Thermal and mechanical degradation of recycled poly-lactic acid filaments for use in 3D printers

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ABSTRACT

Recycling of filaments used in 3-D printing system is beneficial to both the environment and and its manucactures by reducing manufacturing costs. This study investigates how multiple-recycled poly-lactic acid (PLA) filaments affects mechanical properties of fabricated objects.. Mechanical strengths of the printed PLA, as well as the adhesion strengths between 3-D-printed beads, were evaluated by tensile tests of horizontally and vertically fabricated specimens. The mechanical strength of the printed PLA as well as the adhesion strength between 3-D-printed beads were determined through tensile testing of horizontally and vertically fabricated specimens. Subsequent gel permeation chromatography revealed that recycling reduced the molecular weight of the polymer, leading to a loss of mechanical strength in the 3D-printed component. In addition, images of cutting plane using scanning electron microscopy showed that the fabricated bead itself was broken in the case of the horizontally fabricated specimen, while in the case of the vertically fabricated one, the adhered between the beads was found to be broken. This indicates that the mechanical strength of in-plane and out-of-plane direction should be improved by increasing mechanical strength of bead, itself, as well as the adhesion strength between beads.

1. INTRODUCTION

Additive manufacturing (AM) using three-dimensional (3-D) printing technology is a revolutionary, emerging technology suitable for design, rapid prototyping, personalized medical components and component manufacturing [1-4]. As with other AM techniques, components or systems are fabricated through the deposition of successive layers rather than removal of materials from a larger piece, as is the case with subtractive manufacturing (e.g., a lathe) [5]. Among the 3-D printing technologies that have been developed till now, a fused deposition modeling (FDM) is one of the most widely employed modelings in various applications, mainly due to its low cost. In 3-D printers that employ the FDM method, a thermoplastic filament is heated to near its melting point, and then extruded layer-by-layer to create a three dimensional objects. This technology has been employed in a wide range of applications, but this increased use has raised concerns as to whether the filament can be made from more eco-friendly recycled materials. Recently, interest in recycling of polymer wastes has been increasing due to due to problems caused by polymeric wastes accumulation including its impact on the environment. In addition, most of polymeric wastes are produced from oil and gas and it means increase use of polymer products ultimately increases the use of natural resources [6].

There are currently many different raw materials available for FDM type 3D printers, such as acrylonitrile butadiene styrene (ABS), nylon, polycarbonate, high-density polyethylene, high impact polystyrene and poly-lactic acid (PLA). Of these, PLA has been favored for its greater availability and attractive cost structure, with its relatively low melting point (150–160 ℃) also reducing the energy needed to print. In addition, PLA is one of the more important biodegradable polyesters and it can be used as biomedical and pharmaceutical applications such as implant devices, tissue scaffolds, and internal structures. It is derived from renewable resources such as starch and sugar, thus providing a safer alternative to potentially toxic ABS plastic [6-9]. The increased use of PLA has created interest in whether costs and waste can be reduced by recycling it in 3-D printing applications. As with other thermoplastics, mechanical (or physical) recycling has been more widely used for this than chemical recycling or reuse. This process involves mechanically grinding the plastic down into small pieces, and then reprocessing and compounding it at elevated temperature to produce a new component or filament. It is therefore expected to produce similar thermal and mechanical degradation to that observed during injection molding and extrusion [6, 7, 10-12], thus making it critical to understand the degradation of recycled PLA filaments, as well as any object produced from them by FDM type 3-D printing.

This study uses tensile testing to compare the mechanical properties of 3D-printed specimens fabricated from pristine and mechanically recycled PLA. In order to investigate the thermal properties of pristine and recycled PLA, differential scanning calorimetry (DSC) is used. Gel permeation chromatography (GPC) is also used to deeply understand the degradation and measure any change in the molecular weight of the PLA with each recycling, which is directly related with mechanical strength of polymer. Mechanical strength of both horizontally and vertically fabricated specimens were tested and compared each other. The fracture surfaces of specimen were observed by using scanning electron microscopy (SEM) to investigate the fracture mode.

2. EXPERIMENTAL

Recycling of the PLA filament was achieved using a custom mechanical recycling system consisting of shredder, extruder, spooler, sensing and controller parts. With this, failure objects or broken parts fabricated by 3-D printer were broken into small pieces by shredder using an auger driven by an electric motor, which were then heated around the glass transition temperature to be softened. It was forced through a die to extrude PLA filament from softened shredded small pieces. The temperature of heating zone and the speed of extruder were controlled by a closed loop controller in order to regulate the diameter of extruded filament. Details of which can be found elsewhere [13]. In order to investigate the mechanical performance of recycled PLA filament, an open-source FDM type 3-D printer (Cubicon 3DP-110F, Hyvision System Corp.) with a 0.4 mm-diameter nozzle was used to fabricate Type-5 tensile test specimens as shown in Figure 1 using PLA filament with 1.75 mm-diameter, as per ASTM standard D638 for the tensile properties of plastics. In order to investigate the impact of recycling on the mechanical properties of PLA, material in pristine condition was compared against that which had been recycled one and three times.

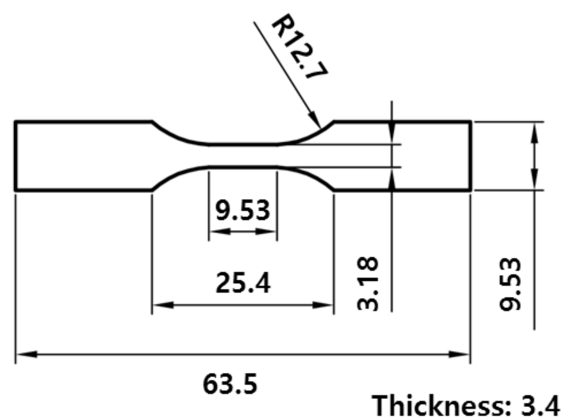

Figure 1. Graphical representation of the tensile test specimen specified in the ASTM standard D638-10 (type 5)

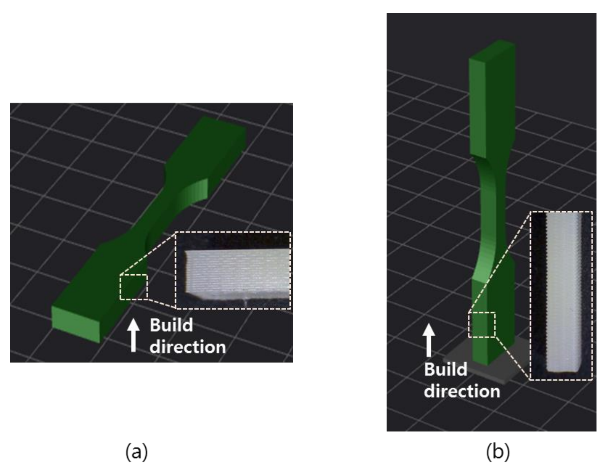

Figure 2. Graphical representation of the tensile test specimen printed in horizontally (a) and vertically (b) including magnified images.

The tensile testing was carried out using a universal testing machine (Instron 5569, Instron Corp.) with a grip speed of 5 mm/min and a distance between the grips of 25.4 mm. At least four samples for each test were used to calculate average value and observe the consistency. All tensile tests were carried out at 25.2 ℃ and 45.5 % relative humidity using the two types of test specimen shown in Figure 2. The specimens fabricated horizontally were used to investigate the mechanical properties of the material itself, while those produced vertically were used to investigate the mechanical properties and the adhesion between fabricated beads. In both instances, the temperature of nozzle was kept at material supplier's recommended temperature of 210 °C, while the heating bed and chamber were maintained at 65 and 45 ℃, respectively. The air gap between the beads of fabricated material was set to zero. The ultimate tensile strength was measured as an average of at least four specimens and used to investigate how well the material could maintain its initial mechanical properties after recycling.

3. RESULT AND DISCUSSIONS

Recycled PLA specimen fabricated using recycled filament were investigated by mechanical tensile tests, DSC, GPC, SEM.

Figure 3 and 4 show the tensile stress and strain curves for pristine and recycled PLA specimens fabricated in the horizontal and vertical direction. Some specimens were broken near the grip place during tensile test and the data from these specimens was excluded. In two types of specimens, the ultimate tensile strength of horizontally fabricated one is higher than that of vertically fabricated one. It indicates that the strength of fabricated PLA material, itself, is higher than the adhesion strength between fabricated beads resulting in typical anisotropic property of FDM type 3-D printed product. Also, there is no elongation after maximum stress before break in the case of vertically fabricated pristine PLA specimen and it means that the fracture occurs between adhesion regions not material itself. In horizontally fabricated specimens shown in Figure 3, both the maximum stress before break and the strain at break are decreased as increasing the number of recycling. It was reported that the degradation of mechanical strength of polymeric material, is due to the reduction in the molecular weight [4, 11, 14-16].

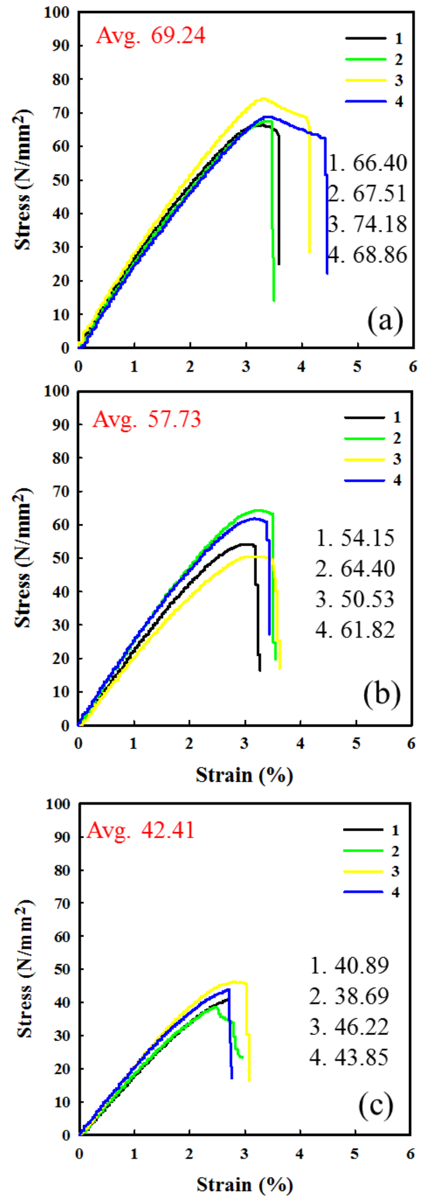

Figure 3. Stress-strain curves for (a) pristine, (b) one time recycling, and (c) three time recycling specimens fabricated horizontally.

This is consistent with reports that mechanical recycling at elevated temperature degrades the macromolecular structure, resulting in chain scission of the polymer structure [4, 11, 14-16]; i.e., shorter chains increase the number of chain ends and the stress at which fracture occurs [17]. Similar observations regarding the degradation of PLA have shown that a correlation generally exists between the tensile strength and molecular weight of polymer materials that can be approximated by the inverse relation [16, 18, 19]:

$$S = S_{\infty} - \frac{A}{M} \quad (1)$$

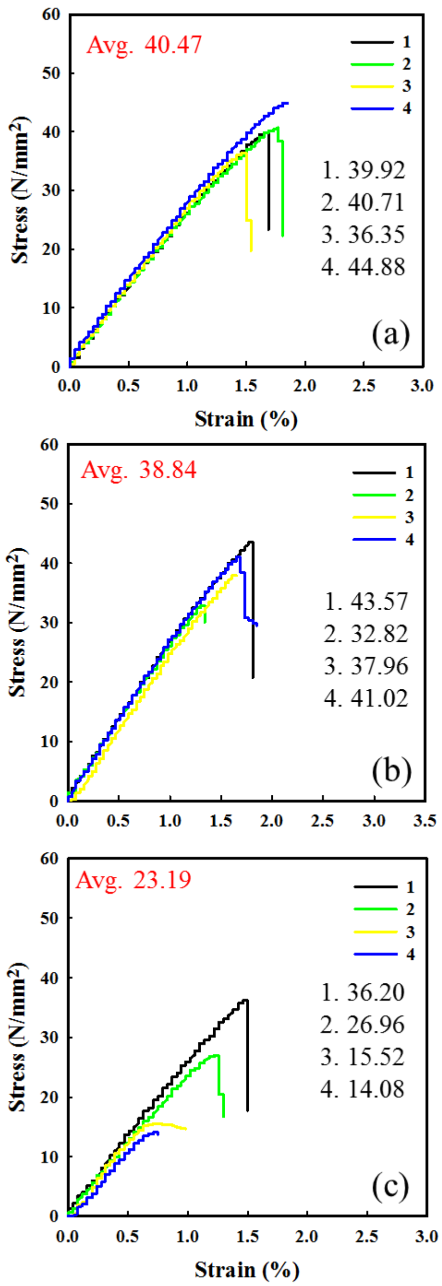

Figure 4. Stress-strain curves for (a) pristine, (b) one time recycling, and (c) three time recycling specimens fabricated vertically.

where S_∞ is the saturated tensile strength for an infinite molecular weight and A is a correction factor for the material type.

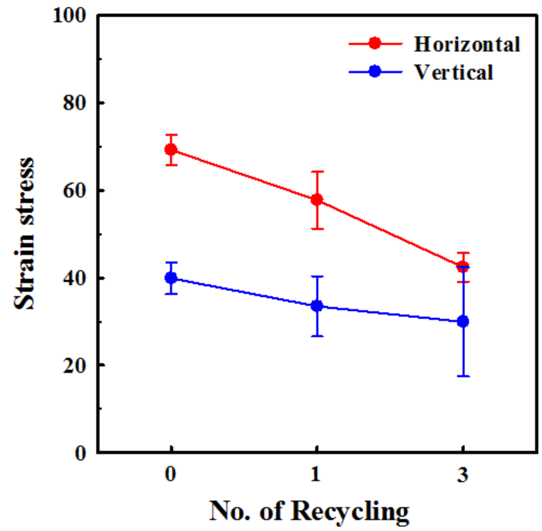

Figure 5. Averaged ultimate tensile strength as a function of the number of recycling time for both horizontally and vertically fabricated specimens.

The ultimate tensile strength of the vertically fabricated PLA specimens decreased with recycling, as shown in Figure 5. This indicates that chain scission of the PLA matrix degrades the strength of adhesion between beads of fabricated PLA, which in the case of a 3-D printed structure, act as an adhesive material. Thus, heating during recycling and 3D printing causes thermally induced chain scission and a reduction in cohesive strength. Based on these results, it is expected that the ultimate tensile strength of vertically fabricated specimens can be improved by adding an adhesion promoter such as poly dopamine (an adhesive polymer derived from mussels) [21], which is currently the subject of further investigation.

The ultimate strength of the vertically fabricated pristine PLA is lower than that of the horizontally fabricated equivalent due to the fact that the strength of a vertically fabricated specimen is dependent upon the adhesion between beads rather than that of the PLA beads themselves. This finding is in a good agreement with previous results [22], and means that vertically fabricated specimens behave in a more brittle manner than horizontally fabricated specimens. That is, they break suddenly if stress is induced by a tensile test, which is not the same behavior exhibited by the material itself. In contrast, horizontally fabricated specimens exhibit elongation even after reaching their ultimate tensile strength, which is consistent with the intrinsic properties of the polymer (especially when produced by injection molding).

4. CONCLUSION

Recycling polymeric materials enables wasted materials into making filament which can be used repeatedly in 3-D printing system. PLA being widely used in 3-D printer is recycled and characterized in order to investigate the effectiveness of recycling filament. Characterization of the mechanical properties of PLA filament for 3-D printers has found that mechanical recycling induces a thermally activated degradation that reduces the molecular weight of the polymer with each successive recycling. This results in chain scission of the PLA and degradation of the mechanical properties of the fabricated object. By using two types of specimen, it has been shown that mechanical recycling degrades both the mechanical strength of the PLA beads, as well as the adhesion between beads. Thus, the mechanical strength of PLA 3D printer filaments is clearly sensitive to thermomechanical recycling, but it may be possible to overcome this issue by using chain extenders or adhesion promoter during recycling.

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