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Toughening of various PLA grades with natural rubber for 3D printing applications

[1]Imre Fekete, [2]László Lendvai

[1]Department of Materials Science and Engineering, Széchenyi István University. Győr, Hungary, fekeim@sze.hu
[2]Department of Materials Science and Engineering, Széchenyi István University. Győr, Hungary, lendvai.laszlo@sze.hu

Abstract

The aim of this present work was to study the toughening efficiency of natural rubber (NR) on various poly(lactic acid) (PLA) grades for 3D printing applications. For this purpose three different types of PLA with varying d-isomer content and average molecular weight were applied. Firstly, PLA-based filaments suitable for fused deposition modeling (FDM) were prepared with 10 wt% NR content using a twin-screw extruder. Subsequently, specimens were fabricated with a desktop FDM printer using two different infill patterns: i) a grid-like infill with an alternating raster angle of ±45° and ii) a unidirectional infill, parallel to the length of the specimens. The quasi-static and dynamic mechanical properties were determined by tensile tests and Charpy impact tests. The results indicated an outstanding toughening efficiency of NR, regardless of the PLA type, however, only for the samples prepared with the unidirectional infill.

Keywords: poly(lactic acid) (PLA), natural rubber (NR), toughening, 3D printing, FDM

1 Introduction

The various additive manufacturing technologies – also known as three-dimensional (3D) printing techniques – have experienced an immense development throughout the last decade. 3D printing has been widely used in various fields, including the aerospace, biomedical, architectural and vehicle industry. Nowadays, the most diffused additive manufacturing methods are the extrusion based ones, such as the fused deposition modeling (FDM). The FDM type 3D printers are generally fed by various thermoplastic polymers, the most common of which is the poly(lactic acid) (PLA) [1, 2].

PLA is a thermoplastic polyester derived from natural feedstocks. It is not simply a bio-based polymer, but it is also compostable, which means that it can be completely biodegraded. Recently, due to increasing environmental awareness, the use of biopolymers, such as PLA has significantly increased. Its mechanical properties are similar to common plastics like poly(ethylene terephthalate) (PET) or polystyrene (PS). Due to its decent properties it is popularly used for various applications [3]. On the other hand, PLA has some serious drawbacks including its brittleness, as evidenced by the short elongation at break and low impact strength. Therefore, researchers have shown an increased interest in the development of PLA-based materials with enhanced toughness in order to expand its fields of applications [4]. One of the most common routes when it comes to increasing the toughness of PLA is to pair it with an elastomeric, rubber-like material [5].

The major objective of this present study was to investigate the toughening efficiency of natural rubber (NR) on various PLA grades for additive manufacturing applications. Therefore, NR-toughened filaments were prepared using three different PLA types. Then, 3D printed specimens were fabricated using those filaments with different infill patterns. The specimens were characterized through tensile tests and Charpy impact tests to analyze the toughening effect of NR under various circumstances.

2 Materials and methods

2.1 Materials

Three grades of PLA with different d-isomer content were purchased from NatureWorks LLC (Minnetonka, MN, USA), namely the Ingeo™ 2003D, the Ingeo™ 8052D and the Ingeo™ 3D850 types. These PLA grades have a d-isomer content of 4.5%, 4.3% and 0.5%, respectively, and a melting temperature (T_m) of 150 °C, 155 °C and 175 °C, respectively. The density of the three types is uniformly 1.24 g/cm^3. The natural rubber used as toughening agent (type SVR-CV60) was obtained from the Vietnam Rubber Association (VRA).

2.2 Preparation of the filaments

A two-step manufacturing process was applied to prepare PLA/NR filaments suitable for 3D printing. Firstly, a melt compounding under higher shear rates was performed in order to achieve a homogenous dispersion of the components. The melt mixing was followed by the extrusion of the filaments with a diameter of approximately 1.75 mm.

Both the NR and the different PLA grades were dried at 80 °C for 4 hours in a DEGA-2500 dehumidifying chamber (DE.GA S.p.A., Corte Franca, Italy) prior to processing. Melt compounding of the desired combinations were performed using a Labtech LTE 20-44 type co-rotating twin-screw extruder (Labtech Engineering Co., Ltd., Samutprakan, Thailand) with a screw diameter of 20 mm and an L/D ratio of 44. The barrel temperature profile from feed zone to die end was set to 155-160-160-165-165-170-170-175-180-185-185 °C and the rotational speed of the screw was 40 1/min. The achieved blends were cooled down in a water tank and then pelletized.

The prepared pellets were dried for another 4 hour at 80 °C. Subsequently, the 3D printing filaments were manufactured with the same twin-screw extruder that was applied for the melt blending. In this case, however, the barrel temperature profile was 170-175-175-175-175-170-170-165-165-160-160 °C and the rotational speed of the screw was set to 15 1/min. The intention was to maintain the same processing temperatures for all materials. However, since the melting temperature of the Ingeo™ 3D850 considerably exceeded the T_m of the two other grades, the temperature of all barrel zones was increased by 20 °C for this specific type. The diameter of the produced filaments was 1.75 ± 0.11 mm.

2.3 3D printing

The prepared PLA and PLA/NR filaments were used to print dumbbell-shaped specimens for tensile tests and prismatic specimens for impact tests. The printing was performed on a Craftbot Plus type desktop FDM printer (CraftUnique Ltd., Budapest, Hungary). The nozzle temperature was set to 215 °C, the nozzle diameter was 0.4 mm and the bed temperature was 60 °C. The layer height was 0.2 mm, the printing speed was 60 mm/min and the filling rate was 100%. Two shell layers of 0.4 mm were applied for all samples. The samples were fabricated using two different infill patterns: i) a grid-like linear infill with an alternating raster angle of ±45° between the layers and ii) an unidirectional linear infill, parallel to the length of the specimens. Schematic graphics of the applied infill patterns is shown in Figure 1.

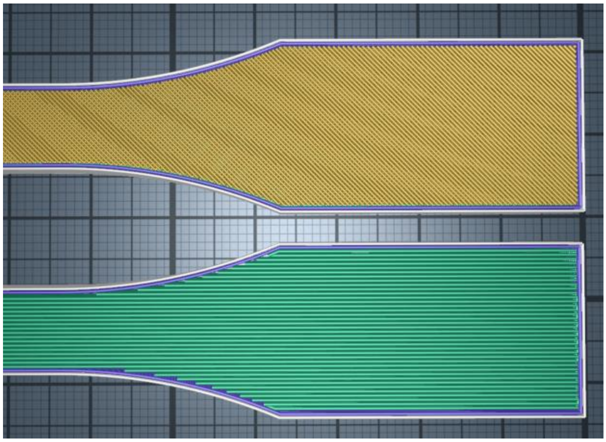

Figure 1. Schematic graphic of the printing orientation with respect to the specimen

The sample code, the formulation and the infill pattern of the prepared samples are summarized in Table 1.

Table 1. The designation, composition and the infill pattern of the fabricated samples

Sample code	PLA grade	PLA amount [wt.%]	NR amount [wt.%]	Printing infill pattern
2003D_PAR	Ingeo™ 2003D	100	-	parallel to length
2003D_GRID	Ingeo™ 2003D	100	-	±45° raster angle
2003D_10NR_PAR	Ingeo™ 2003D	90	10	parallel to length
2003D_10NR_GRID	Ingeo™ 2003D	90	10	±45° raster angle
8052D_PAR	Ingeo™ 8052D	100	-	parallel to length
8052D_GRID	Ingeo™ 8052D	100	-	±45° raster angle
8052D_10NR_PAR	Ingeo™ 8052D	90	10	parallel to length
8052D_10NR_GRID	Ingeo™ 8052D	90	10	±45° raster angle
3D850_PAR	Ingeo™ 3D850	100	-	parallel to length
3D850_GRID	Ingeo™ 3D850	100	-	±45° raster angle
3D850_10NR_PAR	Ingeo™ 3D850	90	10	parallel to length
3D850_10NR_GRID	Ingeo™ 3D850	90	10	±45° raster angle

2.4 Characterization

The tensile mechanical properties of the prepared samples were determined using an Instron® 5582 (Instron Ltd., Norwood, USA) universal tensile testing machine equipped with a 10 kN force sensor. The tests were carried out at a crosshead speed of 5 mm/min. The presented results are the averages of five parallel measurements.

The Charpy impact strength was measured with a Ceast 6545 (Ceast S.p.A., Pianezza, Italy) pendulum-type testing machine equipped with an impact hammer of 2 J. The specimens were unnotched, rectangular bars. The presented results are the averages of five parallel measurements.

3 Results and discussion

3.1 Tensile mechanical properties

The mechanical properties determined through the tensile tests are summarized in Figure 2-4. Figure 2. presents the yield strength of the prepared samples. Based on the results it can be assumed that the lower the d-isomer content of the applied PLA grade, the higher yield strength it exhibits. This statement is valid for both the raw PLA samples and the NR toughened ones. As a consequence of blending PLA with NR the strength values decreased markedly, which is in good agreement with the literature considering the soft rubbery character of NR. This was observed for all samples, regardless of the infill pattern. Interestingly, when using the grid-like infill (Figure 2/a) the drop measured in the yield strength was relatively ~30%, however, with the linear infill pattern parallel to the length of the specimen (Figure 2/b) the decrease was only ca. 15-20%. Whilst the interlayer adhesion has little to no significance in the specimens printed with an orientation parallel to the tensile load, in those samples prepared with ±45° raster angle it is essential. Evidently, the more prominent decrease in the yield strength measured on the toughened samples fabricated using the grid pattern refers to the fact that the presence of NR weakens the adhesion between the printed layers.

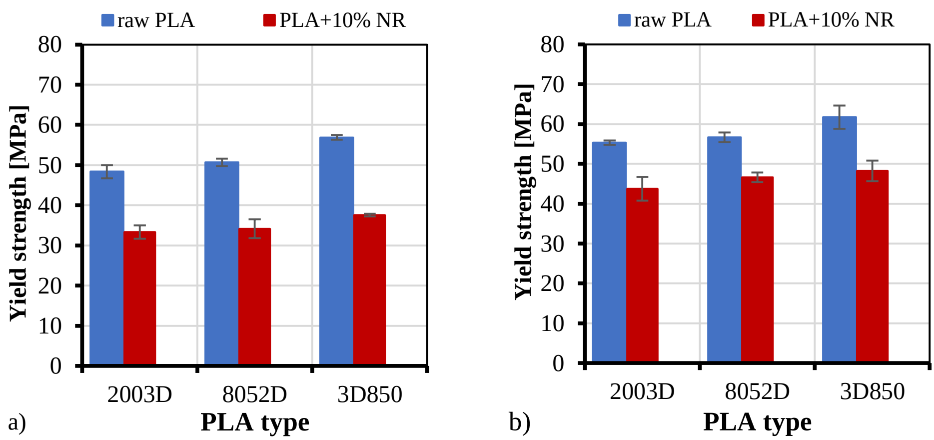

Figure 2. Yield strength of the fabricated samples with (a) grid-type infill pattern and (b) unidirectional infill pattern parallel to the length of the specimens

According to Figure 3. the Young's modulus values of the three PLA grades were in the range of 2.5-3 GPa with the Ingeo™ 3D850 (the type with the lowest d-isomer content) exhibiting the highest stiffness. Similarly to the yield strength, the modulus values of the NR containing samples dropped as well due to the soft nature of the elastomer component. Also, the reduction in stiffness was more notable for samples printed with the grid-like pattern as a result of the weaker interlayer adhesion compared to the ones with the unidirectional linear infill.

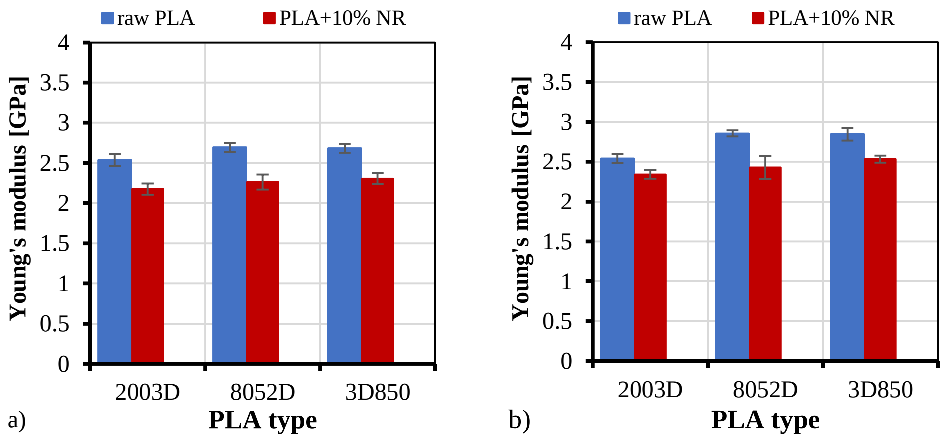

Figure 3. Young's modulus of the fabricated samples with (a) grid-type infill pattern and (b) unidirectional infill pattern parallel to the length of the specimens

Contrary to the strength and modulus, the elongation at break values of the different PLA grades enhanced greatly when blended with 10 wt% NR. There is, however, a marked difference in the achieved improvement depending on the infill type used. Even though the samples prepared by the ±45° raster angle infill (Figure 4/a) already showed an elongation 2-2.5 times as much (7-10%) as the raw PLAs (~4%), the ones with the linear infill parallel to the load (Figure 4/b) all exhibited an elongation higher than 80%, regardless of the PLA grade. In this aspect, the sample 2003D_10NR_PAR outperformed all the other ones by having an elongation at break of ~210%. By also showing the highest deformability (~10%) when using the grid-like infill pattern it can be concluded that most significant improvement was achieved when using the PLA grade with the highest d-isomer content, namely the Ingeo™ 2003D.

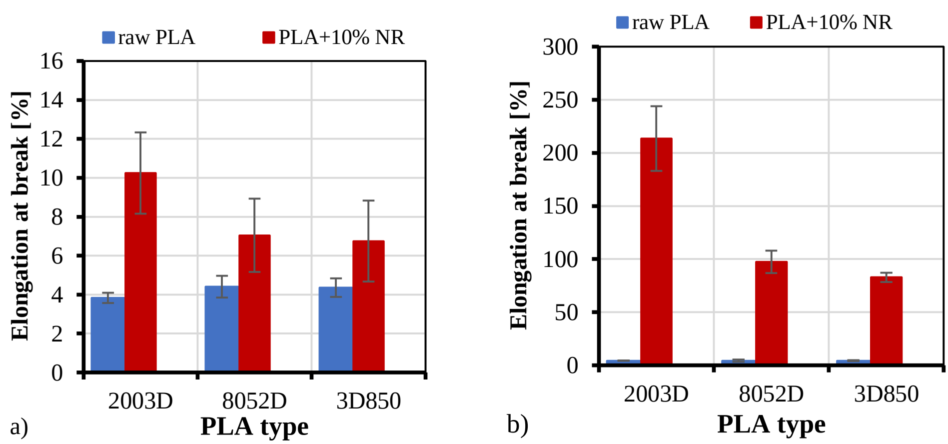

Figure 4. Elongation at break values of the fabricated samples with (a) grid-type infill pattern and (b) unidirectional infill pattern parallel to the length of the specimens

3.2 Impact toughness

The impact properties of the fabricated samples are presented in Figure 5. Apparently, the impact strength of the raw PLAs is independent of the infill patterns used. The Ingeo™ 3D850 is the one with the highest impact toughness (17 kJ/m^2), while the impact strength of the Ingeo™ 2003D, the Ingeo™ 8052D grades are 15.5 kJ/m^2 and 14 kJ/m^2, respectively. The NR-toughened samples prepared with the grid-like infill (Figure 5/a) showed only a slightly higher impact strength compared to the raw PLAs, and the increment was within the deviation range in all cases. On the other hand, the samples with unidirectional infill (Figure 5/b) exhibited a markedly higher impact strength values in the range of 27-32 kJ/m^2, depending on the PLA grade. The rather poor toughening efficiency of NR, when using the grid-type infill can be attributed to the poor interfacial adhesion between the layers, which is in good agreement with the results of the tensile tests.

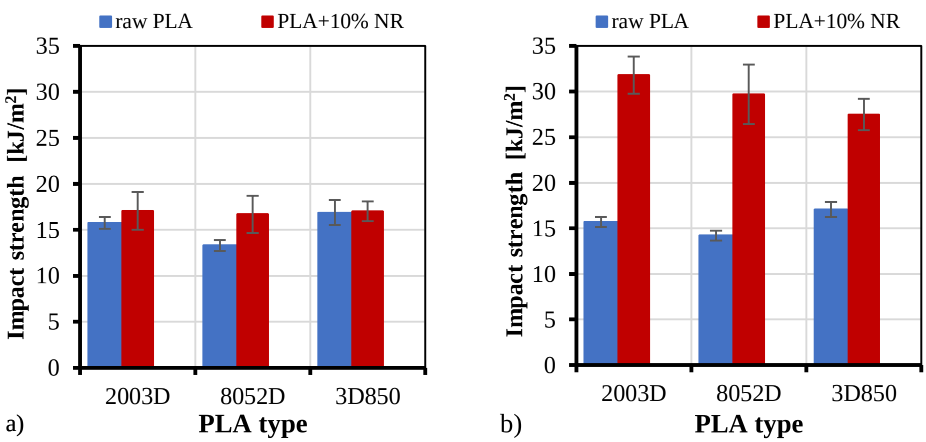

Figure 5. Charpy impact strength of the fabricated samples with (a) grid-type infill pattern and (b) unidirectional infill pattern parallel to the length of the specimens

4 Conclusion

In this present work the efficiency of natural rubber toughening was investigated on various PLA grades for 3D printing purposes. Therefore, 10 wt% NR was mixed into PLA grades with 4.5%, 4.3% and 0.5% d-isomer content *via* melt compounding. Subsequently, filaments were extruded using the prepared PLA/NR blends, which were then used to fabricate specimens by a desktop FDM printer with two different infill patterns. The presence of dispersed NR domains within the PLA matrix resulted in a greatly enhanced deformability and toughness, however, at cost of strength and stiffness. It was found that the improvement in ductility is most prominent when a unidirectional infill pattern is used, which is parallel to the length of the fabricated specimens. Out of the three examined PLA grades the Ingeo™ 2003D was found to be the most suitable to be used as matrix material for NR-toughened 3D printing filaments.

Acknowledgments

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5 References

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