal from the printer bed.

After printing, the samples were post-processed in a Formwash chamber with isopropyl alcohol to clean the specimens, then cured in a UV Formcure oven. Sample batches were cured at 60 ^{o}C for different times. The control samples made of neat, standard clear resin were cured for 15 and 30 minutes as recommended by Formlabs [24]. The 30 minutes cure was to achieve a marginal gain in mechanical properties. The composite resin batch with 5 wt% casein was cured for 30 minutes while two batches containing 10 wt% casein were cured, one for 30 minutes and the other, for 60 minutes, to compare the effect of longer cure time on the properties of the composite.

FFF Printing

PLA powder was blended with 5 wt%, 10 wt%, and 12 wt% casein powder and then extruded into filament for FFF printing. A lab-scale Filabot EX2 extruder was used for filament extrusion. The first extrusion was pelletized and re-extruded a second time to ensure the homogeneity of the final filament intended for printing. The pelletized filament can be seen in Fig. 2 and a sample of PLA/Casein filament is shown in Fig. 3. Tensile test specimens were fabricated on a Creality 10-S 3D printer. The specimens were oriented flat on the print bed, with the long edge parallel to the printer’s y-axis. They were printed with 100% infill settings and a zig-zag deposition pattern.

Figure 2: pelletized PLA/casein filament after the first extrusion.

Figure 3: PLA/casein filament sample.

Results and Discussion

SLA Specimens

The comparison plots for SLA printing are seen in Fig. 4 to Fig. 6 for the tensile strengths, moduli of elasticity, and percent elongations respectively. The designations below each bar on the chart indicate the composition of the material (CL for clear resin), followed by the weight percentage of casein added and the cure time in minutes, thus, CL05C30 indicates clear resin/5 wt% casein cured for 30 minutes. For neat clear resin samples, an increase from 15 to 30 minutes in cure time resulted in better performance across all three material properties measured. Interestingly, with the addition of 10 wt% casein, the change in material properties was varied when comparing 60 minutes cure time to 30. The modulus experienced a 15% reduction while the elongation increased 27%, and the tensile strength remained constant.

Samples with 0 wt%, 5 wt%, and 10 wt% casein were compared at a consistent cure time of 30 minutes. The tensile strength decreased by just under 15% for the composites compared to the neat resin, and the change was close to uniform for both weight fractions. The modulus of elasticity showed an increase with the addition of casein, 34% at 5 wt% casein and 13% for 10 wt% casein. The percent elongation was reduced to nearly half of that of the neat resin with the reduction more marked for 5 wt% casein.

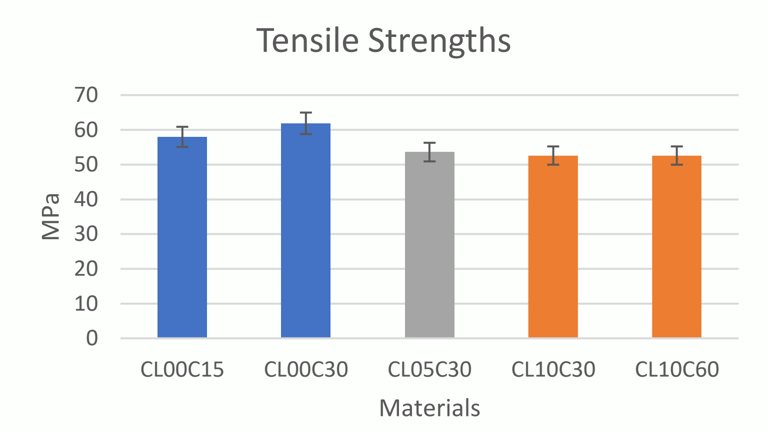

Figure 4: Tensile strength comparison for SLA samples.

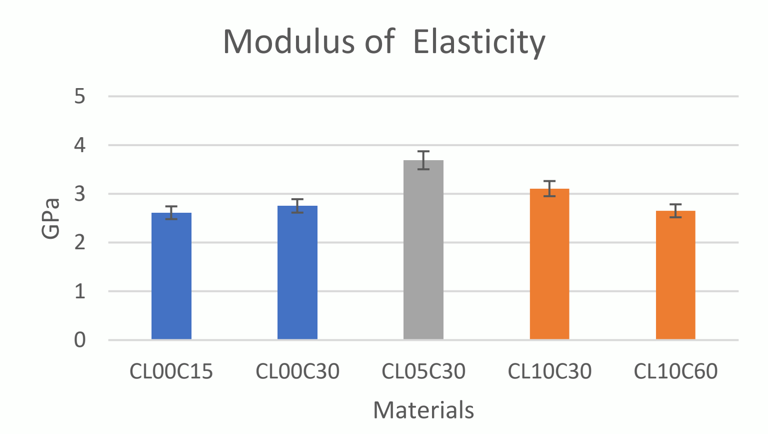

Figure 5: Modulus of elasticity comparison for SLA samples.

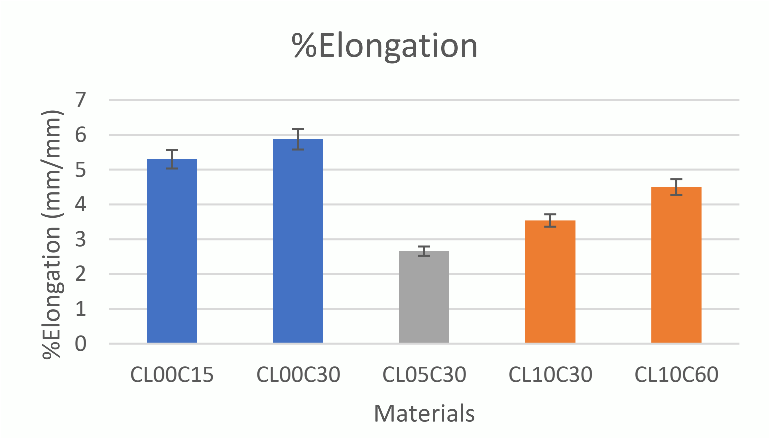

Figure 6: Percent elongation comparison for SLA samples.

FFF Specimens

Figures 7 to 9 show the comparison of the tensile strengths, moduli of elasticity, and percent elongations respectively for FFF specimens. The five-specimen averages for PLA/casein composites made of 5 wt%, 10 wt%, and 12 wt% casein are shown in the plots. Samples of neat PLA were also tested as a control. A slight increase in the modulus of about 4% with the addition of 5 wt% casein was observed and overall, there was only a marginal change in the modulus across all PLA/casein compositions. The tensile strength and percent elongation both experienced varying levels of reduction. The decrease in percent elongation was more significant and ranged from 12% to 35%. This decrease indicated that the addition of casein created a more brittle material compared to the neat PLA samples.

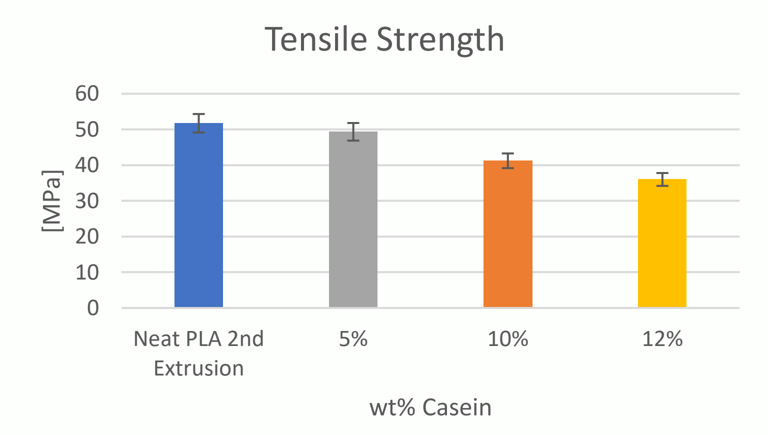

Figure 7: Tensile strength comparison for FFF samples.

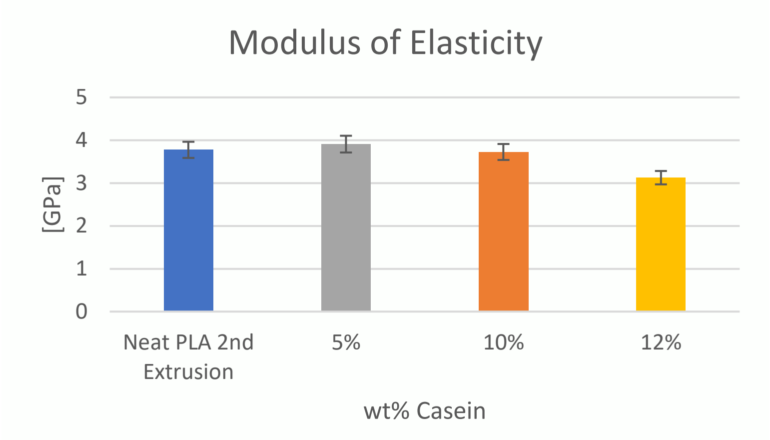

Figure 8: Modulus of elasticity comparison for FFF samples.

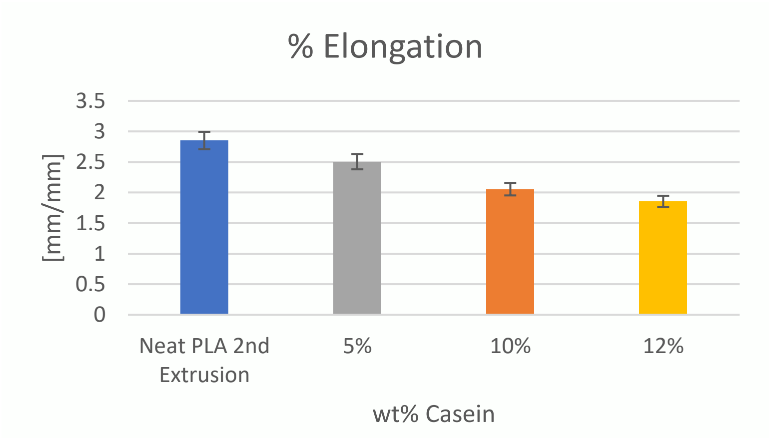

Figure 9: Percent elongation comparison for FFF samples.

SEM Micrographs

Figure 10 presents the SEM images of the fractured surface of FFF samples at several magnifications. Comparing the image of the neat PLA surface in Fig. 10a to the images for 5 wt% in Fig. 10b, 10 wt% casein in Fig. 10c, and 12 wt% in Fig. 10d, very little non-homogeneity in composition is observed. This confirms that the mechanical mixing of the powders and extruding the filament twice is effective in blending the PLA and casein powders. On the surfaces in Fig. 10e and Fig. 10f, at lower magnifications, the layer lines from deposition are visible, creating tiny voids. This is expected and it is characteristic of structure made using the FFF process.

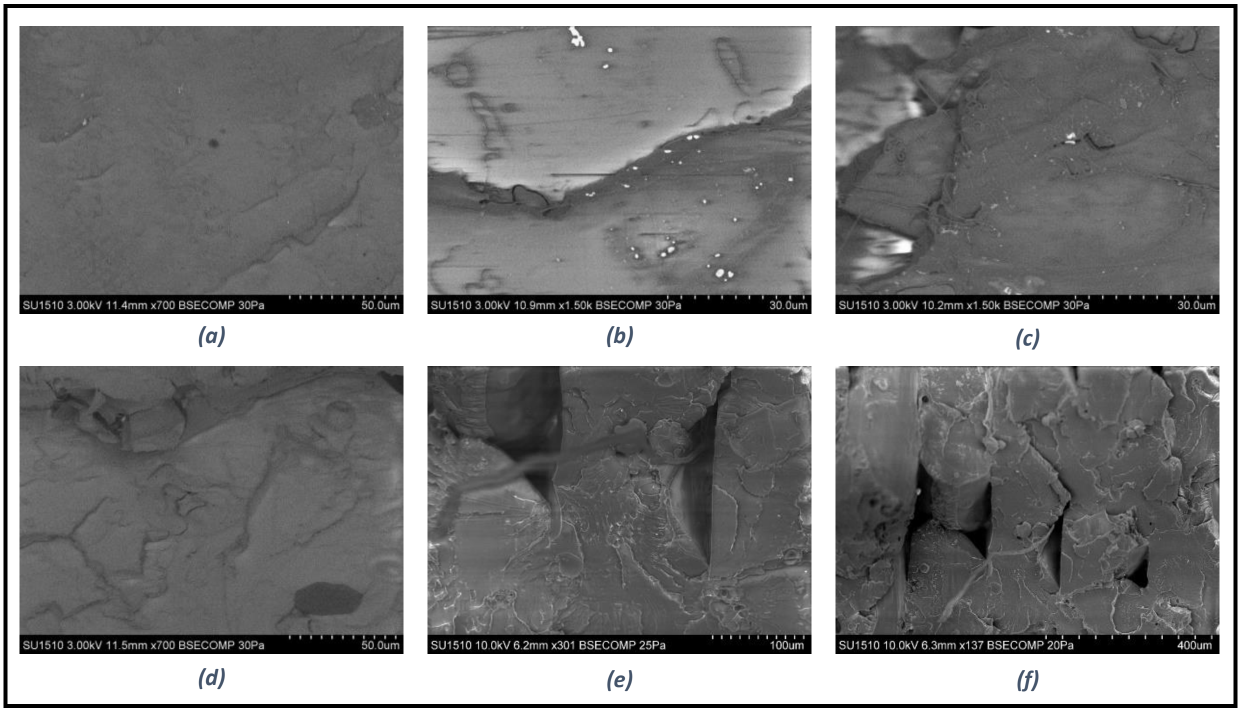

Figure 10: SEM images of fractured surfaces on FFF samples for various compositions and magnifications. (a) neat PLA, 50um, (b) 5% Casein/PLA, 30um, (c) 10% Casein/PLA, 30um, (d) 12% Casein/PLA, 50um, (e) 10% Casein/PLA, 100um, and (f) 10% Casein/PLA, 400um.

Conclusions and Future Work

Casein is shown to be a potential filler in materials for AM. Printability was viable for FFF and SLA printing in the 5 wt%-12 wt% casein filler range examined. Initial testing showed varied mechanical property changes but overall, the composites were more brittle while demonstrating only a slight change to strength and stiffness. For both printing technologies, the 5 wt% casein composites performed the best. The printed material appears homogeneous in SEM imaging. Further refinement of the material blending and printing would improve the process. Additional study includes testing and examining of other weight fractions of casein and incorporating other components such as a plasticizer to reduce the brittleness of the materials.

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