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Centre for Polymer and Material Technologies

FACULTY OF ENGINEERING
AND ARCHITECTURE

DEPARTMENT OF MATERIALS, TEXTILES AND CHEMICAL ENGINEERING
CENTRE FOR POLYMER AND MATERIAL TECHNOLOGIES (CPMT)

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

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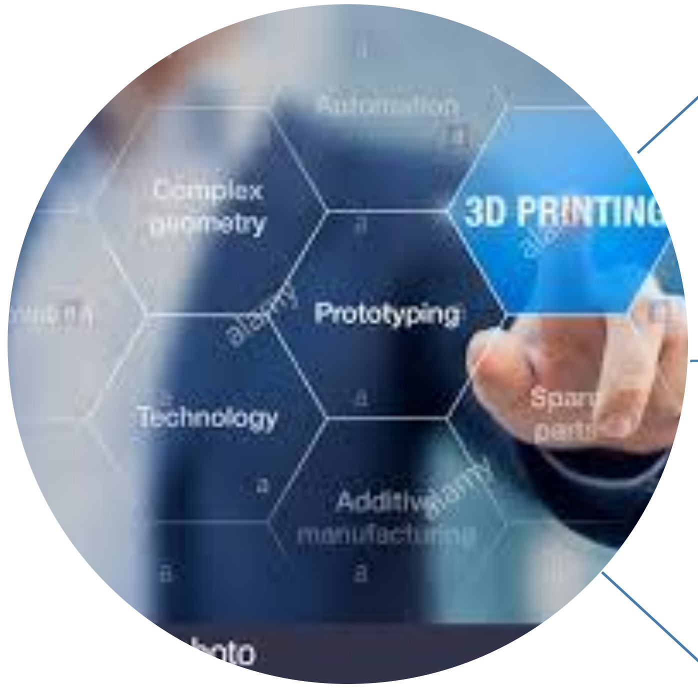
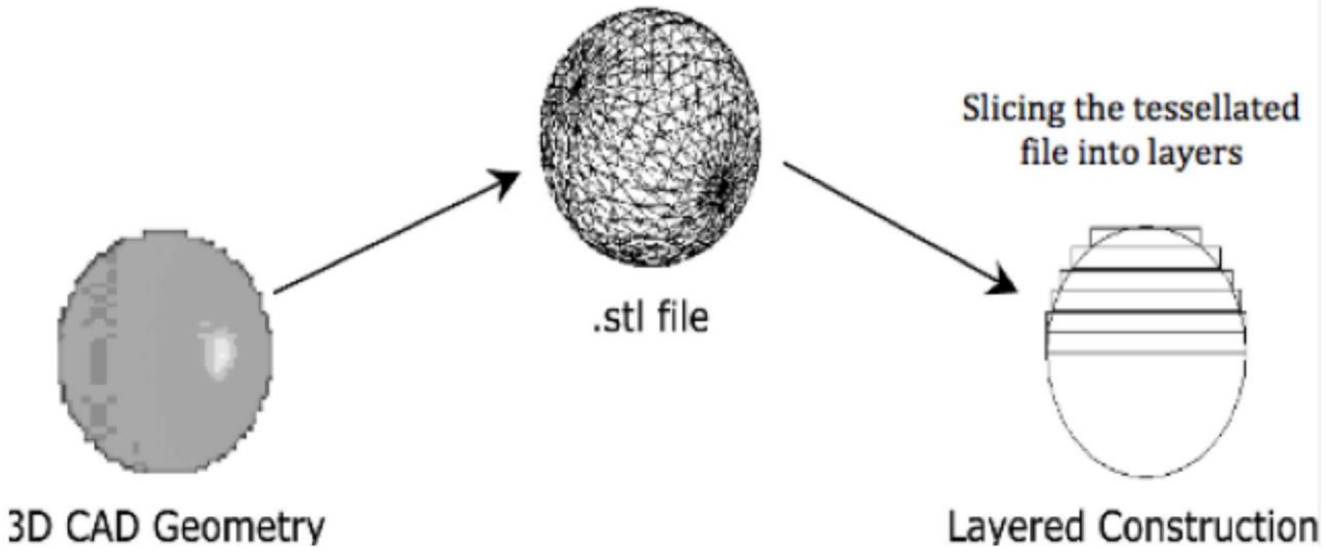
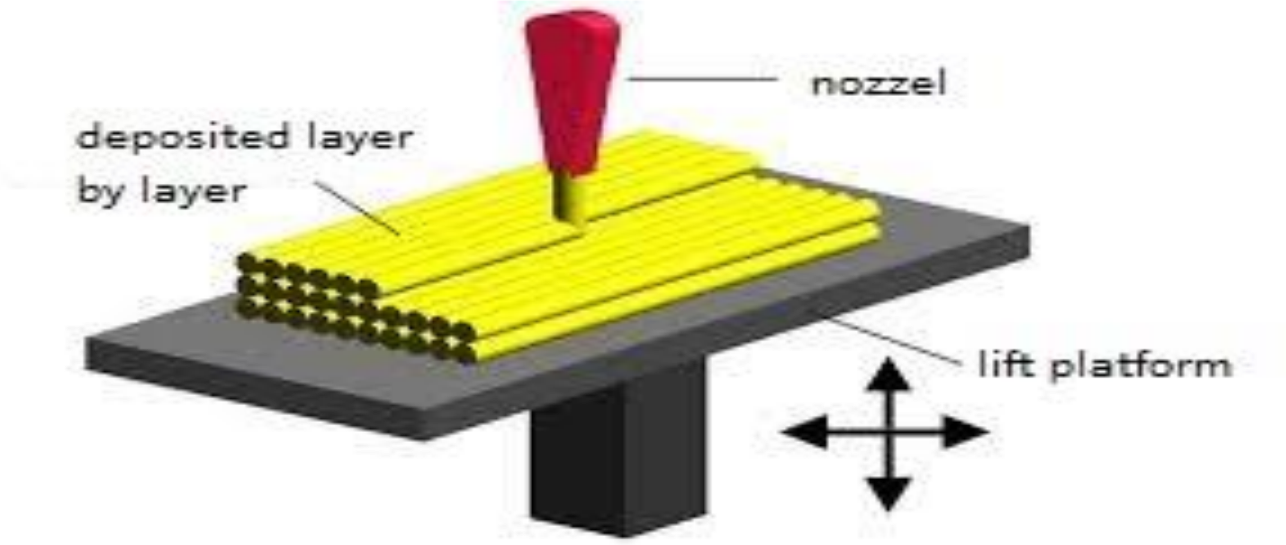
# 1. BACKGROUND




- Material deposition
  - **Extrusion**
- Powder bed
  - Laser sintering
  - Electron beam melting
  - Binder jet
- Liquid bed
  - stereolithography




3D printing employs an additive manufacturing process whereby products are built on a layer-by-layer basis, through a series of cross-sectional slices.

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– **Benefits**

- ✓ EBAM revenues and investments +26 % annual growth
- ✓ Complex geometries
- ✓ Rapid design
- ✓ Less waste

– **Challenges**

- ✓ Waste generation (Failed prints, Discarded support structures)
- ✓ Reduced choice for materials, colors, and surface finishing
- ✓ Common filaments: ABS, HIPS, PET-G, … (Good mechanical properties but not biodegradable)
- ✓ Limited mechanical, physical & chemical characteristics

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| | ABS | PET-G | PLA |
|---|---|---|---|
| Young' modulus (MPa) | 2000 | 2200 | 3500 |
| Strain at break (%) | 20 | 140 | 6 |
| Toughness | Mediocre | Good | Poor |

- PLA used as biodegradable alternative
- Inferior mechanical properites
- Blending with other biodegradable polymers
  - PBAT
- Improve stiffness: cloisite-15

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# RESEARCH GOALS

1

- Develop new biobased thermoplastic composites

2

- Improve the AM processing (rheology, solidification and shrinkage) with optimal final part quality

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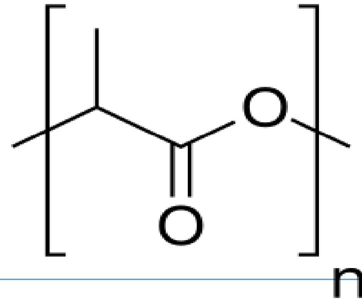
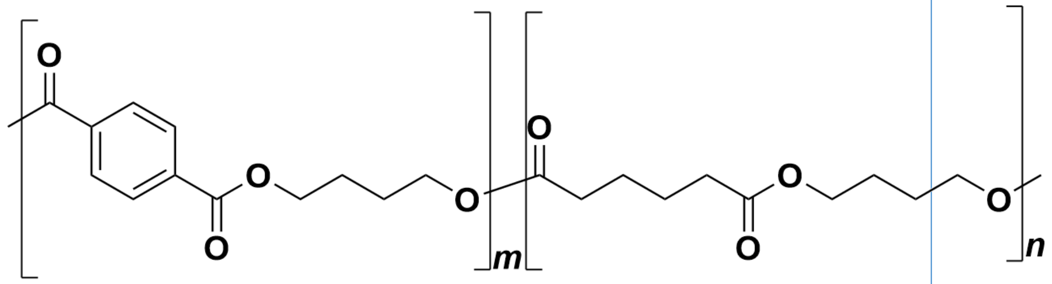
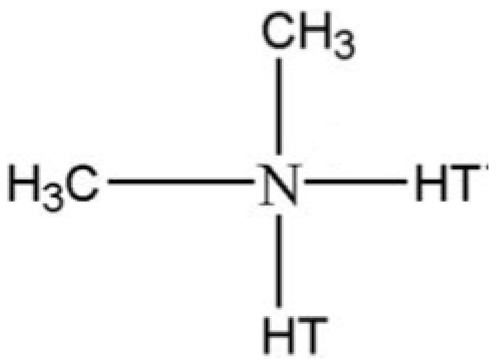
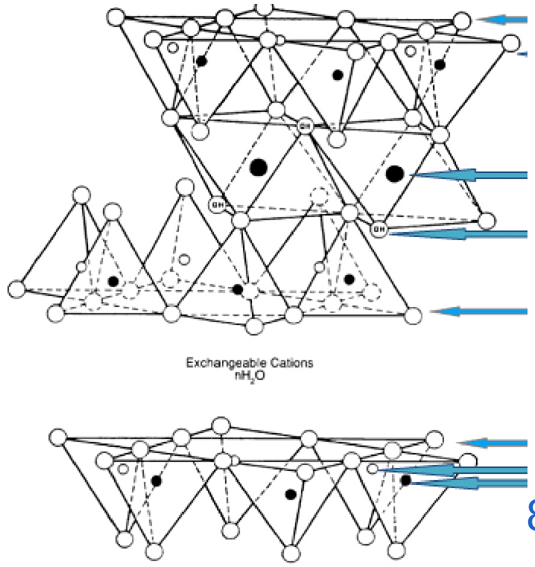
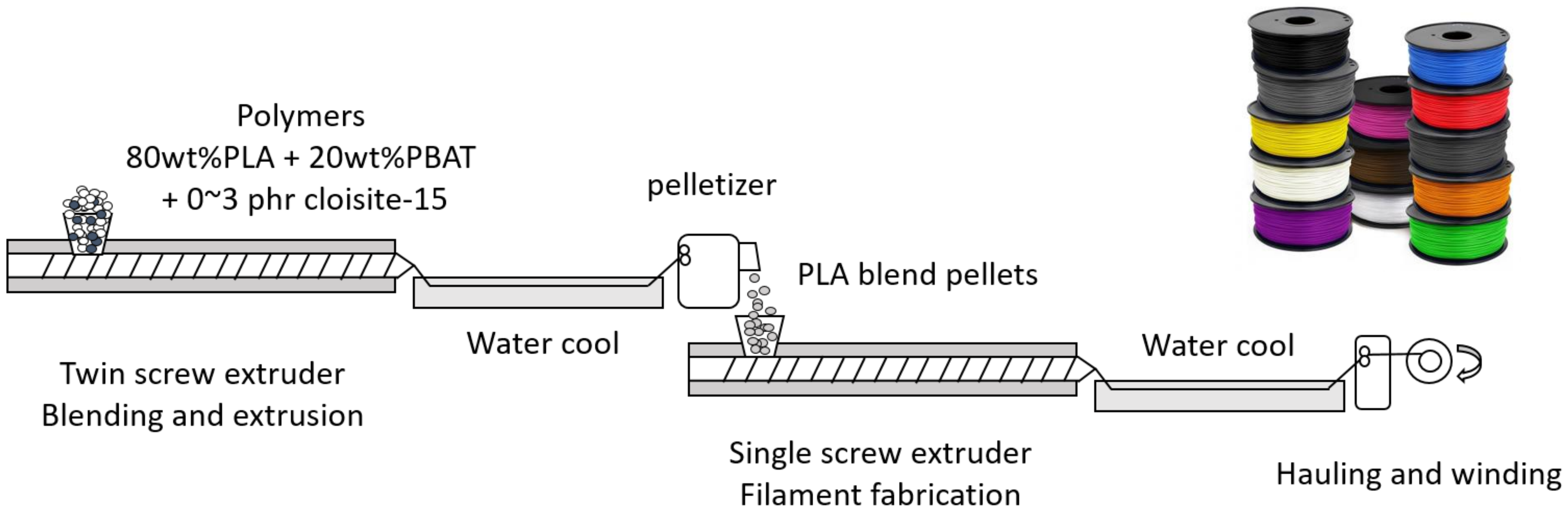
# 2. MATERIAL

| Material | | Supplier | Benifit | Weakness | Chemical formula |
|---|---|---|---|---|---|
| Polylactic acid | PLA, Ingeo 3D850 | NatureWorks | High stiffness (E = 2500 ~ 3500 MPa) | Brittle |  |
| Polybutylene adipate terephthalate<br>- a copolyester of adipic acid, 1,4-butanediol and terephthalic acid (from dimethyl terephthalate) | PBAT, Ecoflex C1200 | BASF | Flexible material (560-710% elongation) | Low stiffness |  |
| Bis(hydrogenated tallow alkyl)dimethyl, salt with bentonite<br>- an organic intercalated nanoclay, acts as filler<br>- $d_{001}$ = 3,63 nm $d_{50}$ < 10 µm | Cloisite-15 | BYK | Good dispersion, miscibility with the thermoplastic systems. Improves various physical properties (reinforcement, flame retardance, barrier properties, enhances flexural and tensile modulus | |   |

# 2. METHODS




| Name | PLA, wt% | PBAT, wt% | Cloisite, phr |
|---|---|---|---|
| PLA | 100 | | |
| PLA/PBAT | 80 | 20 | |
| PLA/PBAT/c1 | 80 | 20 | 1 |
| PLA/PBAT/c3 | 80 | 20 | 3 |

| Printing parameter | Setting |
|---|---|
| Nozzle diameter (mm) | 0.35 |
| Printing bed material | Kapton |
| Printing bed temperature, $T_{bed}$ (°C) | 55 |
| Nozzle temperature, $T_{Nozzle}$ (°C) | 210 |
| Printing speed (mm $s^{-1}$) | 50 |
| Layer thickness (mm) | 0.15 |
| Shell thickness (mm) | 1.05 |
| Infill rate (%) | 100 |
| Strand orientation (°) | 45 |

Characterization

- Melt flow index
- Differential scanning calorimetry analysis
- Thermogravimetric analysis

- Tensile test
- Impact test
- Annealing-Impact test

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# 3. RESULTS & DISCUSSION

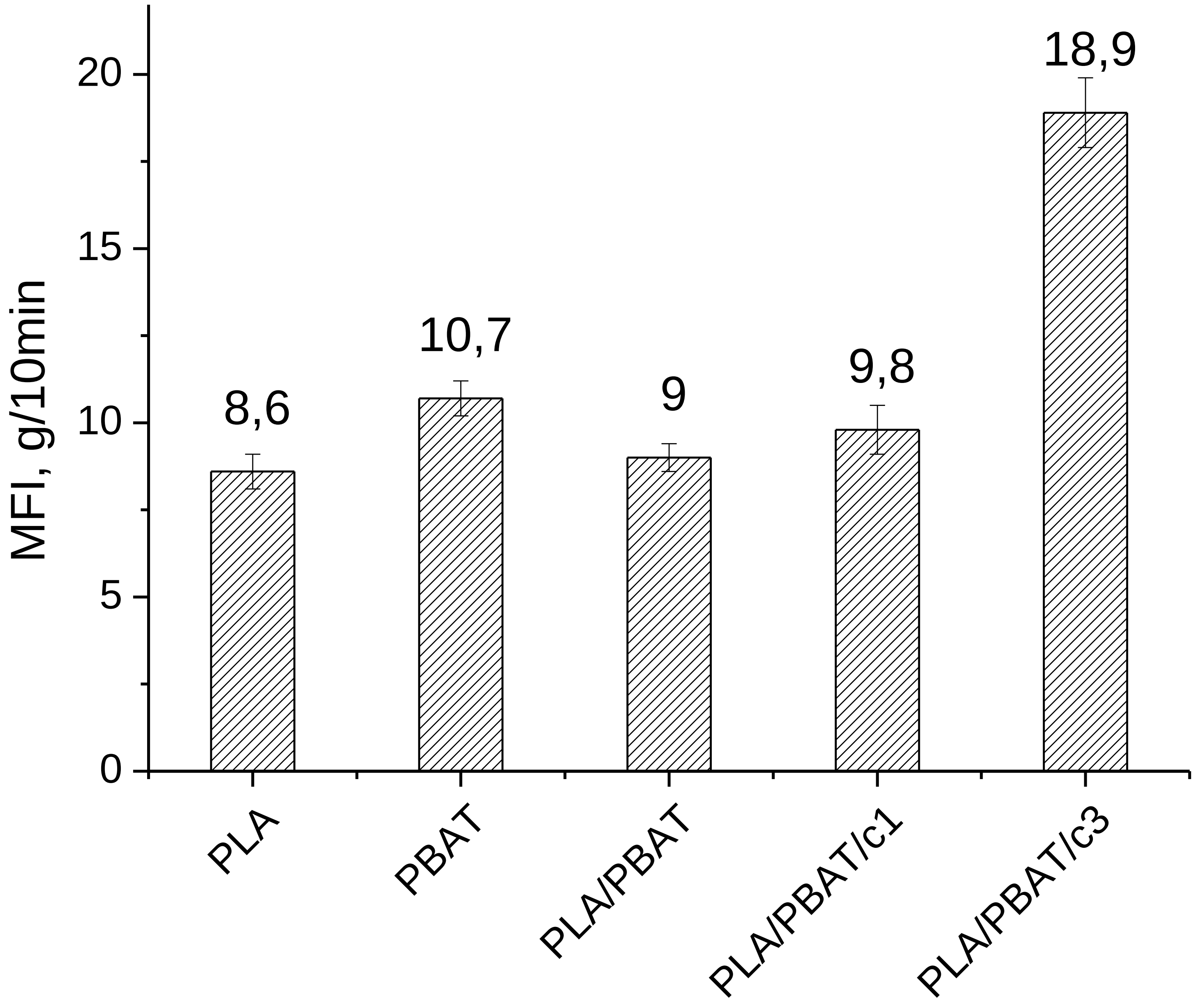


**Figure 1.** MFI of the filaments

Melf flow index test
-ISO 1133
-210°C with a load of 2,16 kg

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.

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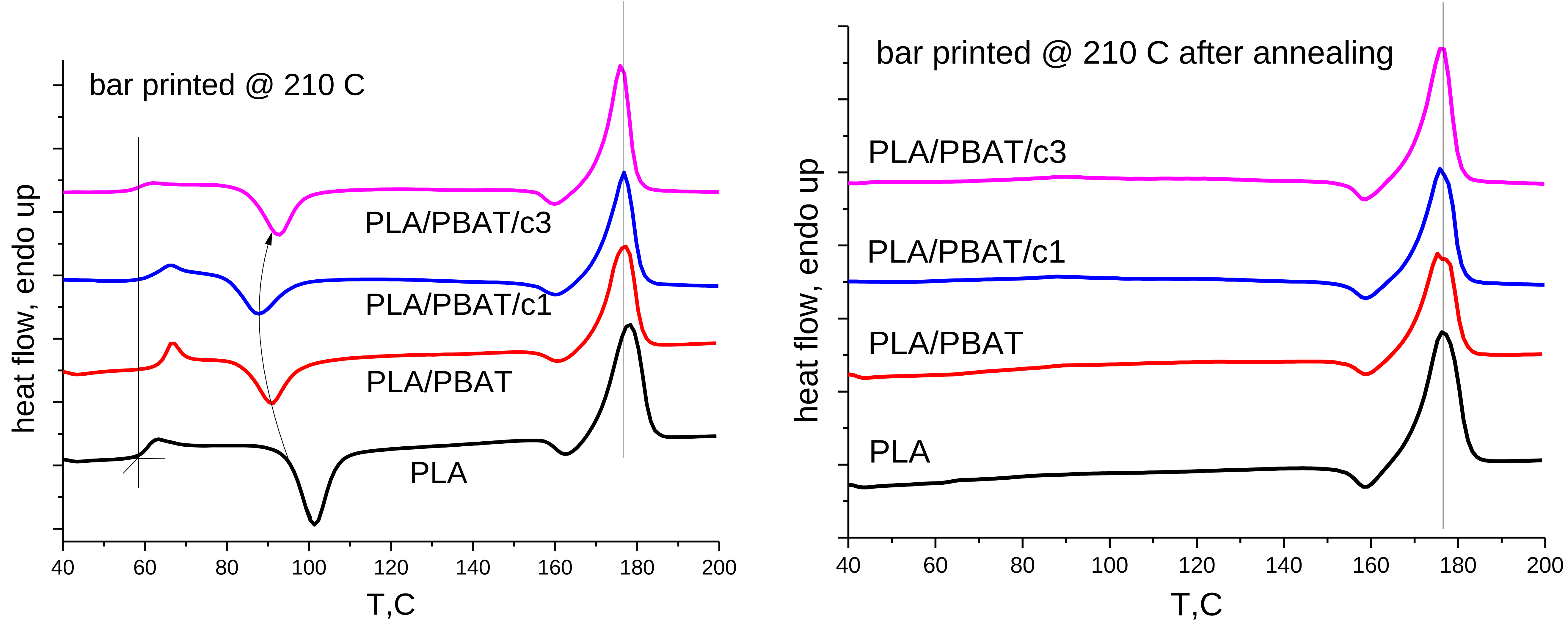


Differential scanning calorimetry test
-20 to 200°C at heating rate of 10°C/min

$$Xc = \frac{\Delta Hcc + \Delta Hm}{\Delta H_m^0 \cdot w_{PLA}} \times 100\%$$

$\Delta H_m^0 = 93$ J/mol

$w_{PLA} = 0.8$ for the blends

**Figure 2.** DSC curve of the printed sample (left: non-annealed, right: annealed)

**Table 1.** DSC data of the printed samples

| $T_{nozzle}$ | composation | Tg, °C | Tcc, °C | ΔHcc, J/g | Tm, °C | ΔHm, J/g | Xc, % |
|---|---|---|---|---|---|---|---|
| Bar printed @ 210°C | PLA | 60 | 101 | -28 | 178 | 43 | 16 |
| | PLA/PBAT | 64 | 91 | -18 | 177 | 36 | 24 |
| | PLA/PBAT/c1 | 62 | 88 | -18 | 177 | 37 | 26 |
| | PLA/PBAT/c3 | 60 | 93 | -19 | 176 | 37 | 24 |
| Annealed bar | PLA | | | | 176 | 46 | 50 |
| | PLA/PBAT | | | | 175 | 35 | 47 |
| | PLA/PBAT/c1 | | | | 176 | 36 | 48 |
| | PLA/PBAT/c3 | | | | 176 | 38 | 51 |

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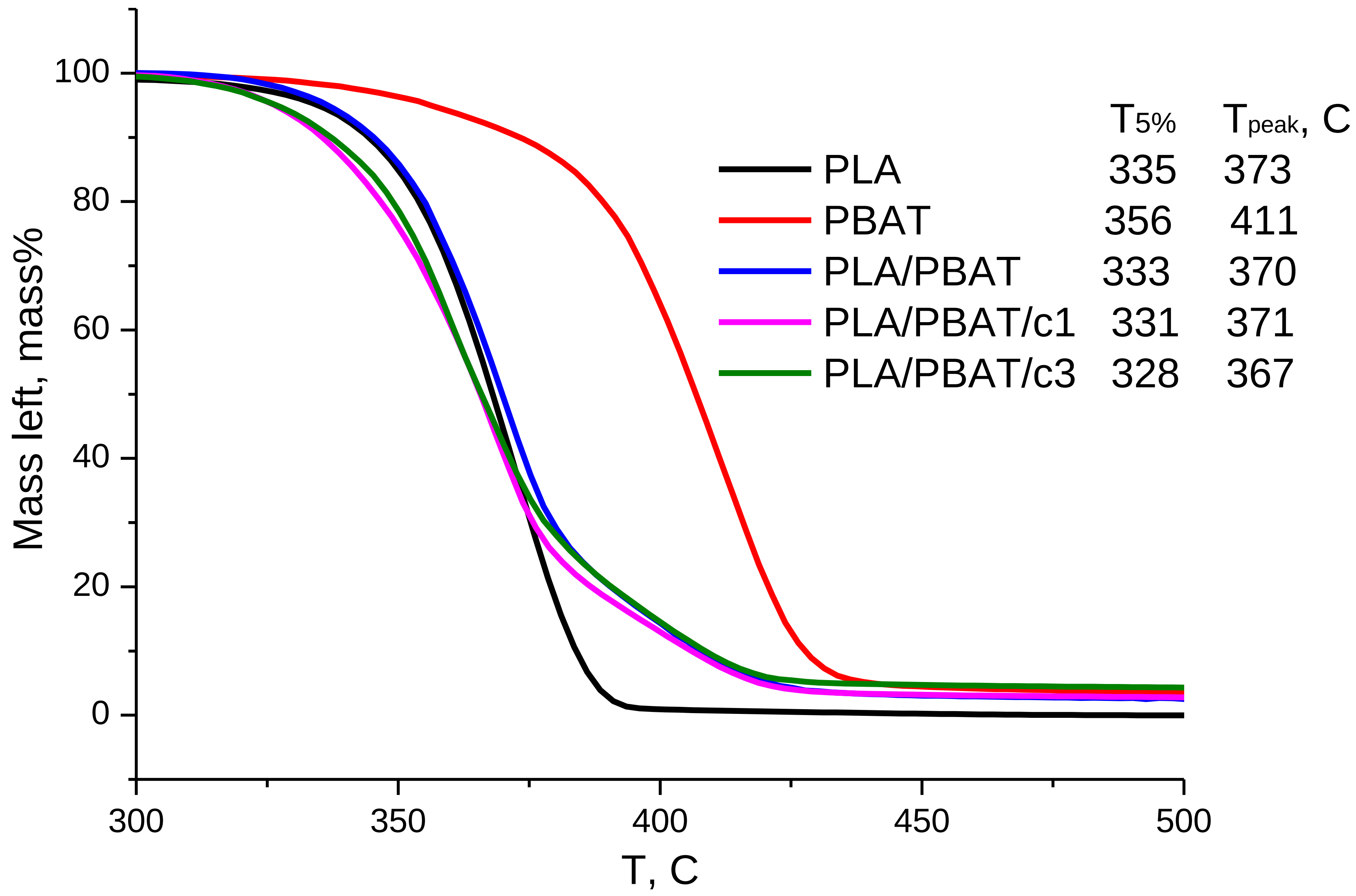


**Figure 3.** TGA curve of the filament sample

Differential scanning calorimetry test
-40 to 550°C at heating rate of 10°C/min
-degradation temperature of 5mass% loss ($T_{5\%}$) and the maximum mass loss point ($T_{peak}$) were recorded

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**Table 2.** 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/c1 | 2617±147 | 47±2 | 28±11 |
| PLA/PBAT/c3 | 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/c1 | 2399±141 | 42±2 | 29±11 |
| PLA/PBAT/c3 | 2540±107 | 41±1 | 15±4 |

Tensile test
-ISO 527
-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.

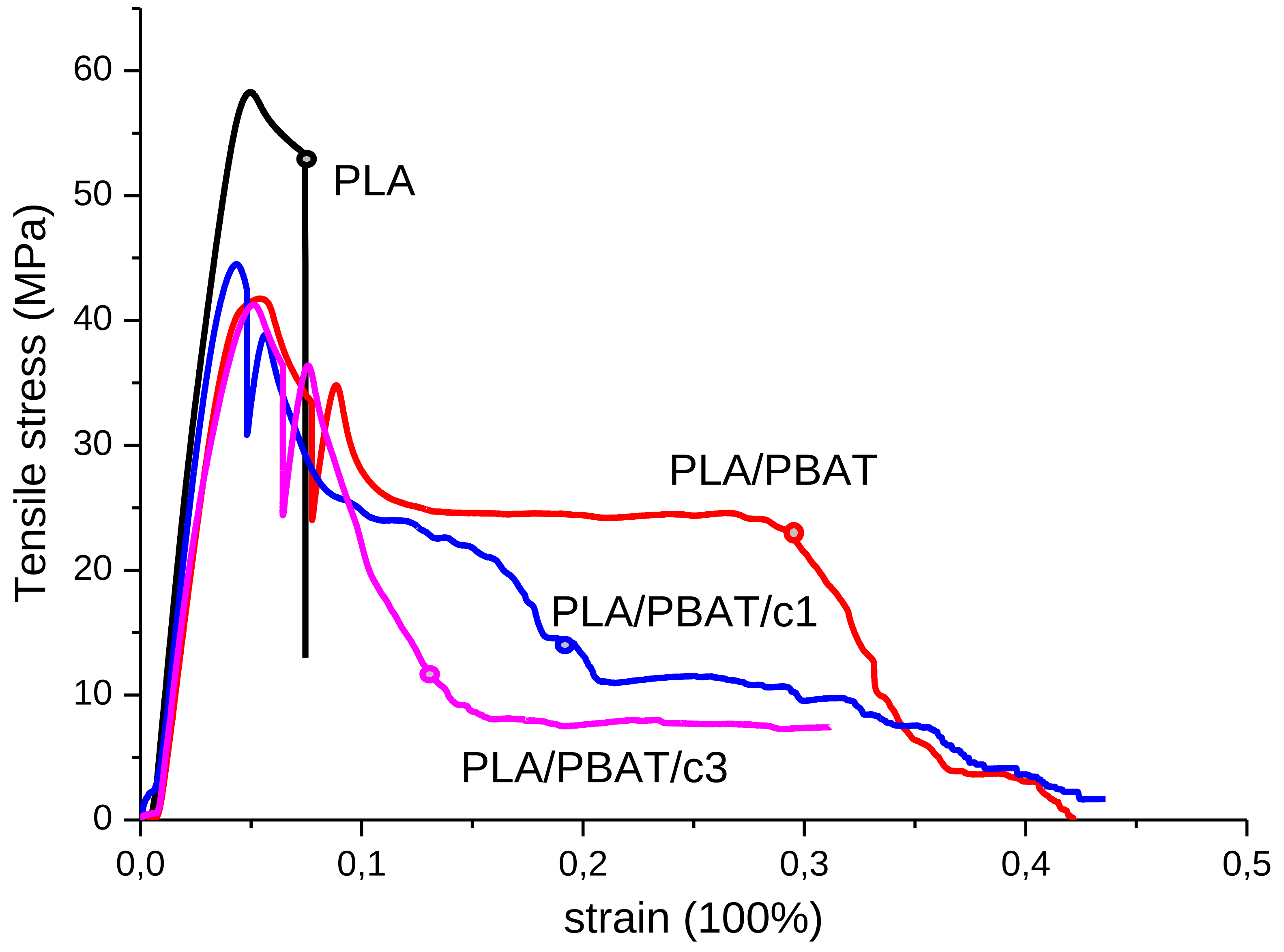


**Figure 4.** Tensile curve of samples printed @ 210°C

Impact test
-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.

+PBAT
Notched impact strength increased from 4 of PLA to 6 $kJ/m^2$.
+cloisite
It increased further from 6 to 8 $kJ/m^2$.
+AN
Impact increased a lot for PLA/PBAT without/with 1 phr cloisite, but increased less for 3 phr cloisite (due to agglomeration)

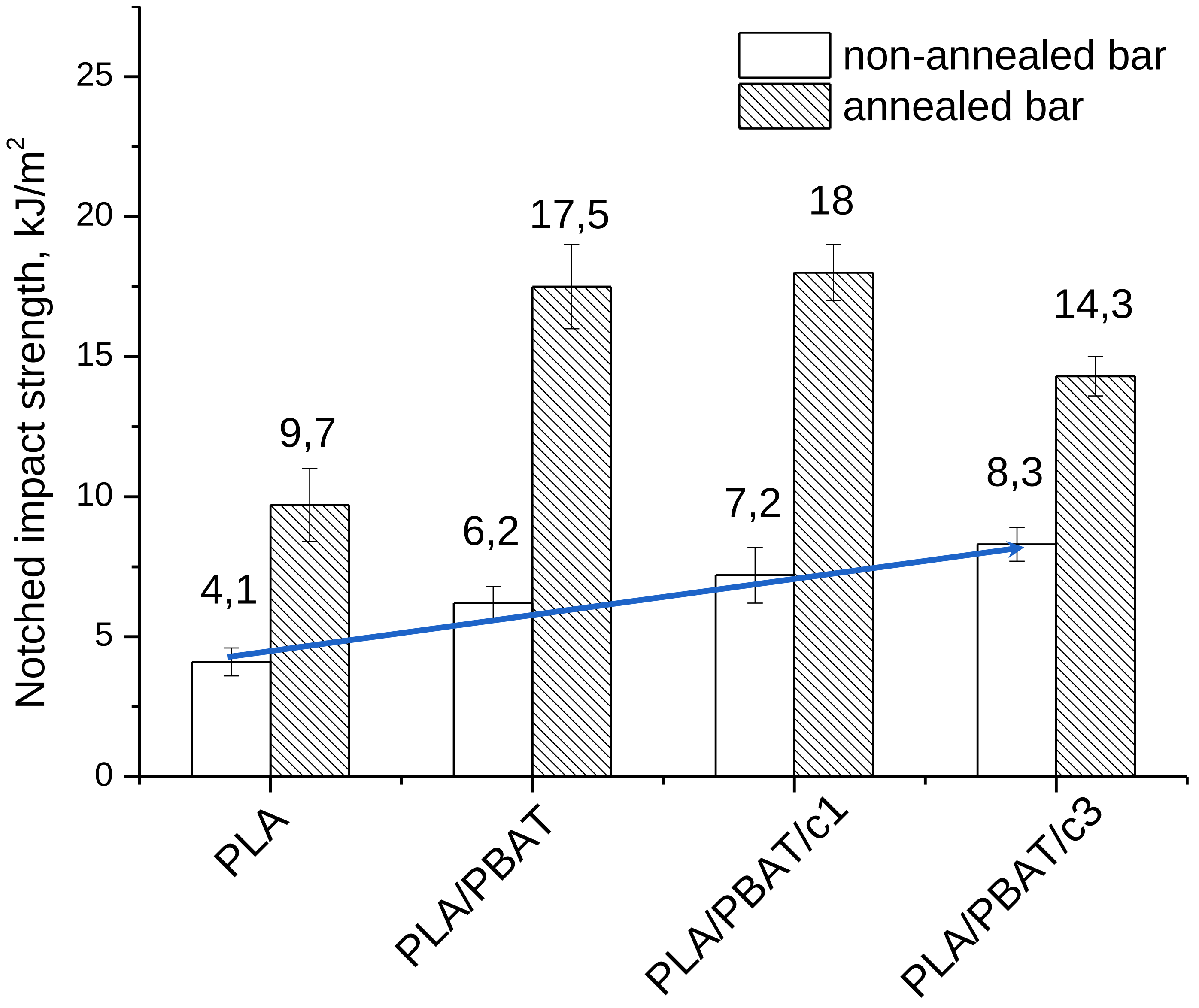


**Figure 5.** The notched impact strength of samples before and after annealing

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# 4. OUTLOOK

- Increase printing temperature
- Add reactive compatibilizer to improve the interface between PLA, PBAT and cloisite. (Najafi, Heuzey et al. 2012) (Meng, Heuzey et al. 2012) (Kumar, Mohanty et al. 2010)

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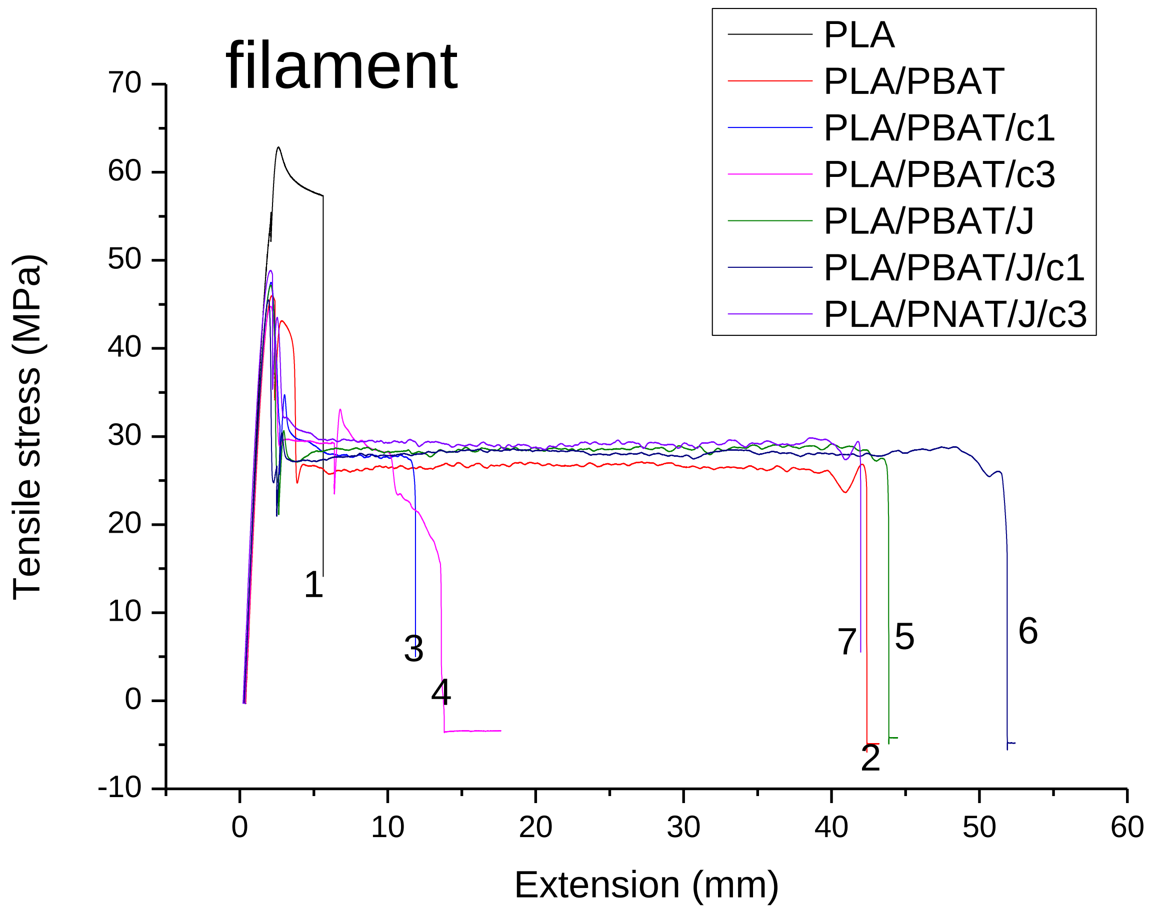
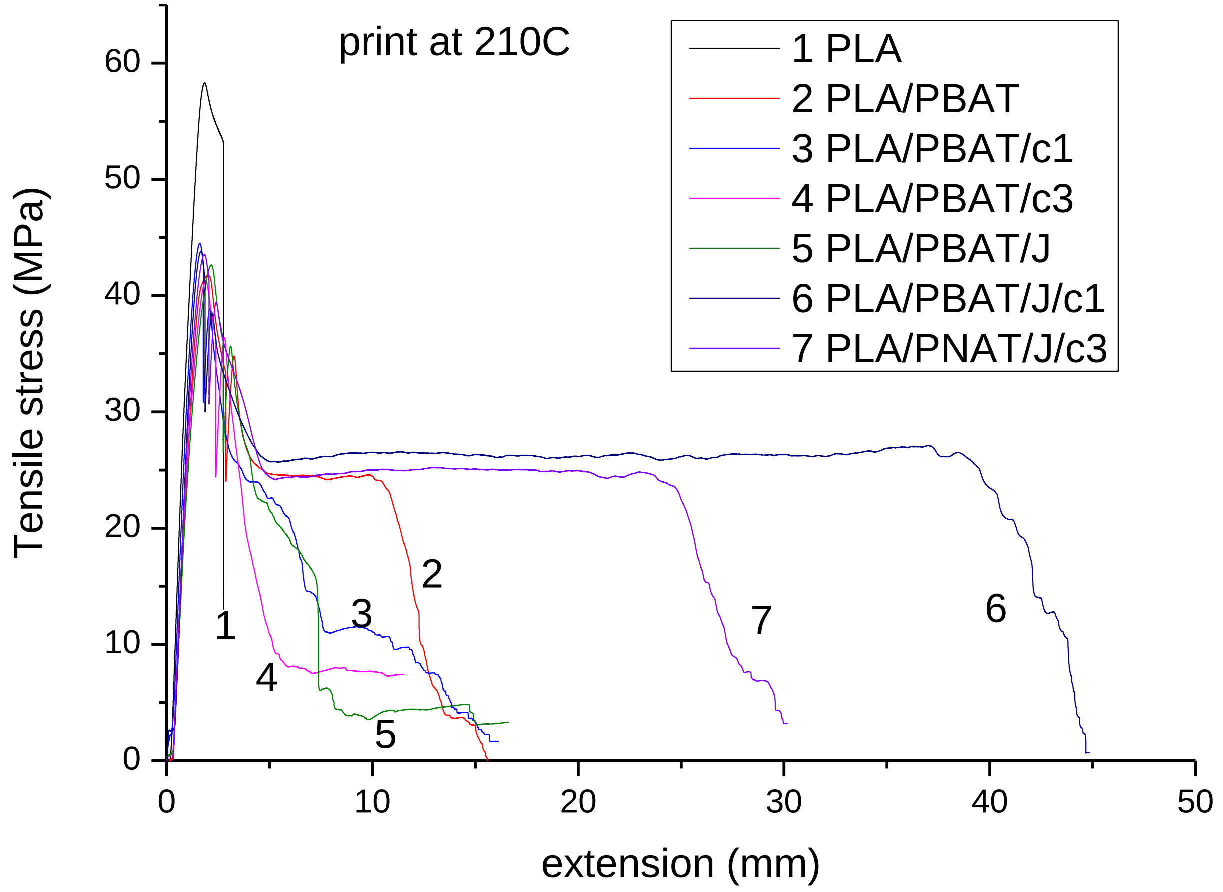
Najafi, N., et al. (2012). "Control of thermal degradation of polylactide (PLA)-clay nanocomposites using chain extenders." Polymer Degradation and Stability **97**(4): 554-565.
Meng, Q., et al. (2012). "Control of thermal degradation of polylactide/clay nanocomposites during melt processing by chain extension reaction." Polymer Degradation and Stability **97**(10): 2010-2020.
Kumar, M., et al. (2010). "Effect of glycidyl methacrylate (GMA) on the thermal, mechanical and morphological property of biodegradable PLA/PBAT blend and its nanocomposites." Bioresource Technology **101**(21): 8406-8415.

# PLA/PBAT/J/cloisite

| $T_{nozzle}$ | Sample | Modulus, MPa | Maximum stress, MPa | Strain at break, % |
|---|---|---|---|---|
| filament | PLA | 3461±345 | 55±3 | 17±4 |
| | PLA/PBAT | 2485±110 | 47±2 | 102±6 |
| | PLA/PBAT/J | 2458±91 | 47±1 | 134±35 |
| | PLA/PBAT/c1 | 2617±147 | 47±2 | 28±11 |
| | PLA/PBAT/c3 | 2758±203 | 44±1 | 26±13 |
| | PLA/PBAT/J/c1 | 2504±34 | 46±1 | 133±34 |
| | PLA/PBAT/J/c3 | 2804±155 | 48±1 | 126±21 |
| Printed bar at 210°C | PLA | 3282±118 | 55±1 | 4±1 |
| | PLA/PBAT | 2471±146 | 41±2 | 38±15 |
| | PLA/PBAT/J | 2429±90 | 43±1 | 25±13 |
| | PLA/PBAT/c1 | 2399±141 | 42±2 | 29±11 |
| | PLA/PBAT/c3 | 2540±107 | 41±1 | 15±4 |
| | PLA/PBAT/J/c1 | 2638±77 | 44±1 | 118±40 |
| | PLA/PBAT/J/c3 | 2811±53 | 44±2 | 70±21 |

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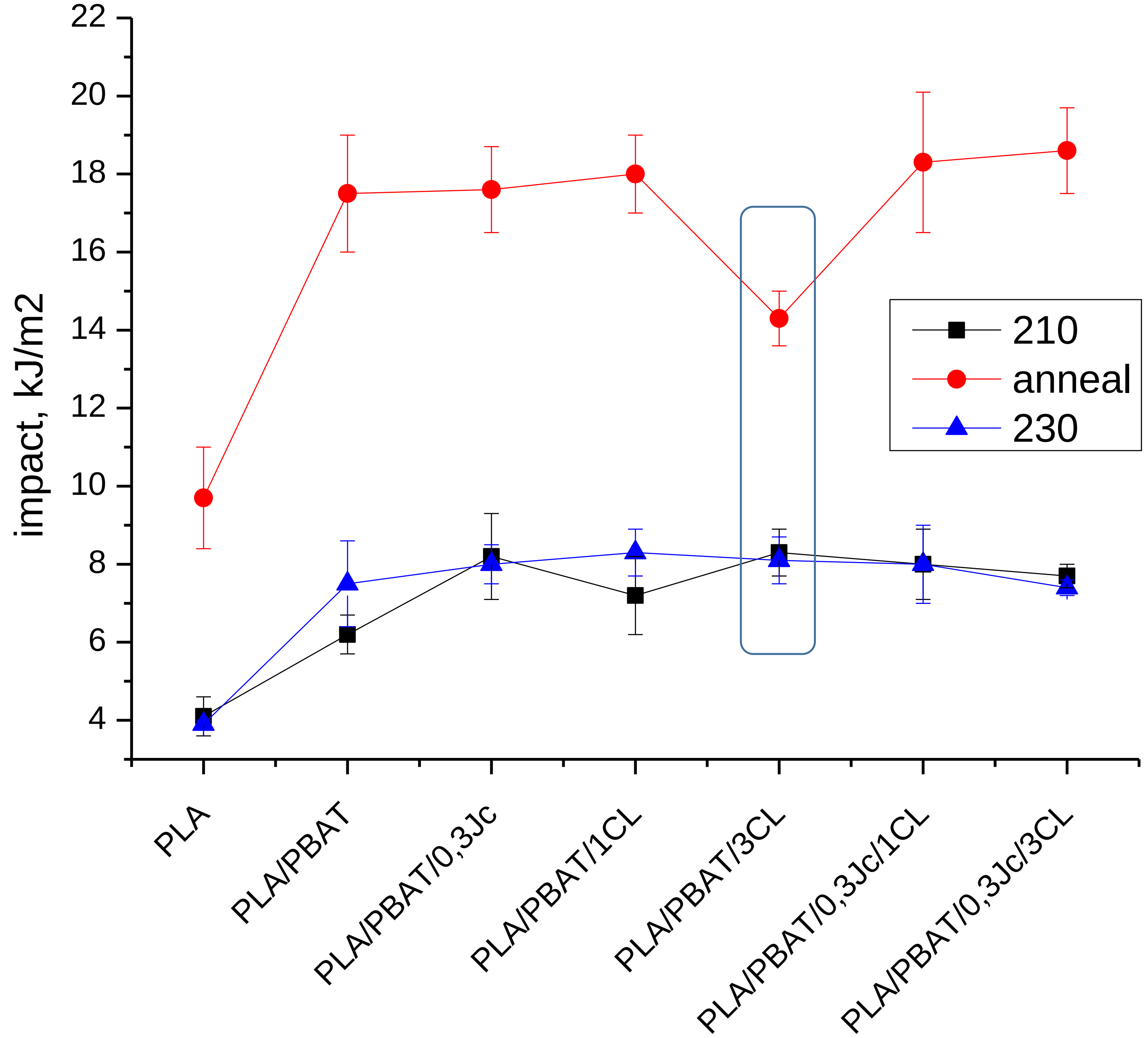
+cloisite&Joncryl
Increase strain a lot




# After annealing impact strength of samples increased

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