## STUDY OF THERMO-STABILIZATION OF BIODEGRADABLE POLYMERS DURING EXTRUSION PROCESS

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# Introduction

The increasing use of plastic front of the other materials have been causing an increase of this kind of residue in landfills, dumps and even in streets and rivers due to inappropriate disposal. As an alternative to solve the environmental problem, biodegradable plastics have achieved a prominent position in the academic community and industry<sup>1,2</sup>. However, the population has the stigma that biodegradable polymers must be used in products of short life cycles. This project aims to study the thermostabilization of poly(buthylene adipate-co-terephthlate) – PBAT and poly(lactide acid) – PLA. It is hoped that the results will lead to materials with high life cycles, stable during the processing, and recyclability while maintaining its characteristic of biodegradability.

## Experimental

The polymers used were poly(buthylene adipate-co-terephthlate) – PBAT and poly(lactide acid) – PLA. A processing stabilizer was used for both polymers: Tris(2,4-di-tert-butylphenyl) phosphite. To PBAT were used stabilizer concentrations of 0.1 and 0.5% (w/w) and to PLA were used 0.05 and 0.1% (w/w). The neat polymers and stabilized ones were submitted to five cycles of extrusion cycles in an extruder Haaker. Different temperatures profiles were used:

PBAT: 170 °C – 180 °C – 190 °C – 200 °C

PLA:  $190 \,^{\circ}\text{C} - 200 \,^{\circ}\text{C} - 210 \,^{\circ}\text{C} - 230 \,^{\circ}\text{C}$ 

After each cycle a quantity of the sample was collected to posterior analysis. Firstly, Melt Flow Index (MFI) analysis were done because the

short time to obtain the results. After MFI analysis, Size Exclusion Chromatography (SEC) and Infrared spectroscopy (FTIR) analysis were done.

## **Results and discussion**

The results from MFI analysis are showed on Table 1 and 2, for PBAT and PLA, respectively. The data from polymers without stabilizer show that scission reactions are the main phenomena on the degradative process. The presence of processing stabilizer was effective. Similar results were seen on SEC analysis for both polymers (see Table 3 and 4).

| Extrusion<br>cycles | Samples             |                    |                     |
|---------------------|---------------------|--------------------|---------------------|
|                     | neat PBAT           | <i>PBAT</i> + 0,1% | <i>PBAT</i> + 0,5%  |
| 0                   | $7,00 \pm 0,13$     | $7,\!30\pm0,\!17$  | $7,\!10 \pm 0,\!03$ |
| 1                   | $6{,}98 \pm 0{,}48$ | $7,\!13\pm0,\!56$  | $6{,}98 \pm 0{,}38$ |
| 2                   | $7{,}96 \pm 0{,}51$ | $7,\!19\pm0,\!29$  | $7{,}56\pm0{,}39$   |
| 3                   | $8,\!44 \pm 0,\!21$ | $7,\!26\pm0,\!47$  | $7,73\pm0,57$       |
| 4                   | $8,73\pm0,29$       | $7,74\pm0,52$      | $8,01 \pm 0,39$     |
| 5                   | $9{,}29\pm0{,}48$   | $8,67 \pm 0,29$    | $8,\!45\pm0,\!45$   |

Table 1: MFI results (g/10min) of PBAT with and without processing stabilizer.

Table 2: MFI results (g/10min) of PLA with and without processing stabilizer.

| Extrusion<br>cycles | Samples          |                  |                   |
|---------------------|------------------|------------------|-------------------|
|                     | neat PLA         | PLA + 0,05%      | <i>PLA</i> + 0,1% |
| 0                   | $14.57\pm0.76$   | $18.71 \pm 0.52$ | $15.07\pm0.25$    |
| 1                   | $13.57\pm0.88$   | $20.28\pm0.66$   | $16.19\pm0.52$    |
| 2                   | $17.49\pm0.36$   | $25.09\pm0.54$   | $22.83\pm0.29$    |
| 3                   | $20.59\pm0.87$   | $25.65\pm0.48$   | $22.89\pm0.45$    |
| 4                   | $27.11 \pm 1.00$ | $26.05 \pm 1.20$ | $26.69\pm0.75$    |
| 5                   | $36.76\pm0.74$   | $28.33 \pm 2.83$ | $29.96\pm0.60$    |

| Extrusion cycles | Samples   |                    |             |
|------------------|-----------|--------------------|-------------|
|                  | neat PBAT | <i>PBAT</i> + 0,1% | PBAT + 0.5% |
| 0                | 41350     | 41350              | 41350       |
| 1                | 35100     | 41400              | 42000       |
| 3                | 31300     | 42200              | 39350       |
| 5                | 37600     | 41400              | 41600       |

Table 3: Molecular weight ( $\overline{M}_n$ ) of PBAT with and without processing stabilizer.

Table 2: Molecular weight ( $\overline{M}_n$ ) of PLA with and without processing stabilizer.

| Extrusion<br>cycles | Samples  |             |            |
|---------------------|----------|-------------|------------|
|                     | neat PLA | PLA + 0,05% | PLA + 0,1% |
| 0                   | 65000    | 65000       | 65000      |
| 1                   | 66350    | 61300       | 61600      |
| 3                   | 61400    | 58900       | 62200      |
| 5                   | 49000    | 58650       | 56200      |

PBAT and PLA have carbonyl groups in its backbone. This carbonyl group is responsible to became them susceptible to microorganism attack; however, the same group became this polymer thermo-sensible. The Figure 1 and 2 show spectrum of PBAT and PLA, respectively.



Figure 1 – Spectrum of neat PBAT (read), neat PBAT after 5 cycles (green), PBAT + 0.1% after 5 cycles (blue) and PBAT + 0.5% after 5 cycles (black).



Figure 2 – Spectrum of neat PLA (read), neat PLA after 5 cycles (green), PLA + 0.05% after 5 cycles (blue) and PLA + 0.1% after 5 cycles (black).

In Figure 1 a broadening of carbonyl (C=O) peak were observed after 5 cycles for neat PBAT. The left shoulder (1790 and 1750 cm<sup>-1</sup>) indicates the formation of free C=O, and the right shoulder represents the formation of a lower molecular weight ester<sup>3</sup>. A minor effect was observed for PBAT samples containing stabilizer. In Figure 2 a narrowing of carbonyl peak were observed for neat PLA after 5 cycles. It is confirmed that the degradation mechanism was predominantly by scission of ester linkage<sup>4</sup>. These scissions were suppressed by presence of processing stabilizer.

### Conclusions

Similar to commodities polymers, the results show the importance of the previous study about thermo-stabilization and the correct choice of additive for a particular polymer.

#### References

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