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Mechanical Properties Characterization for Polyamide Matrix Dairy Protein Composites Fabricated Using Selective Laser Sintering Process

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Abstract

This work investigates the viability of casein protein for manufacturing engineering structures. Polyamide 12 (PA12) was used as a matrix for different compositions of casein up to 20 wt%. Test samples were fabricated for neat PA12 and the composites using selective laser sintering for mechanical properties comparisons. The results show significant increases of the tensile strengths up to 71% for the composite materials over the neat PA12. Stiffnesses also increased up to 157%. The composite samples were embrittled in comparison with the neat PA12 samples, however, with the addition of a plasticizer, significant improvement in ductility was obtained from near 2% to over 6% percent elongation with marginal loss in strength. The investigation shows the dependencies of mechanical properties of the composites on the type of filler casein and treatments.

Introduction

Polymers have increasingly been relied upon for manufacturing engineering products. This is because of several factors, among which are cost and weight reduction in comparison to metals. Today, most of the polymers used for engineering grade applications are derived from petroleum-based materials. However, environmental concerns, impacts on human health, and marine ecosystems are some of the driving forces behind recent advances aimed at developing environmentally friendly and competitive alternatives from renewable resources [1-4]. Additive manufacturing (AM) technologies offers the most viable platforms for economical processing and rapid turn arounds of novel material developments. Some naturally occurring biopolymers have been formulated into composites and evaluated for mechanical, thermal, and some other properties of interest using AM. Two material matrices – petroleum-based and biopolymer-based - have been generally adopted. Composites based on petroleum-derived matrices are sometimes developed for the purposed of property modification of the matrix materials, effecting partial biodegradability, and in some cases investigating new applications for the filler biomaterials. This include the use of lignin, a biopolymer derived from plants and trees for developing polymer composites using various petroleum-derived materials as matrices including polyurethane, polypropylene, polystyrene, poly(methyl methacrylate) [5-8]. Composites based on biopolymer matrices are mostly aimed at finding biobased renewable alternatives with low carbon footprint and the potential to substitute petroleum derived materials. Recent work on this includes the development of biocomposites using lignin, cellulose, or hemicellulose as filler materials in PLA matrix [9-15].

While most of the recent work involve lignocellulosic materials from plants, proteins sourced from both plants and animals have historically been used for plastic manufacturing. The common proteins used include casein, zein, soy, feather meal, fish proteins, horn meal, leather scraps as well as waste protein from cotton and linseed [16]. In the present work, a pioneering effort is being made at investigating the use of dairy protein for engineering polymer development through 3D printing. Dairy milk contains proteins, about 80% of which is casein in cow milk, and the balance, whey [17]. These proteins are vital sources of nutrition and are consumed by humans and as animal feeds; and are also used for medical applications. Casein is a hetero-polymer consisting of multiple amino acids and other functional groups that are capable of establishing chemical bonds with other materials [16] under the right processing conditions. As natural biopolymers, they have the potential for useful engineering products. However, rather than compete with casein that are used for food and medical applications, the primary aim is to valorize protein from dairy waste waters and from discarded milk that are dumped into the environments mostly due to supply chain problems [18]. Ability to convert these waste resources would ease economic waste to farmers and the various dairy companies and provide a path to finding alternative polymers that could reduce dependencies on petroleum-derived materials, and promote circular bioeconomy.

The use of AM for casein material processing have been primarily for food and medical applications [19-21]. In this work, the printability and performance of casein filled PA12 composites are explored. The aim is to develop composites that can provide avenue for valorizing casein derived from dairy wastes. Different composites of casein and PA12 blends were prepared up to 20 wt% casein and used to print test samples using selective laser sintering (SLS) process. The mechanical properties of fabricated samples were evaluated.

Experimental Procedures

The PA12 powder used in this work was obtained from Sinterit sp. z o.o., Poland, the manufacturer of the Lisa Pro SLS machine used for all sample fabrications. The filler casein powder was sourced from Fischer Scientific, USA and used for all composite materials fabrication. The SLS machine is a lab scale machine equipped with 5 watts infrared diode laser and 808 nm wavelength. All sample fabrications were made using 125 um layer height. The print surface temperature was offset on the SLS machine by -1°C, relative to the standard setting for the PA12 supplied by the original equipment manufacturer. The PA12 powder consist of almost round particles with size range: 40 μm to 80 μm (US mesh size +400/-170). Also, the casein powder was made of irregular, spongy shape and was received with particle size range: 90 μm to 500 μm (US mesh size +170/-35). Initial samples were fabricated using the casein powder as received, subsequently referred to as “coarse casein”. To assess the dependencies of mechanical properties of fabricated samples on powder particle sizes, subsequent samples were made using finer particle sizes in the range: 90 μm to 250 μm (US mesh size +170/-60). These are subsequently referred to as “fine casein”. Figure 1 shows micrographs of PA12 and casein powder particles obtained using scanning electron microscope (SEM). The casein powders were dried in vacuum oven at 60 ^{o}C temperature for 24 hours before use. To investigate the potential effects of incorporating plasticizers on the mechanical properties of test samples, polyethylene oxide (PEO) was added as a plasticizer in some samples. All powder materials were mechanically mixed to achieve homogeneous distribution before they were used for sample fabrications.

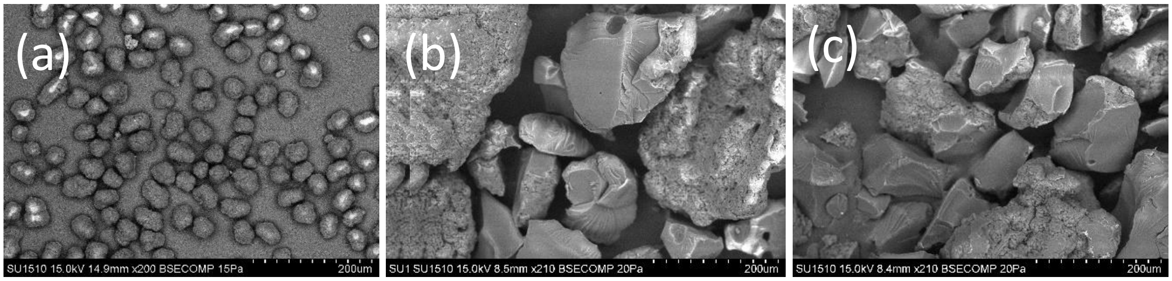


Figure 1: SEM micrographs of (a) PA12, (b) coarse casein, and (c) fine casein particles

Different batches of experimental samples were printed in different orientations, and all sample treatments were printed with five replicates. The samples were in the vertical, horizontal, and at 45^{o} slanting orientations as illustrated in Fig. 2. The different batches include those made of neat PA12 that serve as control. The composites were made of 10, 15, and 20 wt% casein compositions. Initial composite samples were fabricated using coarse casein particles at 10 wt% and 20 wt% casein as a screening step. Upon evaluation of the mechanical properties and SEM micrographs of fractured test samples, additional composite samples with the fine casein particles were fabricated. From previous works published in the literature, finer particles result in better powder packing density prior to sintering on the SLS AM machine bed leading to better density and strengths of the fabricated parts [22]. Test samples made of composites containing 10 wt% and 15 wt% fine casein were fabricated to evaluate their properties in comparison with those made of coarse casein. Furthermore, to study the effect of plasticizers on fabricated composite test samples made of fine casein, 4 wt% PEO were added as a plasticizer to another

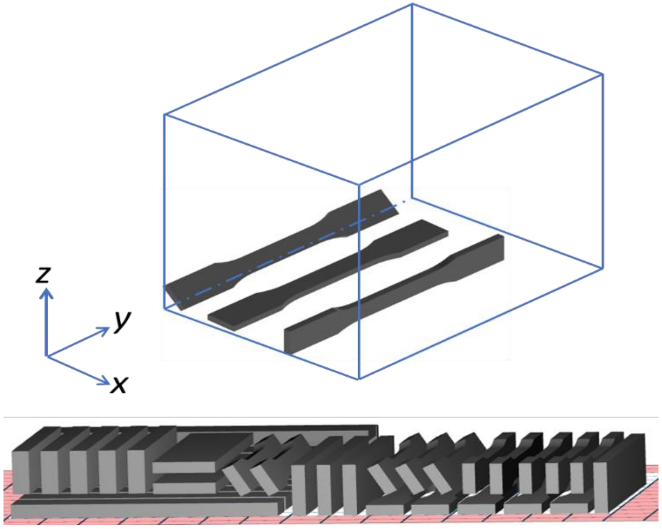


Figure 2 showing the orientation of each batch of test samples fabricated set of samples with 10 wt% and 15 wt% casein. In this paper, the samples are named and differentiated based on the weight fraction of the casein, the fineness or coarseness of the casein particles, and the orientation of the test samples during print. As an example, a sample with 10wt% coarse casein in the vertical orientation is named: *PA-10CT-V*; and a sample with 10 wt% fine casein in the vertical orientation is named: *PA-10CT-VF*. Also, a sample with 10 wt% fine casein and 4 wt% PEO plasticizer in the vertical orientation is named: *PA-10CT-4P-VF*. All samples were sandblasted after removal from the SLS machine to remove all loose, unbound particles and kept in a desiccator until tested. A 50 kN MTS tensile testing machine was used for testing tensile specimens using parameters that conform to ASTM D638 standards.

Results and Discussions

The print qualities of the test samples had surface finish that are typical of parts printed using SLS process, although the composite test samples had rougher surfaces compared to those printed with neat PA12 because of the larger casein particles. Figure 3 shows an image for samples fabricated using neat PA12.

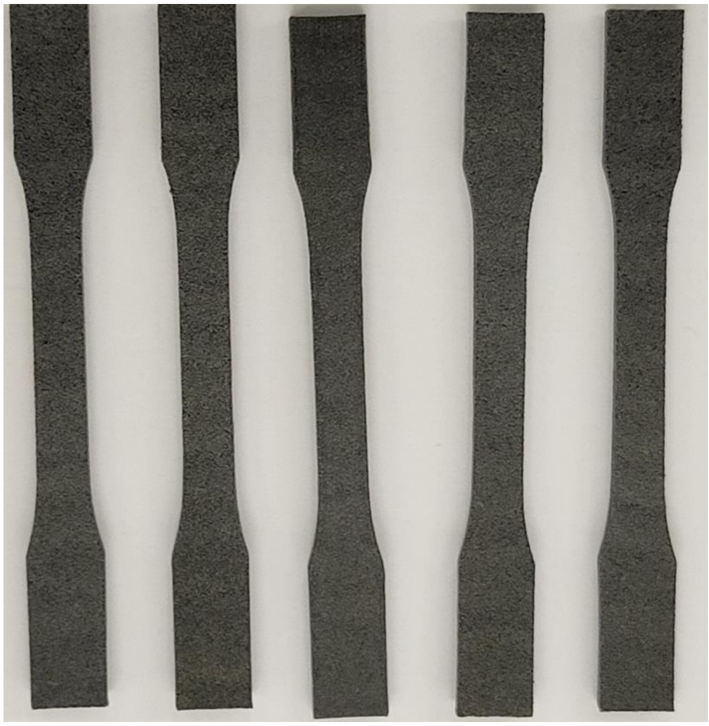


Figure3: Tensile test samples made of neat PA12

Tensile testing results are shown in Fig. 4 to Fig. 6. Figure 4 shows that test samples made of the neat PA12 had 33.48 MPa tensile strength. Composite samples made of 10 wt% coarse casein yielded an average of 40.565 MPa for those with slanting orientation, 39.42 for vertical samples, and 39.92 MPa for horizontal samples. There is no significant difference between the samples based on orientation, but the strengths are significantly higher than the neat

PA12 materials. As shown in Fig. 5, there is significant increase of 71% in stiffness over the neat PA12 samples. However, the composite samples were significantly embrittled with a much lower percent elongation at a little over 2 % compared to the neat PA12, as shown in Fig. 6. Samples made of 20 wt% coarse casein did not have any significant difference in strength when compared with those with 10 wt% coarse casein, both the stiffness and percent elongation are in the same range as the samples made of 10 wt% coarse casein. With fine casein, significantly higher strength values were obtained for all sample orientations than for all the samples made of coarse casein. Samples in slanting orientation have the highest average strength of 57.3 MPa, there was, however, no significant difference between the stiffness of the 10 wt% fine casein samples in comparison with the samples based on coarse casein. 10 wt% fine casein samples with plasticizer yielded comparable strength values when compared to those with basic 10 wt% fine casein. The plasticizer addition resulted in significant increase in percent elongation as shown in Fig. 6. This was a desirable effect for load bearing applications, to avoid unpredictable failure due to embrittlement.

The samples with 15 wt% fine casein and with plasticizer applied, recorded marginal decrease in strengths in comparison to those with 10 wt% fine casein. Horizontal samples recorded the lowest average strength for all composites made of fine casein. The relaxation of the bonding strengths of the constituent materials also led to much lower stiffness for samples made of 15 wt% fine casein with plasticizer in comparison to all the samples made with other composite material formulations. In the same manner as the tensile strengths, the percent elongation reduced marginally.

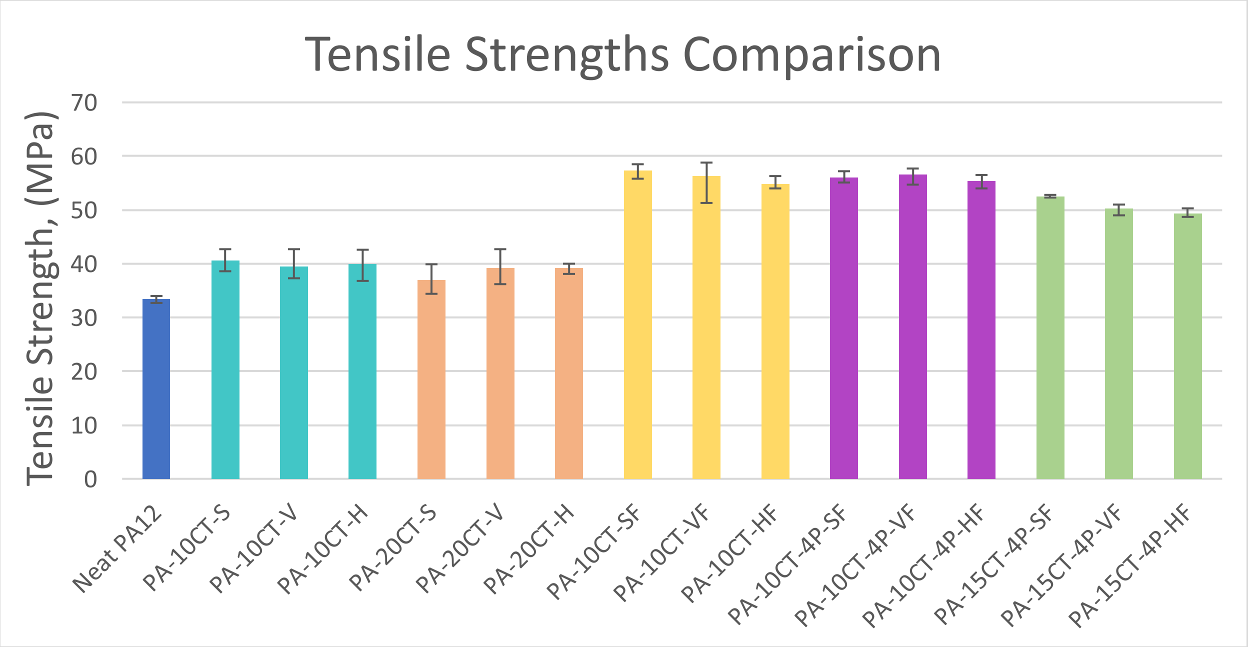


Figure 4: Tensile strengths comparison for samples fabricated using the control, neat PA12 and the composite materials

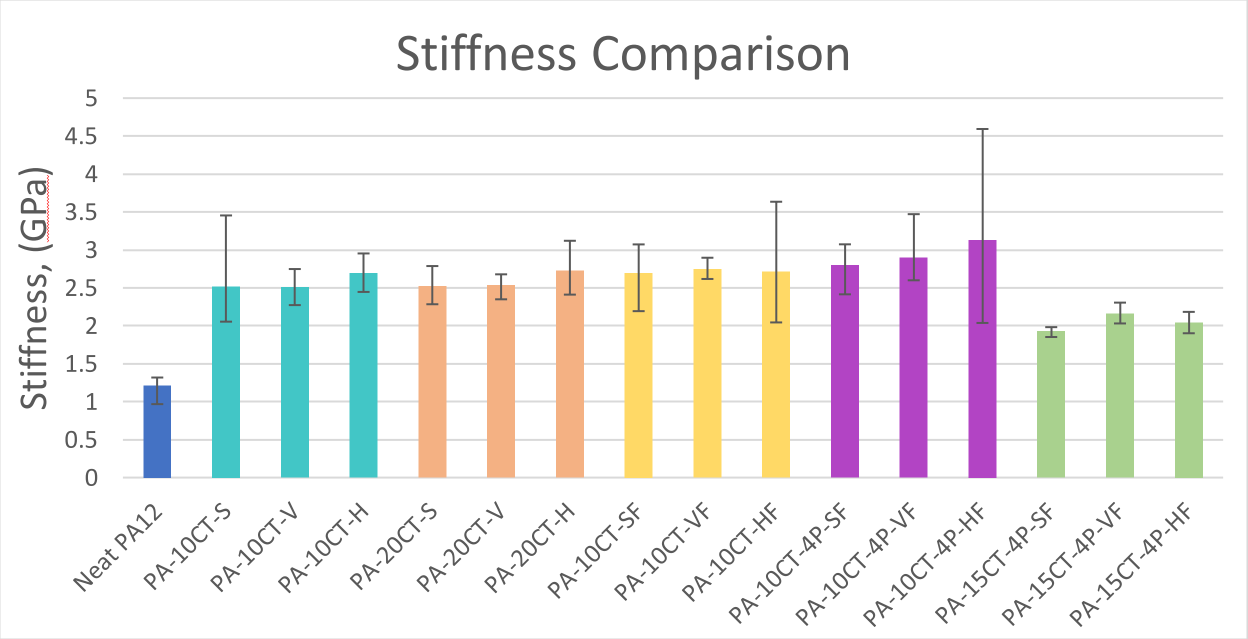


Figure 5: Stiffness comparison for samples fabricated using the control, neat PA12 and the composite materials

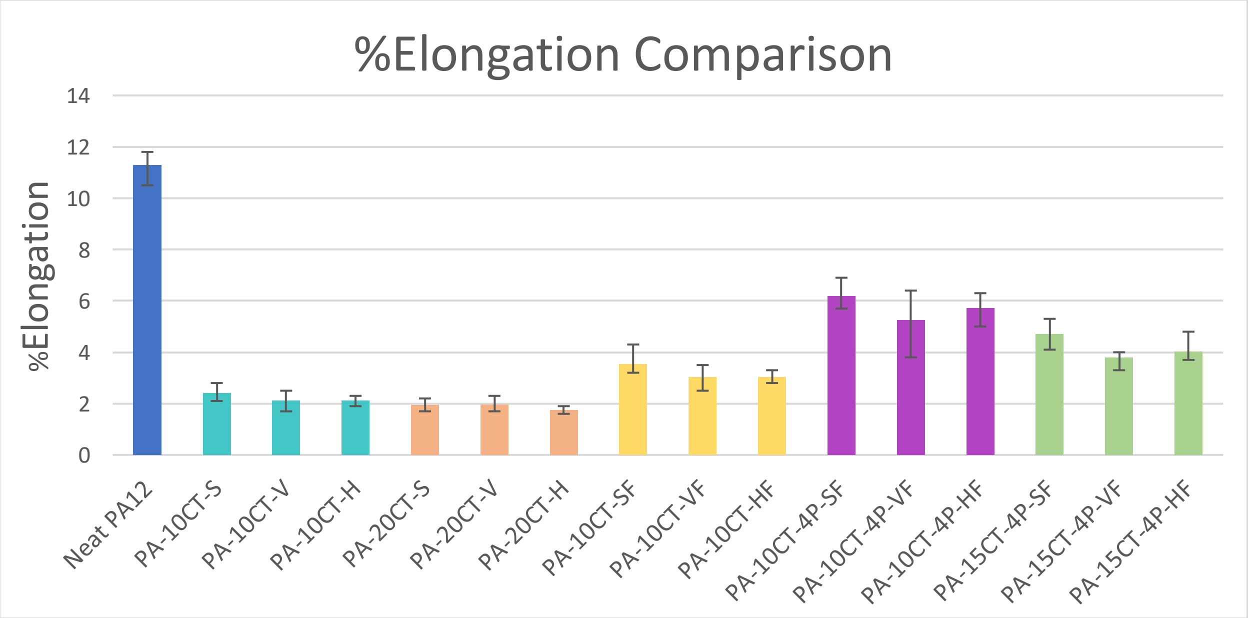
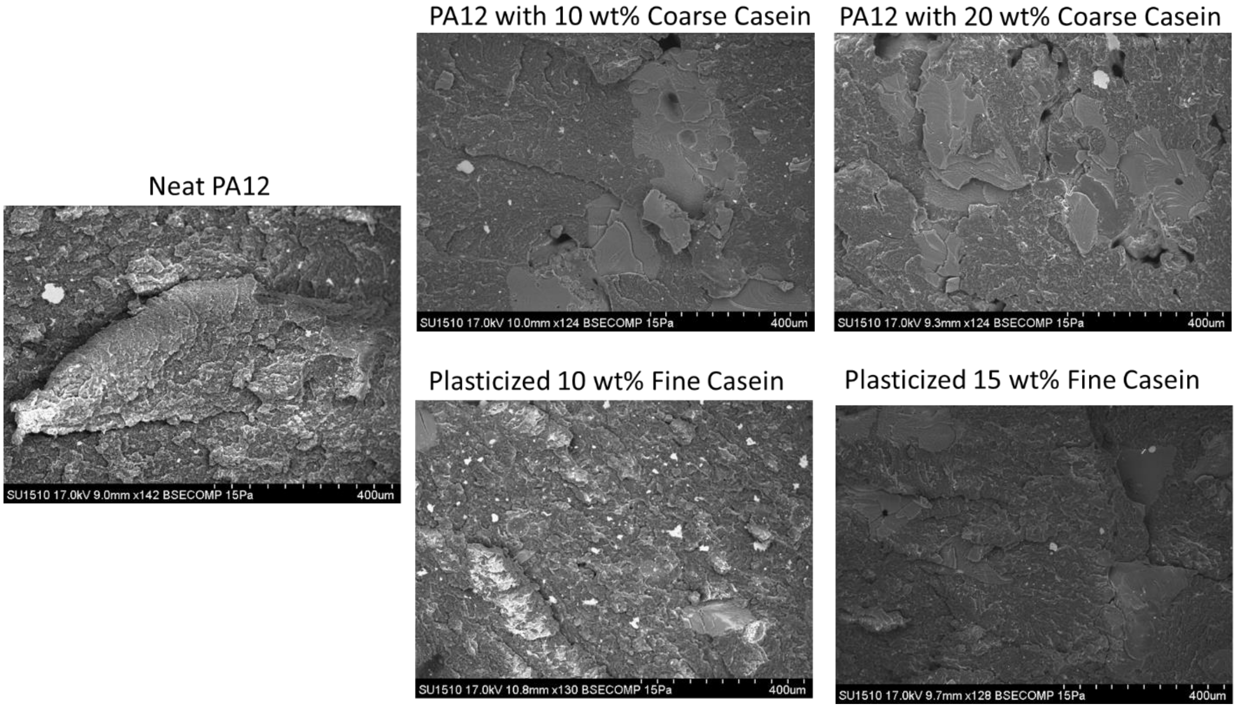


Figure 6: Percent elongation comparison for samples fabricated using the control, neat PA12 and the composite materials

SEM Microscopy

Figure 7 shows the SEM micrographs of the fractured surfaces of tensile test samples. The micrographs show evidence of agglomeration of casein in the PA12 matrix. The sizes of the agglomerates are much bigger in the composite samples made of 10 wt% and 20 wt% coarse casein. These coarse casein-based composites also have porosities that are evidence of low powder bed densities due to larger casein particles that could result in brittle chacteristics. In comparison to the neat PA12 samples, most of the samples based on composite materials exhibit features of brittle fracture surface morphologies.


Neat PA12

PA12 with 10 wt% Coarse Casein

PA12 with 20 wt% Coarse Casein

Plasticized 10 wt% Fine Casein

Plasticized 15 wt% Fine Casein

Figure 7: SEM micrographs of fractured sample surfaces.

Conclusions

This work has demonstrated the viability and potentials of casein, a dairy protein and biopolymer for load bearing engineering applications. Both the tensile strengths and stiffnesses of composite materials made using casein as a filler in PA12 were higher than the neat PA12 at the compositions tested. The increases in tensile strengths over the neat PA12 is dependent on the particle sizes of the filler casein. Finer particle sizes yielded much higher strengths, as the powder packing density increases on the print bed before sintering. The study also shows that the addition of casein leads to embrittlement of the composites. The embrittlement is mitigated by the addition of PEO as a plasticizing agent. Composites with PEO demonstrated a significant increase in percent elongation over those without significant change in tensile strengths.

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