BIO-MATERIAL POLYLACTIC ACID/POLY(BUTYLENE ADIPATE-CO-TEREPHTHALATE) BLEND DEVELOPMENT FOR EXTRUSION-BASED ADDITIVE MANUFACTURING

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ABSTRACT

Bio-material polylactic acid and poly(butylene adipate-co-terephthalate) were blended to achieve increased ductility of the blend. Cloisite was added to improve the stiffness of the blend. The blends were made into filament suitable for extrusion-based additive manufacturing. Melt flow index of the filament and mechanical properties of the printed bars were tested. Preliminary results showed that the melt flow index increases significantly with cloisite and the modulus of polylactic acid/poly(butylene adipate-co-terephthalate) improved slightly. The notched impact strength of the blend increased with increasing content of cloisite, and it increased significantly after annealing, especially for blends without cloisite.

Key Words: Polylactic acid, poly(butylene adipate-co-terephthalate), additive manufacturing, annealing

1. INTRODUCTION

Additive Manufacturing (AM) or 3D Printing is a process that enables the production of physical objects by deposition of successive layers of material. Extrusion-based AM such as fused filament fabrication (FFF) or fused deposition modeling (FDM) is a widely used AM technique. [1] Polylactic acid (PLA) [2, 3] is a commercial biodegradable thermoplastic for AM. However, the PLA's brittleness, slow crystallization rate, and poor heat resistance may limit its usage in practical applications. The elastomer, poly(butylene adipate-co-terephthalate) (PBAT) which is also a bio-material was blended with PLA to improve its flexibility and impact strength. [4, 5] To improve the performance of AM-fabricated thermoplastic parts in a further step, reinforcing the materials with high strength fibers or fillers [6-8] is one of the possible methods, and another possible way is annealing. Annealing increases diffusion, bonding of beads and crystallinity. [6, 9] In the present communication, it is highlighted that the modulus and impact strength of a PLA/PBAT blend improves with the incorporation of cloisite-15 nanoclay, and the impact strength increases significantly after annealing.

2. Experimental

2.1 Materials

Polylactic acid (Ingeo™ 3D850; abbreviated as PLA3D), a grade developed for manufacturing 3D printer monofilaments, was purchased from NatureWorks in pellets with following specifications: 0.5% d-isomer, density: 1.24 g/cm^3, melting point: 176°C, and melt flow index (MFI) of 7-9 g/10min[1] at 210°C with a load of 2.16 kg. Poly(butylene adipate-co-terephthalate) (PBAT), brand name ecoflex® F Blend C1200 was obtained from BASF. It is aliphatic-aromatic copolyester based on the monomers 1,4-butanediol, adipic acid and terephtalic acid. Cloisite-

15 from BYK is bis(hydrogenated tallow alkyl)dimethyl, salt with bentonite. It has a typical dry particle size, d_{50}<10µm, density 1.66 g/cm^3, and d_{001}=3.63nm. The polymers were dried overnight at 50°C before processing. Cloisite was predried at 100°C for 5h.

2.2 Sample Preparation

PLA/PBAT blend (80/20 by mass ratio) with cloisite (0, 1, 3phr) was first made into granules by a twin extruder (Coperion ZSK18ML) with a screw diameter of 18 mm and L/D of 40. The temperature profile was set as 160-210°C from zone 1 to zone 9. A screw speed of 120 rpm and a feeding rate of 0.5kg·h^{-1} were used. The extrudates were water cooled and cut into granules for the next processing step. The single screw extruder (Brabender PL2000) was used to make suited filament production with the diameter of 1.75mm for the 3D printer. The screw diameter is 19 mm and L/D is 25 for the single screw extruder. The temperature variation was 180, 190, 200 and 210°C from the feed zone to die. The screw speed was set at 30 rpm and the hauling speed was 8 m/min. PLA filament was prepared with the same processing as a comparison.

2.3 Characterization

The rheology of the blends is assessed via the melt flow index (MFI) test. Samples are tested under 210°C with a load of 2,16 kg referring to ISO 1133.

Tensile property of filaments and printed bars were measured on an Instron 5565 machine according to ISO 527. The extensometer 2620-603 Instron with Gauge length 25 mm is used to calculate accurate results at the beginning of the stress-strain curve. A 1 mm/min tensile rate is applied until 0.3% strain to determine Young's modulus. Afterward, 10 mm/min is executed until the material breaks. Impact tests were conducted on a Tinius Olsen Impact model 503 according to ISO 179. A V-notch was applied with a depth of 2 mm. The weight of pendulum was 0.462 kg, which supplies impact energy of 2.82 J and a released velocity of 3.46 m/s. All tests were carried after 2 days conditioning in the standard atmosphere (23°C and 50% humidity). At least five samples were tested to get an average value.

3. RESULTS

3.1 Melt flow behavior of filaments

Melt flow index (MFI) results of filaments are shown in Figure 1. Pure PLA and PBAT possess MFI value about 10 g/10min, PLA/PBAT blend and blend with only 1 phr of cloisite have similar MFI. With up to 3 phr cloisite, the MFI increases significantly.

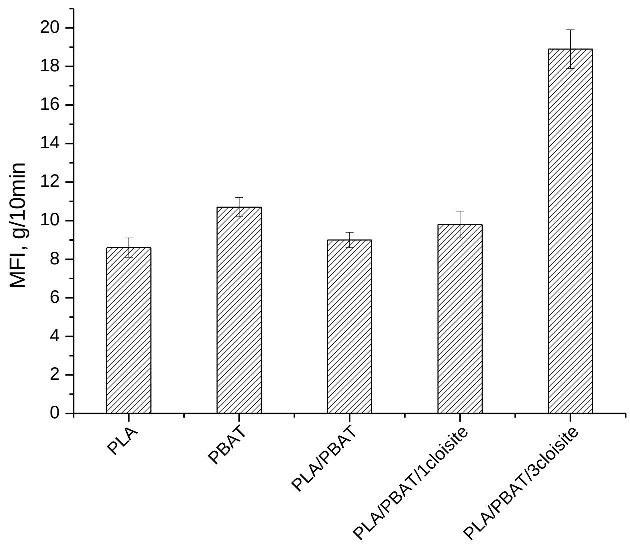

Figure 1. MFI of the filaments

3.2 Mechanical properties of blends

Tensile properties of PLA, PLA/PBAT, and PLA/PBAT/cloisite filaments were tested, with the results listed in Table 1. Modulus and stress at break of PLA dropped significantly, but strain at break increased dramatically due to the introduction of flexible material, PBAT. [4, 5] With the addition of cloisite, the modulus of PLA/PBAT improved slightly because of the filler contributing to the stiffness. [8] However, elongation of PLA/PBAT reduced to 30% with cloisite ascribed to its easy agglomeration. Tensile properties of printed bars are similar to its filaments, the stress and strain are a little lower than the filaments because of the existence of voids in the printed bars.

The notched impact strength of samples before and after annealing are shown in Figure 2. The impact strength of PLA increased from 4 to 6 kJ/m^2 after PBAT was added, and it rose further to 8 kJ/m^2 with the incorporation of 3 phr cloisite. The impact strength increased significantly after annealing due to the increased crystallinity and better diffusion. [6, 9] The impact strength of annealed PLA/PBAT is more than 3 times (20 kJ/m^2) than the non-annealed sample. However, the value dropped to 12 kJ/m^2 for annealed PLA/PBAT/3cloisite which is likely due to phase coalesce during annealing.

Table 1. Tensile property of the filament and printed samples

Sample	Modulus, MPa	Stress at break, MPa	Strain at break, %
filament			
PLA	3461±345	55±3	17±4
PLA/PBAT	2485±110	47±2	117±6
PLA/PBAT/1cloisite	2617±147	47±2	28±11
PLA/PBAT/3cloisite	2758±203	44±1	26±13
Printed bar			
PLA	3282±118	55±1	4±1
PLA/PBAT	2471±146	41±2	38±15
PLA/PBAT/1cloisite	2399±141	42±2	29±11
PLA/PBAT/3cloisite	2540±107	41±1	15±4

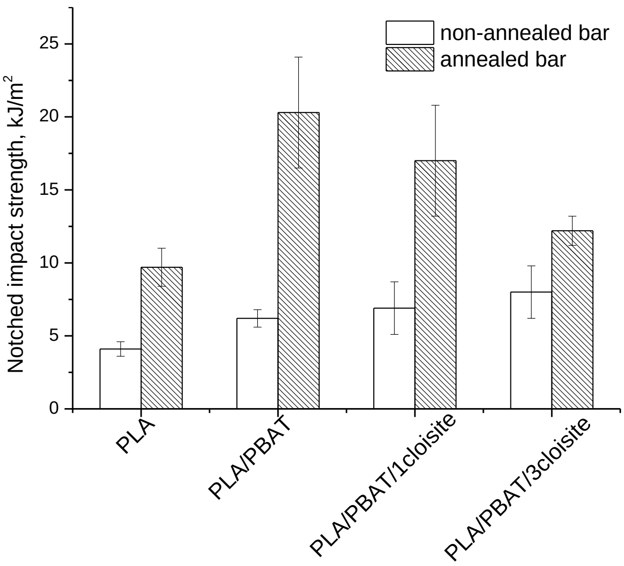

Figure 2. The notched impact strength of samples before and after annealing

4. CONCLUSION

Melt flow index increase significantly with cloisite, while the modulus of polylactic acid/poly(butylene adipate-co-terephthalate) improved slightly. The notched impact strength of the blend increased with increasing content of cloisite, and it increases significantly after annealing, especially for PLA/PBAT blend.

5. REFERENCES

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