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MODIFIED POLYLACTIDE FILAMENTS FOR 3D PRINTING WITH IMPROVED MECHANICAL PROPERTIES

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Abstract: We investigated the effects of two different types of impact modifiers, i.e. core-shell rubber and aliphatic polyester, on the mechanical and thermal properties of polylactide (PLA) filaments for 3D printing. First, PLA/impact modifier blends with various concentrations of impact modifiers were prepared by melt blending in a co-rotating twin screw extruder and test specimens by injection molding. The mechanical and thermal properties of blends were investigated by tensile and bending tests, dynamic mechanical analysis (DMA) and Charpy impact test. It was found that core-shell rubber remarkably improved Charpy impact strength at loadings above 5 wt % (up to 746 %). As shown by DMA, the PLA/10 wt % core-shell rubber blend exhibited better damping performance as compared to neat PLA over the whole examined frequency range, especially at high frequencies, which explained the increase in impact strength. The filament for a fused deposition modeling (FDM), 3D printer was prepared from blend with the highest impact strength (PLA/10 wt % core-shell rubber), whereas PLA and acrylonitrile-butadiene-styrene copolymer (ABS) filaments were used for reference. Test specimens were prepared by using a consumer FDM 3D printer. The mechanical and thermal properties were investigated by tensile and bending tests, DMA, Charpy impact test, and ultra-fast differential scanning calorimetry (Flash DSC). Specimens from PLA blend exhibited 109 % increase in Charpy impact strength as compared to neat PLA. In contrast to injection molded specimens, 3D printed PLA blend exhibited higher tensile E modulus than neat PLA, which was ascribed to improved interlayer adhesion. Moreover, DMA and Flash DSC analysis of 3D printed specimens showed an increase in the glass transition temperature as compared to injection molded specimens. This phenomenon was ascribed to reduction of free volume because of slow cooling in 3D printing process, which is also the reason for increased tensile E modulus of the PLA blend. All tested PLA, PLA blend and ABS filaments were in amorphous state as shown by Flash DSC analysis. Bending test showed an increased toughness of PLA blend in comparison to neat PLA and also higher toughness as compared to ABS. The modified polylactide (PLA/10 wt % core-shell rubber) filament thus combines easy processability of PLA filament and impact toughness of ABS filament.

Keywords: Polylactide, Impact modification, Core-shell rubber, 3D printing, Fused deposition modeling.

1. INTRODUCTION

Fused deposition modeling 3D printing is commonly used method for rapid prototyping (RP). A FDM 3D printer is fed by a thermoplastic filament usually made of PLA or ABS. The heated nozzle moves across sectional profile and deposits molten material layer by layer. Because PLA does not evolve an irritating odor during printing and does not warp, it has become more popular polymer material for 3D printing than ABS.[1]

PLA is linear thermoplastic polyester produced by the ring opening polymerization of lactide. PLA is most promising biopolymer, since it offers unique features of biodegradability as well as thermoplastic processability. PLA is used for many different applications, from packaging to agricultural products and disposable materials, as well as in medical, surgical and pharmaceutical fields.[2] However, despite its numerous advantages such as good optical, physical and mechanical properties (high flexural and tensile moduli and strengths), the inherent brittleness significantly impedes its application in many fields, especially when a high level of mechanical strength is required.[3]

Many efforts have been made to improve brittleness of PLA such as modifying its crystalline structure, blending it with plasticizers or other ducti-

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le polymers, and reactive blending, but none of them dealt with this effect in connection to the 3D printed parts.[3-8] One of the main limitations facing RP manufacturing of parts for end-use are the properties of the parts produced. Improvements in material properties, most notably with FDM 3D printing, have induced a steady increase of the range of applications for FDM materials. However, further improvements, particularly with respect to stiffness, strength and toughness, are required to enlarge the envelope of applications.[9]

The aim of the present work was to develop filament for 3D printing based on PLA with increased impact toughness and improved processability as compared to neat PLA filament. For this purpose, two different types of impact modifier were selected: core-shell rubber and aliphatic polyester. They were compounded with PLA, test specimens were fabricated by injection molding and mechanical properties as well as thermal ones were investigated. The filament for 3D printing was fabricated from the PLA blend with the highest impact strength. The mechanical and thermal properties of 3D printed test specimens were evaluated using tensile test, bending test, Charpy impact test, DMA and Flash DSC.

2. EXPERIMENTAL

2.1. Materials

PLA (Ingeo 2003D), recommended for extrusion, was supplied by Natureworks LLC (Minnetonka, MN, USA). PLA has a density of 1.24 g/cm^3, while its melt flow index (MFI) is 6.0 g/10 min at 210 °C and 2.16 kg load. ABS (HF-380), recommended for injection molding, was supplied by LG Chem (Seul, South Korea). ABS has a density of 1.05 g/cm^3, while MFI is 42.0 g/10 min at 220 °C and 10.0 kg load. Commercial names of two impact modifiers, core-shell rubber and aliphatic polyester, cannot be revealed due to trade secret of the project partner.

2.2. Specimens preparation

2.2.1. Blend preparation

PLA was dried prior to extrusion in laboratory oven at 80 °C, below 0.02 wt % moisture content. Blends were prepared in a twin screw extruder (Labtech LTE 20-44), with screw diameter 20 mm and L/D ratio 44. Screw speed was 100 min^{-1}, barrel temperature was 175 °C. Compositions of specimens are summarized in table 1.

Table 1. Specimens compositions

Specimen	PLA [wt %]	Core-shell rubber [wt %]	Aliphatic polyester [wt %]
1	98	2	0
2	95	5	0
3	90	10	0
4	90	0	10
5	85	0	15
6	80	0	20
7	100	0	0

2.2.2. Injection molding

Prepared blends were dried prior to injection molding in laboratory oven at 60 °C, below 0.02 wt % moisture content. Test specimens according to ISO 527, ISO 168 and ISO 179 standards were prepared by injection molding (Krauss Maffei 50-180 CX). Injection speed was 60 mm/s, barrel temperature was 175 °C and mold temperature was 35 °C.

2.2.3. Filament preparation

Based on results from injection molded specimens, we chose the most suitable blend (specimen 3P with 10 wt % of core-shell rubber). Filament for 3D printing was prepared by single screw extruder (Noztek). The prepared blend was dried prior to extrusion in laboratory oven at 60 °C, below 0.02 wt % moisture content. Filament for 3D printing was 1.75 mm in diameter. We also prepared PLA (specimen 7P) and ABS (specimen 8P) filaments for reference. Barrel temperature was set to 220 °C for PLA based specimens and to 230 °C for ABS specimen.

2.2.4. 3D printing

All specimens were prepared on a consumer FDM 3D printer (Solidoodle 4). G code was prepared with Slic3r software using standard settings (Z axis resolution 0.3 mm, 20 % infill). All specimens were prepared perpendicular to the heated bed. Nozzle temperature was set to 230 °C for all specimens and heated bed to 55 °C for PLA based specimens and to 110 °C for ABS specimen. Filament flow was calibrated for each specimen so that width to thickness ratio was 1.4:1. Specimens are marked as injection molded analogues with added letter P, e.g. 3D printed specimen made from specimen 3 is marked as 3P.

2.3. Characterization

2.3.1. Tensile test

Tensile properties were determined using a universal testing machine (Shimadzu AG-X plus 10 kN. Injection molded specimens were tested according to ISO 527 standard. 3D printed specimens were made from 3D model for 1 BA test specimens according to ISO 527 standard. Test speed was set at 1 mm/min from 0 to 0.25 % strain and at 50 mm/min above 0.25 % strain for all specimens.

2.3.2. Bending test

Bending properties were determined using a universal testing machine (Shimadzu AG-X plus 10 kN). Injection molded specimens were tested according to ISO 178 standard. 3D printed specimens were made from 3D model for ISO 178 test specimens. Test speed was set at 2 mm/min for all specimens.

2.3.3. Charpy impact test

Charpy impact strength was determined using pendulum impact tester (Zwick). Injection molded specimens were tested according to ISO 179 standard. 3D printed specimens were 80 mm in long, 10 mm wide and 8 mm thick. All specimens were tested using 4.54 kg hammer.

2.3.4. Dynamic mechanical analysis

Dynamic mechanical properties were determined on a dynamic mechanical analyzer (Perkin Elmer DMA 8000). All specimens were tested in dual cantilever bending mode. Frequency was 10 Hz, amplitude 0.04 mm, the specimens were heated with a heating rate of 2 °C/min from room temperature to 90 °C for PLA specimens and to 150 °C for ABS specimens. Dynamic mechanical properties as a function of frequency were tested in dual cantilever bending mode. Frequency was set logarithmically from 0.1 Hz to 100 Hz, with 3 points per decade, the specimens were heated from 30 °C to 90 °C with 10 °C step and heating rate of 2 °C/min. Injection molded specimens were prepared from ISO 527 test specimens and 3D printed specimens were prepared from tensile test specimens.

2.3.5. Ultra-fast differential scanning calorimetry

Thermal properties were determined using Mettler Toledo Flash DSC 1 with Huber intercooler TC45 and nitrogen purge gas (50 ml/min). Injection molded specimens were prepared from ISO 527 test specimens. 3D printed specimens were prepared from bending test specimens. Specimens were cooled from melt (200 °C) to desired temperature and then crystalized for a fixed time (first 100 s at 90 °C, then 600 s at various temperatures). Rapid cooling (1,000 °C/s) was performed before and after isothermal segments to prevent crystallization during cooling. First heating run was performed from 15 °C to 200 °C with a heating rate of 1,000 °C/s.

The specimen's mass was estimated from normalized specific heat capacity change at the glass transition to 0.48 J/gK for fully amorphous PLA as found in literature.[10] The degree of crystallinity was evaluated according to the following Eq. (1):

$$\%Crystallinity = \left[\frac{\Delta H_m - \Delta H_c}{\Delta H_f} \right] \quad (1)$$

where ΔH_f is the enthalpy of fusion, ΔH_c is the enthalpy of crystallization and ΔH_m is the enthalpy of fusion of a wholly crystalline PLA (93 J/g).[10]

3. RESULTS AND DISCUSSION

3.1. Tensile test

Table 2 summarizes the mechanical properties of neat PLA and PLA blends prepared by injection molding. With addition of impact modifiers, tensile modulus reduces from 3.5 GPa to 2.8 GPa (- 20 %) at highest loading of both modifiers. Tensile strength also reduces from 68 MPa to 54 MPa (- 21 %) at 10 % loading of core-shell rubber and to 58 MPa (- 15 %) at 20 % loading of aliphatic polyester. Strain at tensile strength decreases for PLA with the addition of 2 % and 10 % core-shell rubber, while at 5 % loading it increases. Strain at break decreases with 2 % and 5 % loading of core-shell rubber while at 10 % loading it increases from 4.7 % to 7 % (+ 49 %). Strain at tensile strength increases for PLA with addition of aliphatic polyester at all tested concentrations. Strain at break is also higher for all tested concentrations, but it drops at 20 % loading. Both impact modifiers reduce stiffness and strength and enhance strain at break at concentrations higher that 10 %. Decrease of strain at break for 20 % loading of aliphatic polyester indicates poor compatibility between matrix and impact modifier.

Table 3 summarizes tensile properties of 3D printed specimens. Specimen with 10 wt % loading of core-shell rubber has higher tensile modulus, lower tensile strength and lower strain at tensile strength as well as strain at break than neat PLA. Compared to ABS, neat PLA and PLA blend have higher tensile modulus and tensile strength but lower

strain at break. Neat PLA has the highest strain at tensile strength while PLA blend has the lowest one.

Higher stiffness of PLA blend was ascribed to improved inter-layer adhesion. Higher stiffness in comparison to injection molded specimens was ascribed to reduction of free volume because of slow cooling in 3D printing process, which was also supported by higher glass transition temperatures determined by DMA and Flash DSC.[11] 3D printed specimens exhibited lower tensile strength, strain at tensile strength and strain at break (Table 3) as compared to injection molded specimens (Table 2), which could be explained by higher number of structural defects due to low adhesion between layers, low filling and lower pressures in 3D printing process.

Table 2. Tensile properties of injection molded specimens

Specimen	Tensile modulus [GPa]	Tensile strength [MPa]	Strain at tensile strength [%]	Strain at break [%]
1	3.4	61	3.6	4.0
2	3.2	57	3.8	4.1
3	2.8	54	3.4	7.0
4	3.0	64	4.2	5.4
5	2.9	60	4.0	6.4
6	2.8	58	4.0	5.7
7	3.5	68	3.7	4.7

Table 2. Tensile properties of 3D printed specimens

Specimen	Tensile modulus [GPa]	Tensile strength [MPa]	Strain at tensile strength [%]	Strain at break [%]
3P	3.2	49	3.2	4.4
7P	3.0	60	4.0	4.5
8P	2.5	38	3.5	5.1

3.2. Bending test

Table 4 summarizes the bending properties of injection molded specimens. The flexural modulus of PLA with addition of impact modifier reduces from 3 GPa to 2.5 GPa (- 33 %) as compared to neat PLA. Flexural strength for highest loading of both impact modifiers decreases from 92 MPa to 71 MPa (- 23 %) for 10 wt % loading of core-shell rubber type modifier and to 74 MPa (- 20 %) for 20 wt % loading of aliphatic polyester modifier. Flexural strain at flexural strength also decreases with addition of impact modifiers and has the lowest value for 10 wt % and 15 wt % loading of aliphatic polyester (from 4.6 % for neat PLA to 3.6 %, - 22 %). Specimens with added impact modifier didn't break during the test, which indicated high bending toughness.

Table 4. Flexural properties of injection molded specimens

Specimen	Flexural modulus [GPa]	Flexural strength [MPa]	Flexural strain at flexural strength [%]	Strain at break (flexural) [%]
1	2.9	88	4.3	/
2	2.7	81	3.8	/
3	2.5	71	3.7	/
4	2.6	78	3.6	/
5	2.6	76	3.6	/
6	2.5	74	3.9	/
7	3.0	92	4.6	5.7

Figure 1 shows the stress-strain curves of 3D printed specimens. PLA blend and neat PLA exhibit the same flexural modulus (2.5 GPa), whereas flexural modulus of ABS is lower (2.0 GPa, - 20 %). Neat PLA exhibits the highest flexural strength (71 MPa), while with addition of core-shell rubber to PLA flexural strength decreases (68 MPa, - 4 %), however, flexural strength of ABS is the lowest (52

MPa, - 25 %). ABS exhibits higher flexural strain at flexural strength than neat PLA (3.8 %, - 12 %) and PLA blend (3.6 %, - 16 %). PLA blend specimens didn't break during measurements thus showing improved flexural toughness also for 3D printed specimens. Lower reduction of flexural strength of 3D printed PLA blend as compared to injection molded specimens was ascribed to improved inter-layer adhesion.

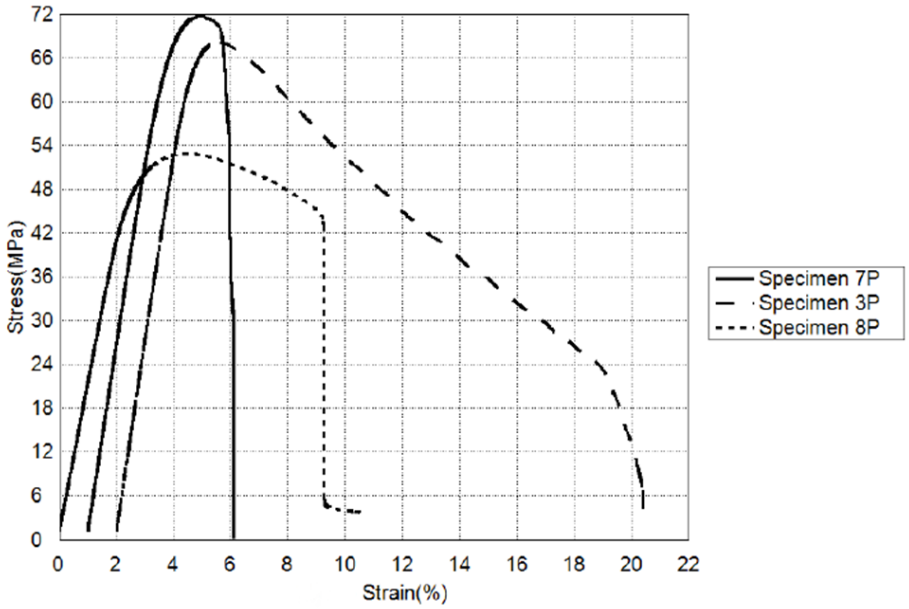

Figure 1. Representative stress-strain curves for bending test of 3D printed specimens (dashed line – PLA blend, full line – PLA, dotted line – ABS)

3.3. Charpy impact test

The highest increase of Charpy impact strength was determined for PLA/core-shell rubber blends, but only at high loadings: 5 wt % loading (20 kJ/m^2, + 54 %) and 10 wt % loading (111 kJ/m^2, + 746 %) as shown in Figure 2. Other specimens did not exhibit statistically important increases.

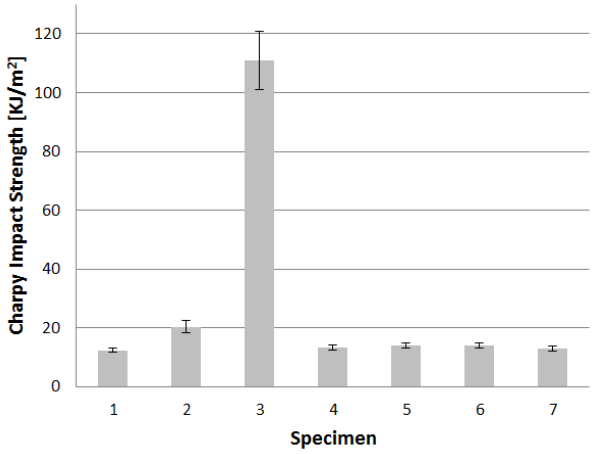

Figure 2. Charpy impact strength of injection molded specimens

Charpy impact strength of 3D printed specimens is shown in Figure 3. PLA blend exhibits the highest Charpy impact strength (23 kJ/m^2, + 109 %) and ABS exhibits only slightly lower impact strength (22 kJ/m^2, + 100 %), but statistically not relevant.

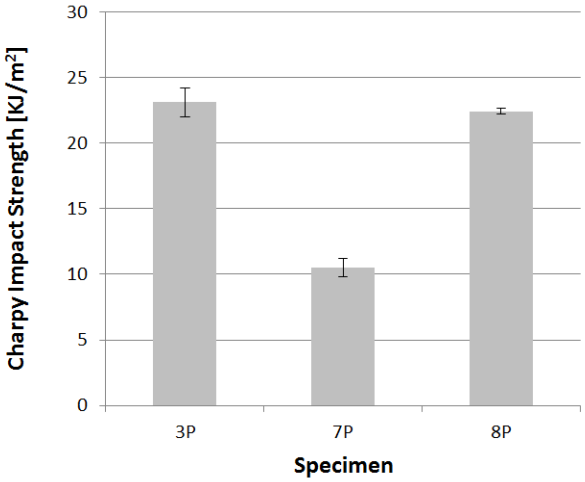

Figure 3. Charpy impact strength of 3D printed specimens

3.4. Dynamic mechanical analysis

Storage modulus (E') of all specimens was measured by DMA at 30 °C and 80 °C (Figure 4). At 30 °C, storage moduli of PLA blends with both impact modifiers decrease. E' of PLA with 10 wt %

loading of core-shell rubber drops from 3,005 MPa (for PLA) to 2,407 MPa (- 20 %) and for 20 wt % loading of aliphatic polyester it drops to 2,537 MPa (- 16 %). At 80 °C, E' first increases at 2 wt % loading of core-shell rubber (32 MPa, + 7 %) and at 5 wt % loading (36 MPa, + 20 %), then at 10 wt % loading drops to level of neat PLA (30 MPa). The reason for such uneven value distribution could be sterically hindered molecular motion by dispersed core-shell particles or by increased degree of crystallinity due to nucleating effect of impact modifier. At higher loadings of the impact modifier, E' decreases due to its low modulus.

E' at 80 °C of PLA with addition of 10 wt % of aliphatic polyester increases (36 MPa, + 20 %), which could be explained by increased crystallinity because of enhanced and prolonged crystallization due to the effect of impact modifier on solidification process or its nucleation effect. E' at 80 °C for higher loadings of aliphatic polyester decreases, which is ascribed to predominating low modulus effect. The lowered glass transition (T_g) of blend indicates some degree of interaction between PLA matrix and aliphatic polyester modifier.

Figure 5 shows loss factor (tan δ) as a function of frequency for neat PLA and PLA/10 wt % core-shell rubber blend. PLA blend exhibits higher tan δ across the whole tested frequency range which indicates better damping performance. This effect is especially noticeable at higher frequencies, which means that macromolecules in PLA blend relax and respond much faster at fast loads and, consequently, the increase in Charpy impact strength is remarkable.[12] Reduction of tan δ at 0.2 Hz is most likely due to resonance effect of a sample-instrument system[13].

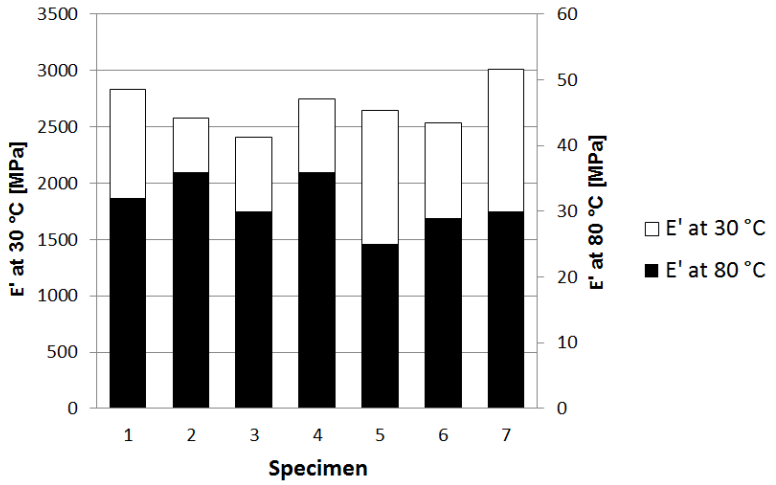

Figure 4. Dynamic mechanical properties of injection molded specimens

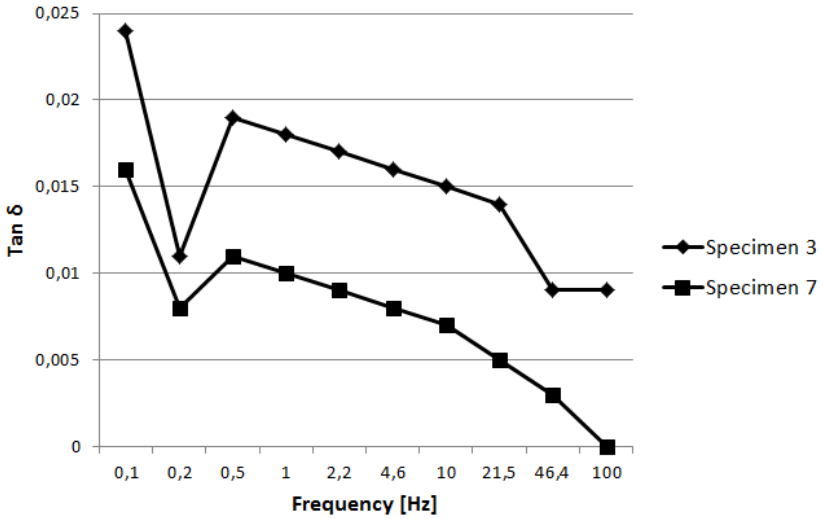

Figure 5. Tan δ as a function of frequency for injection molded specimens

Figure 6 shows storage modulus of 3D printed specimens as a function of temperature. Highest E' at 30 °C was determined for neat PLA (2,491 MPa), while with addition of core-shell rubber E' drops to 2,083 MPa (- 16 %). ABS exhibits lowest E' at 30 °C (1,477 MPa, - 41 %). In comparison to ABS, PLA exhibits much lower glass transition temperature (73.3 °C – determined by tan δ peak versus 126.3 °C) thus limiting its use due to low thermal stability. The glass transition temperature of 3D printed specimens of neat PLA and PLA blend is higher than of injection molded specimens. This phenomenon is ascribed due to greater reduction of free volume caused by slower cooling in 3D printing process due to poor heat transfer.

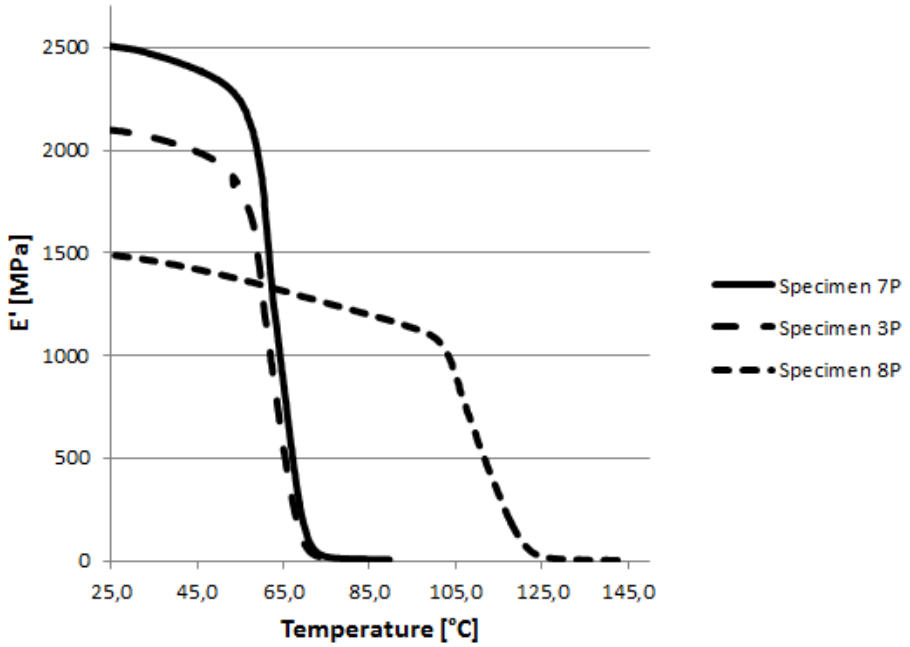

Figure 6. Storage modulus of 3D printed specimens as a function of temperature

3.5. Ultra-fast differential scanning calorimetry (Flash DSC)

Table 5 summarizes the thermal properties of injection molded PLA/core-shell rubber blend determined by Flash DSC. Highest degree of crystallinity (23.6 %) was determined at isothermal crystallization temperature of 120 °C. The melting point shifts to higher values with increased crystallization temperature indicating an increase in size of crystalline spherulites at higher crystallization temperatures.[14]

Table 5. Thermal properties of injection molded PLA/10 wt % core-shell blend as determined by Flash DSC

T *[°C]	T_g [°C]	ΔC_p [J/gK]	Crystallinity [%]	T_m [°C]
90	75.5	0.43	/	/
100	74.8	0.41	3.7	150.5
110	75.0	0.35	18.7	157.9
120	74.8	0.33	23.6	164.9
130	75.0	0.42	1.98	170.0
140	75.5	0.43	/	/

* Isothermal crystallization temperature

Table 6 summarizes the thermal properties of injection molded neat PLA as determined by Flash DSC. The highest degree of crystallinity (14.6 %) was determined at crystallization temperature of 120 °C, the same as for PLA blend. T_m increases with increasing temperature of isothermal crystallization.

PLA/core-shell rubber blend specimens exhibit higher degree of crystallinity as compared to neat PLA indicating that core-shell particles act as a nucleating agent and promote heterogeneous crystallization. The optimal temperature for isothermal crystallization for both PLA and PLA blend is around 120 °C.

Table 6. Thermal properties of injection molded neat PLA as determined by Flash DSC

T * [°C]	T_g [°C]	ΔC_p [J/gK]	Crystallinity [%]	T_m [°C]
90	75.2	0.48	/	/
100	74.7	0.47	1.8	149.7
110	75.1	0.42	12.6	158.4
120	73.1	0.41	14.6	165.3
130	75.7	0.48	/	/
140	74.5	0.48	/	/

* Isothermal crystallization temperature

Table 7 summarizes the thermal properties of injection molded and 3D printed PLA and PLA blend determined in the first heating run by Flash DSC. 3D printed specimens exhibit higher glass transition temperature (from 2.1 °C to 4.4 °C) than injection molded specimens as confirmed by DMA. None of the specimens tested did not show melting peak in the first heating run thus indicating that all specimens were in amorphous state.

Table 7. Comparison of thermal properties of injection molded and 3D printed PLA and PLA blend determined by Flash DSC in the first heating run

Specimen	Mass [ng]	ΔC_p [J/gK]	T_g [°C]
3	12.8	0.43	70.2
7	27.1	0.48	72.0
3P	28.5	0.43	74.6
7P	11.7	0.48	74.1

4. CONCLUSION

Flexural and impact toughness of PLA was remarkably improved with addition of 10 wt % core-shell rubber. Injection molded specimens showed 746 % increase in Charpy impact strength while 3D printed specimens exhibited 109 % increase in impact strength. Improved damping performance, especially at high frequencies, explains increase in impact strength. PLA/core-shell rubber specimens did not break during flexural test indicating improved flexural toughness. The core-shell rubber particles, dispersed in PLA matrix, acted as a nucleating agent and thus promoted crystallization as shown by Flash DSC. With addition of core-shell rubber, we prepared PLA based filament with processing properties like PLA filament and better mechanical properties (stiffness, strength and toughness) than ABS filament. Further work will need to address low thermal stability of PLA to fully broaden its range of applications.

5. ACKNOWLEDGEMENT

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МОДИФИКОВАНИ ФИЛАМЕНТИ ПОЛИЛАКТИДА ЗА 3Д ШТАМПАЊЕ СА ПОБОЉШАНИМ МЕХАНИЧКИМ СВОЈСТВИМА

Абстракт: Испитивали смо ефекте двију различитих врста модификатора удара, тј. гуму језгро−омотач и алифатски полиестер, на механичка и термална својства филамената полилактида (ПЛА) за 3Д штампање. Најприје је направљена мјешавина ПЛА/модификатора удара са различитим концентрацијама модификатора удара путем мијешања отапањем у коротацијским двопужним екструдерима и инјекцијски пресани узорци за тестирање. Механичка и термална својства мјешавина испитивана су путем влачног испитивања и испитивања савијања, динамичко-механичке анализе (ДМА) и удара Charpy клатном.

Утврђено је да је гума језгро−омотач значајно побољшала снагу удара Charpy клатном при пуњењу изнад 5 wt % (до 746 %). Како је показала ДМА, ПЛА/10 wt % мјешавина гуме језгро-омотач је показала бољу дампинг перформансу у поређењу са чистим ПЛА у читавом тестираном обиму фреквенција, посебно при високим фреквенцијама, што објашњава пораст снаге удара. Филамент за *fused deposition modeling* (FDM) за 3Д штампач је припремљен од мјешавине са највишом снагом удара (ПЛА/10 wt % гума језгро−омотач), док су филаменти ПЛА и ацрулонитриле-бутадиене-стурене цополумер (АБС) кориштени информативно. Узорци за тестирање су припремљени коришћењем потрошачког FDM 3Д штампача.

Механичка и термална својства су испитивана су тестовима влачног испитивања и испитивања савијања, ДМА, тестом удара Charpy клатном, и ултрабрзом диференцијалном скен калориметријом (Flash DSC). Узорци из ПЛА мјешавине су показали пораст од 109% у снази удара Charpy клатном у поређењу са чистим ПЛА. За разлику од инјекцијски пресаних узорака, 3Д штампана ПЛА мјешавина је показала виши вучни Е модул од чистог ПЛА, што се приписало побољшаној адхезији међу слојевима. Штовише, ДМА и Flash DSC анализе 3Д штампаних узорака су показали пораст температуре стакластог прилеза у поређењу са инјекцијски пресаним узорцима. Ова појава је приписана смањењу слободне запремине због спорог хлађења у процесу 3Д штампања, што је такође разлог за повећани вучни Е модул ПЛА мјешавине. Сви тестирани ПЛА, ПЛА мјешавина и АБС филаменти су били у аморфном стању као што је приказано путем Flash ДСЦ анализе. Тест савијања је показао повећану жилавост ПЛА мјешавине у поређењу са чистим ПЛА и такође већу жилавост у поређењу са АБС. Филамент модификованог полилактида (ПЛА/10 wt % гума језгро−омотач) тиме комбинује лаку процесабилност ПЛА филамента и жилавост удара АБС филамента.

Кључне ријечи: полилактид, модификација удара, гума језгро−омотач, 3Д штампање, Fused deposition modeling.