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3D PRINTING SUSTAINABLE BIOCOMPOSITES FROM RECYCLED PLA AND MICRO-CRYSTALLINE CELLULOSE

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Abstract

The motivation for this work was to increase the economic life of recycled poly(lactic acid) (rPLA) (30 wt%) by utilizing it with virgin PLA (70 wt%) in the presence of a fiber-based reinforcing filler, micro-crystalline cellulose (MCC) and an epoxy-based chain extender. A conventional melt extrusion technique was used to fabricate the strands with and without MCC and chain extender in the PLA/rPLA blend matrix. It was observed that the complex viscosity of rPLA was improved significantly after the addition of the chain extender, which resolved the issue related to excessive polymer flow during processing and hence made it possible for use in fused deposition modeling (FDM)-based 3D printing. The addition of the chain extender improved the impact strength of 3D the printed PLA/rPLA specimens. The voids in the 3D printed material contributed to the reduced weight of the developed sustainable composites. The modulus and tensile strength of the 3D printed sustainable biocomposites were improved significantly, and impact strength increased by ~10% by reinforcing the blended matrix with 5% of MCC.

Introduction

The manufacturing of intricate designs using an advanced software called computer aided design (CAD) is grown as an engineering research stream in three-dimensional (3D) printing. The restrictions in polymer printing ability based on the material's properties and mechanical properties have inspired the researchers to continue evolving high performance of 3D printed polymer-based materials that bring numerous benefits such as reduced cost, higher accuracy, decrement in polymer leftover, nominal chemical utilization and intricated objects. The utmost rapid prototyping techniques in additive manufacturing is FDM, which has the foremost advantage of several materials' usage. Multiple materials consumption, densification and printing resolution are the three main factors, which illustrate objects printed by FDM [1].

PLA, a biodegradable and compostable polymer, belongs to the aliphatic polyester family, is one of the most used polymers. It has the capability to replace a few synthetic thermoplastics available in the market due to its low cost, higher strength and modulus [2]. The lower melting point of PLA works as an advantage that supports 3D printing due to the reduced energy consumption compared to other widely used polymers i.e. ABS and polyamides [3]. As stated in the literature, PLA was combined with numerous reinforcing materials, plasticizing agents and compatibilizing agents as microparticles, micro/nano fibers and nanospheres to avoid compatibility issues and brittleness. Cellulose, one of most used reinforcing materials, can be prepared from various resources such as plants, fungi, algae and bacteria. Water insolubility, toughness and fibrous structure are the main properties of cellulose, which makes cellulose a promising additive that can enhance properties like crystallinity and thermomechanical properties of printed biocomposites [4].

In the current research work, an evaluation of properties like mechanical, rheological and surface morphology of 3D printed, and injection molded samples were performed, in which rPLA from coffee pod waste was used. An epoxy-based chain extender was introduced to the PLA/rPLA composite to improve its processing behavior. Moreover, the mixing of micro-crystalline cellulose (MCC) as a reinforcing material to PLA/rPLA-based biocomposites brought thermal stabilization. The goal of the conducted research was to explore 3D printing to encourage reutilization of polymer waste and polymer sustainability by adding rPLA into virgin PLA without disturbing the thermomechanical properties.

Experimental Section

Materials

The used matrix was fabricated by blending post-industrial PLA and pristine PLA. The PLA waste and virgin PLA were obtained from compostable coffee pods, PurPod100 (Club Coffee, Canada) and 4043D grade (Nature Works LLC, USA), respectively. MCC (powder form) provided by MP Biomedicals (USA) and ADR-4368C (Joncryl) (BASF, Germany) were consumed as reinforcing agent and chain extender, respectively.

Methods

Prior processing, virgin PLA and rPLA were dried overnight at 70°C. The distinct polymer strands were fabricated and named as 70% poly (lactic acid)/30% recycled poly (lactic acid) (PLA/rPLA), 70% PLA/30% rPLA/0.5 phr epoxy-based chain extender (PLA/rPLA/0.5J), and 95% [70% PLA/30% rPLA]/5% micro-crystalline cellulose (MCC)/0.5 phr epoxy-based chain extender (PLA/rPLA/5MCC/0.5J) as mentioned elsewhere [5]. The as received post-industrial PLA mesh was processed by twin-screw extruder (Leistritz advance technologies corporation, USA). After cooling the strands using a water bath, the extruded strands were pelletized. Prior to the processing of blend, all waste PLA, pristine PLA and MCC were dried at 75°C. The feed rate and screw speed used in the process was 5 kg/h and 100 rpm, respectively. The temperatures were fixed from 165°C to 180°C (zone-1 to zone-12) with a temperature difference of 5°C. The collected strands were kept for drying at 70°C for 24 h.

Injection Molding

Before injection molding, the prepared filaments were pelletized by a pelletizer (Bullet 64, US) followed by keeping the pellets at room temperature. A mini-jector (MPM model, US) with single screw was used at 180°C to prepare the specimens. Before testing, all the samples were stored at room temperature for 48 h.

3D Printing

The prepared strands of all formulations were evaluated for FDM-based 3D printing by following the ASTM tensile (type IV), and printed specimens by LulzBot TAZ 6), which was operated at 200°C (nozzle temperature) with bed temperature, layer thickness and fill density of 60°C, 2.5 mm and 100%, respectively.

Characterizations

Surface Morphology

The morphology of all the specimens was conducted on the cross-section of samples after an impact test. The images of gold coated samples were captured by scanning electron microscope (Phenom ProX, Netherlands), at 10 kV.

Mechanical Properties

The samples were stored at 23°C and 50% RH for 48 h. The tensile properties of both types (injection molded, and 3D printed) of samples were measured by a universal test machine (UTM) (Instron 3382). The analysis was conducted based on ASTM D638.

Rheology

The distinct properties of 3D printed, and injection molded specimens were analyzed using a rheometer (MCR 302, Antor Paar, Germany). A frequency sweeps test was performed from 0.01 to 100 rad/s to find out the linear viscoelastic range, with 1% strain at 200°C, using an attached parallel-plate geometry.

Results and Discussion

Surface Morphology

Figure 1 displays the microstructures of 3D printed and injection molded samples. The images showed in Figure 1(a) and (b) correspond to PLA/rPLA/5MCC/0.5J. These two images present an interruption in the designs observed in previous samples. Injection line patterns were more pronounced when the chain extender was added [see Figure 1(a)]. The image corresponding to the 3D printed sample displays the existence of pores due to the layer deposition during the printing process. These holes revealed quasi-triangular shaped pores that is very common in FDM-based 3D printing [1,6]. This printing pattern showed lower density of 3D printed samples.

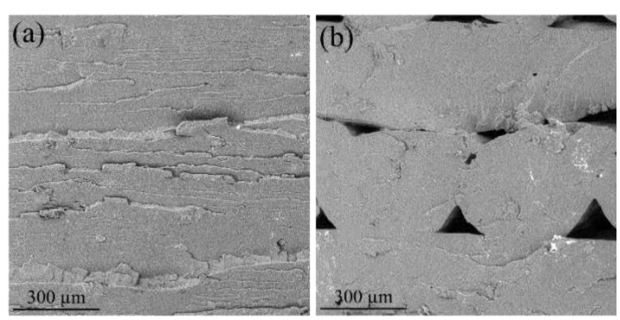


Figure 1: Surface topography of (a) and (b) PLA/rPLA/5MCC/0.5J, developed using injection molding and 3D printing, respectively.

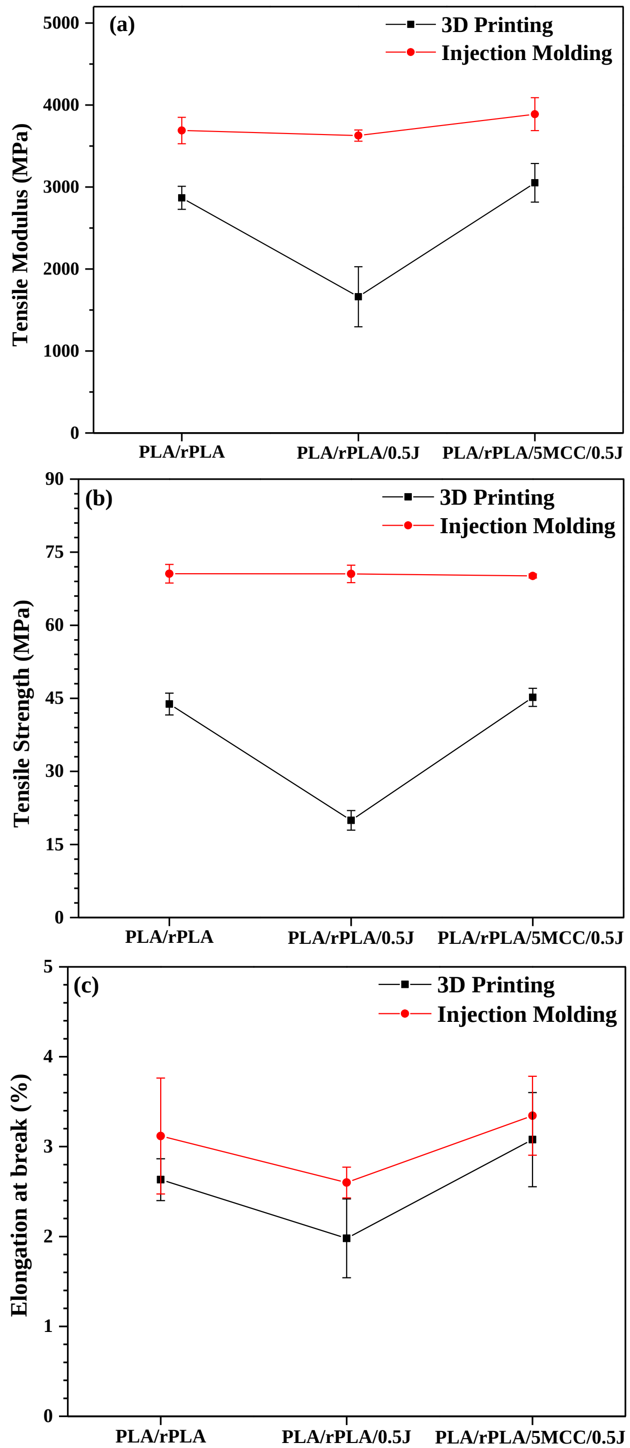
Mechanical Properties

Figure 2(a) presents the tensile modulus of injection and 3D printed specimens. The modulus of injection molded PLA/rPLA blend reduced to some extent after adding chain extender. Fascinatingly, the amount of MCC in the blend enhanced the modulus values significantly as compared to PLA/rPLA/0.5J blend. It was observed as a small improvement compared to the PLA/rPLA blend.

The MCC (with a higher modulus) addition resulted in the development of biocomposites with enhanced stiffness [4]. The stiffness was pointedly improved by up to 88% in the case of 3D printed samples and amplified by 7% in the case of injection molded samples as compared to its 3D printed and injection molded virgin PLA specimens, respectively. The MCC addition leads to superior mechanical properties regardless of the porous structure of the PLA/rPLA-based sustainable biocomposites.

Figure 2(b) shows data for tensile strength vs. injection molded and 3D printed biocomposites used, shows an identical behavior to modulus. Higher tensile strength i.e. ~70 MPa was observed for injection molded specimens compared with 3D printed specimens. The decrement in modulus and strength is possibly as a result of highly porous structure of 3D printed PLA/rPLA/0.5J specimens, as supported by SEM analysis. The tensile properties of biocomposites (in the case of injection molding) are not affected significantly after adding MCC. However, MMC addition in PLA/rPLA/0.5J (in the case of 3D printing) increased the tensile properties significantly.

The %elongation at break for injection molded and 3D printed specimens demonstrates similar pattern as shown in Figure 2(c). Further, notched Izod impact strength for injection molded and 3D printed specimens is shown in Figure 2(d). The addition of chain extender has improved the impact strength of PLA/rPLA in the case of injection molding, which signifies the formation of less brittle blend compared to PLA. The 3D printed PLA/rPLA/5MCC/0.5J biocomposite showed improved impact strength ~7% compared to injection counterpart and ~9% improvement in impact strength was observed in 3D printed PLA/rPLA/5MCC/0.5J compared to 3D printed PLA/rPLA.



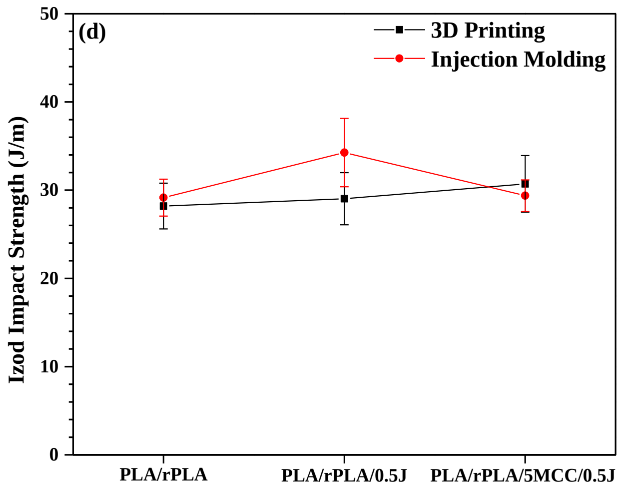


Figure 2: (a) Tensile modulus, (b) tensile strength, (c) %elongation at break and (d) Izod impact strength of injection and 3D printed samples.

Rheology

It was observed that the rheological properties of the 3D printed specimens were improved, compared to that of the injection molded materials due to the thermal degradation of matrix material through processing, which was suppressed in 3D printing. The shear rate is much higher in the case of the injection molding samples, compared to the 3D printing. The biodegradable materials like PLA are sensitive to processing shear rate and temperature [7].

The effect of chain extension was clearly observed by the improved rheological properties. The modulus and viscosity of PLA/rPLA/0.5J blend were much higher compared to the PLA/rPLA blend as shown in Figure 3(a), (b) and (c). The chain scission of polymer chains in PLA/rPLA/0.5J blend was an ideal example of shear thinning phenomenon. PLA/rPLA/0.5J/5MCC showed lower modulus and viscosity as compared to PLA/rPLA/0.5J blend.

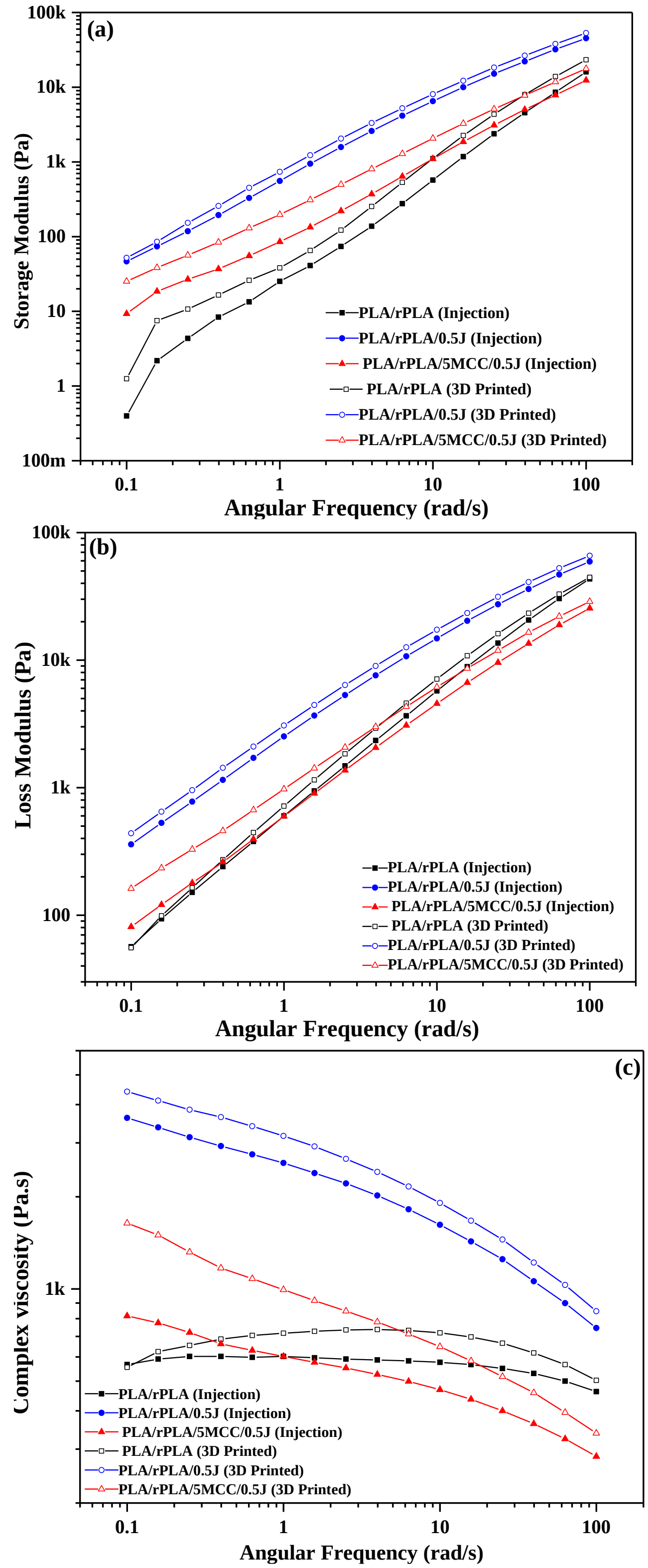


Figure 3: Rheological properties of PLA/rPLA-based samples; frequency vs: (a) storage, (b) loss modulus and (c) complex viscosity.

Conclusions

PLA/rPLA-based sustainable biocomposites were successfully developed by FDM-based 3D printing after incorporating natural fibers. The improvement in rheological properties of PLA after adding chain extender was a key factor in the appropriateness for 3D printing. Micro-crystalline cellulose was utilized as a reinforcing material to enhance mechanical properties of PLA/rPLA-based sustainable biocomposites. The intrinsic porosity in 3D printed samples was observed by SEM, which is responsible for its lightweight or reduced density as compared to injection samples. In conclusion, the FDM-based 3D printing technology is a better substitute to develop customized sustainable biocomposites using recycled polymers and natural fibers.

Acknowledgments

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