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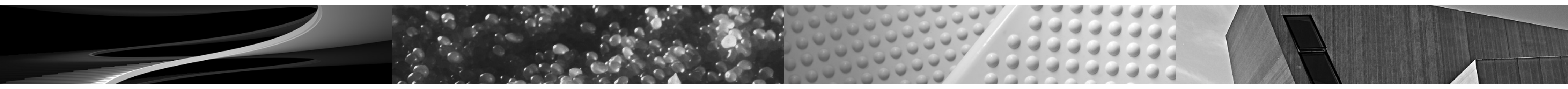

Effects of Reprocessing on Thermal and Mechanical Properties of Biodegradable PLA and Biobased PA 410

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1 Introduction

Over more than the last three decades the practice of recycling, especially in-house recycling, reprocessing, has been encouraged and promoted by increasing focus on environmental issues and the subsequent desire to save resources. Together with the relative high cost of polymers and sometimes high levels of scrap material generated during manufacture, recycling becomes a viable and attractive option. The recycling with scrap material, and mixing with virgin material, is the most common solution. For conventional petrobased polymers and polymer blends long term extensive research in this field reflects the rule rather than the exception of this practice [1-3].

Furthermore, concern for the environment and the limited resource of petroleum and natural gas has driven recent research and development regarding polymerisation of biopolymers, and now several biopolymers are commercially available. However, for biobased and biodegradable polymers to substitute petrobased polymers they should be able to be reprocessed, to save resources and costs, as well as fulfil all other requirements regarding physical, chemical and mechanical properties.

Therefore the feasibility of reprocessing has been investigated for a biodegradable as well as a biobased polymer, more specifically a biodegradable poly lactic acid (PLA) and a biobased poly amide (PA 410). The effect on thermal and mechanical properties of these two polymers undergoing 7 respectively 10 reprocessing cycles, were analysed. Furthermore, the aim of this study is benchmarking of the selected biodegradable and biobased polymers against conventional petrobased polymers, which they are intended to substitute. It is primarily polyethylene therephthalate (PET), polystyrene (PS) [4] and acrylonitrile-butadiene styrene (ABS) [5], which is substituted with PLA, therefore in this study PLA is benchmarked against ABS. Likewise, PA 410, which is intended to substitute PA 66 [6], is benchmarked. However, no studies concerning reprocessing of PA66 was available. PA 66 and PA6 are very similar, thus, it is benchmarked against PA6.

2 Experimental

2.1 Materials

EcoVIO C1335, a biodegradable PLA from BASF and EcoPaXX Q-FP4, a biobased PA 410 from DSM engineering is selected for this study.

2.2 Material reprocessing and sample preparation

The injection moulding cycles were carried out in a Sumito DEMAG injection moulding machine model Systec 25-80. The operating gradient temperature of injection moulding was 180 – 195°C for PLA and 275-285°C for PA.

For PLA this process was repeated 7 times under the same operating conditions. For PA 410 the process was repeated 5 times, after which the gradient temperature were decreased 5 °C. Five more reprocessing cycles were carried out. The test plan is shown in Fig 1a. In every injection cycle app. 50 specimens for tensile- and impact testing were sampled. The rest of the material was grinded in an AB RAPID granulator type 1521. A sample of app. 500g regrinded material was taken for subsequent evaluation as well as for the steady state blend. The steady state blend represents in-house reprocessing with 30% regrind and 70% virgin material is shown in Fig. 1b. The rest of the grinded material was the starting material for the following reprocessing cycles.

2.3 Analysis techniques

Alterations in chemical structure were evaluated by FTIR analysis carried out on a ThermoScientific Nicolet™ iS5 instrument. The measurement is carried out in the 650-4000 cm^{-1} range.

The thermal properties were determined using a Mettler Toledo 822^e differential scanning calorimeter (DSC) at a heating, cooling, heating temperature scan from 30 to 450°C at a scan rate of 20°C /min and a Mettler Toledo TGA/ADTA 851^e thermobalance (TGA) heating from 25 C to 700°C with a scan rate of 20°C /min. Samples of about 4 and 10 mg respectively were used.

Mechanical tests were, in so far, carried out on PLA. Tensile testing were conducted using a Lloyd LR50K plus apparatus according to ISO 527, and charpy notched impact strength were carried out using a CEAST Torino impact tester according to ISO 179-1/1eA.

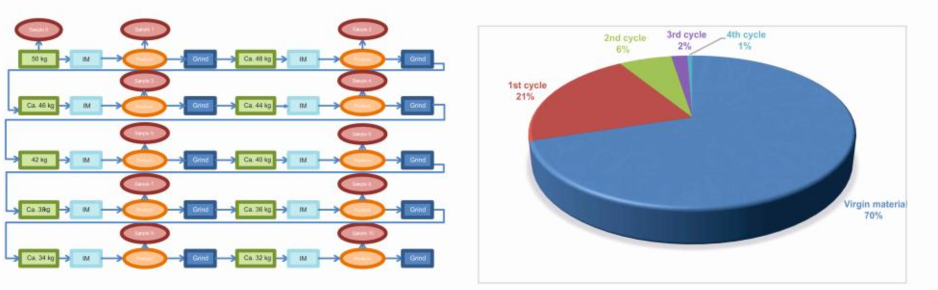

Figure 1: Test plan and steady state blend.

3 Results

Chemical structure: In FTIR observation of new absorption bands at wave numbers app. 3400 and 1735 cm^{-1} indicates a thermo oxidative degradation has occurred, resulting in the formation of –OH and –CO containing groups. The results concerning reprocessing of PLA shows a larger peak at around 1750 cm^{-1}, arising from oxidation products, for sample 7, reprocessed 6 times, compared to sample 1, injection moulded from virgin material. However, the difference although significant is only 6 % transmittance (T), slightly above the threshold of the noise level of 2-3% T. See Fig 2.

For PA 410 the FTIR analysis of virgin material, samples 1 -10 and the steady state blend, showed no significant alteration of the chemical structure.

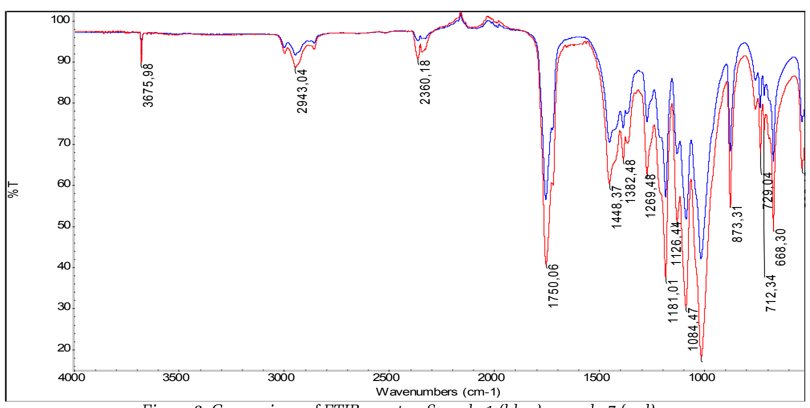

Figure 2: Comparison of FTIR spectra: Sample 1 (blue), sample 7 (red).

Thermal properties: As expected the DSC results for PLA exhibits a reduction in T_g and T_m and an increase in T_c as a result of the repeating recycling. Even though, the difference is not great, a clear tendency is shown. Furthermore, the double peak arising from melting of the two different PLA crystals (α and α') [7], becomes less and less prominent, indicating that the difference in the crystalline structure becomes more and more homogeneous. *Cf.* with the DSC thermogram found in Fig 3 and Table 1.

Table 1: Overview of DSC results for samples 1-7

DSC	T_g [°C]	T_m [°C]	X_c [%]	T_c [°C]
Sample 1	60,65	160,57 167,30	23,90	110,15
Sample 2	60,36	160,75 167,41	24,06	110,31
Sample 3	59,38	159,74 166,07	24,77	111,64
Sample 4	56,72	160,02 165,93	24,64	111,97
Sample 5	56,9	158,77 164,94	24,70	112,64
Sample 6	56,46	156,35 162,52	23,27	112,63
Sample 7	53,16	153,33 159,98	24,48	112,34

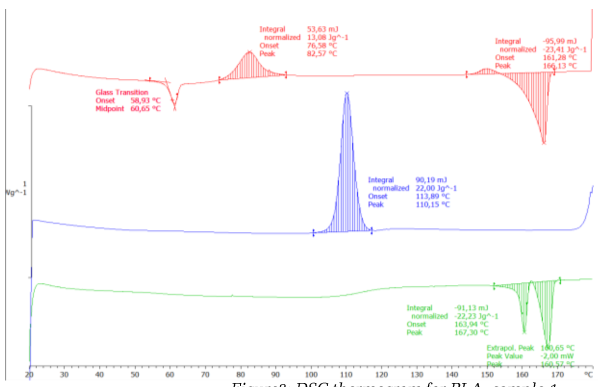

Figure3: DSC thermogram for PLA, sample 1.

For PA 410 no significant change is determined in T_g, T_m, X_c and T_c as the results obtained are nearly constant. TGA is applied to obtain information regarding thermal stability of the material. T_{10}, the temperature where 10% of the material is decomposed, is compared for PLA samples 1 to 7. The results shows that the thermal stability of the material is reduced with 8°C already after the first reprocessing cycle and that T_{10} is reduced at least 4°C further with each following cycle. T_{10} for PA 410 samples 1 – 10 and steady state shows no significant change when compared to virgin material.

Mechanical properties: Results of the tensile tests concerning PLA showed a significant reduction of yield strength, strength at break, and strain at break when comparing samples 1 – 7, *cf.* Fig 3. However, for strength at break a significant increase were observed for the first couple of reprocessing cycles; i.e. sample 2 and 3, which was accompanied with a decrease in strain of brake for these samples.

For PLA an initial notched impact strength of 6 kJ/m^2 is determined, and a significant decrease is found. In fact, for sample 5, i.e. the 4th cycle and further, notched impact strength is below the detection limit of the instrument.

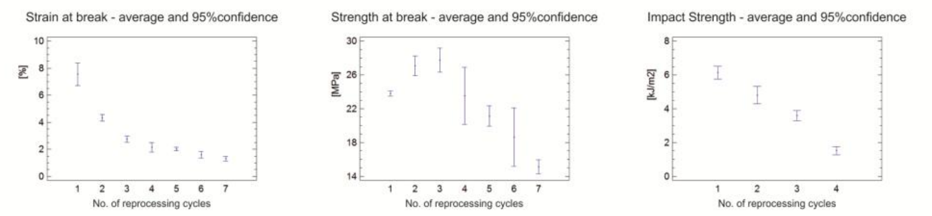

Figure 4: Mechanical properties as a function of cycle, PLA. Left: Strain at break, center: Strength at break, right: Impact strength.

4 Discussion

Sourodi et al [8] presents an overview of recyclability of bioplastics, where reprocessing is included. In this study various types of PLA were injection moulded and reprocessed 7 and 5 times. Pilin et al [9] reports on the effect of thermo-mechanical cycles, reprocessing, on the physio-chemical properties of poly lactic acid of the PLLA type. The material was reprocessed 7 times and rheological, mechanical and thermal properties were evaluated. In this case the thermal properties, T_g and T_m were reduced, M_w were reduced as well as the mechanical properties strength and strain, as a consequence of chain scission caused by the thermooxidative degradation process associated with reprocessing. E-modulus and hardness did not alter significantly. Furthermore, Badia et al [10] investigated an amorphous PLA from NatureWorks, where the material were reprocessed 5 times and mechanical tests as well DSC, FTIR, capillary viscosity and DTMA analysis were carried out. Amongst other findings the study showed a reduction of all properties subsequent to the second reprocessing cycle. These results are all in good agreement with the presented results, where T_g, and T_m are reduced as well as the mechanical properties; yield strength, strength at break, strain at brake and impact strength. No studies concerning thermo mechanical reprocessing of PA 410 or other biobased polyamides were available.

5 Benchmarking

Several articles are concerned with the reprocessing of ABS of various types [11-13]. Thermal and mechanical properties were investigated. It is concluded that a reprocessing of up to 10 times did not have a significant effect on tensile properties, whereas impact strength were reduced due to alterations in the poly butadiene phase. Thus, when comparing the reprocessing of PLA with that of ABS, PLA is inferior in respect to mechanical properties, specifically tensile properties.

As mentioned, PA 410 is benchmarked against PA 6 instead of PA66. Reprocessing of PA 6 were studied by Lozano-Gonzalez et al [14] and Su et al [15] who investigated PA 6 from Celanese and Sunlyon 6N, respectively. In [14] the material was reprocessed 10 times followed by mechanical tests, GPC and MFI analysis. In this study it was shown that the material could be reprocessed 7 times without significant degradation, for subsequent reprocessing cycles especially the mechanical properties were significantly altered. In [15] the material was reprocessed 16 times and changes were studied via FTIR, GPC, MFI and DSC. Mechanical properties were determined as well. Mw was reduced, a broader MWD were found, but alteration in the chemical structure could be determined. When comparing these studies with the presented results for PA 410 showing no alterations of T_g, T_m, X_c and T_{10} as well as no change in chemical structure, it seems very likely to substitute PA 6 with PA 410.

6 Conclusions

The effect of reprocessing on PLA and PA 410's thermal and mechanical properties has been studied. It showed that for PLA T_g and T_m are reduced and yield strength, strength at break, strain at brake and impact strength are reduced as well. For PA 410 no change in T_g, T_m, X_c and T_{10} as well as in chemical structure were found.

Furthermore PLA and PA 410 were benchmarked against ABS and PA 6, respectively.

It is concluded that when comparing the reprocessing of PLA with that of ABS, PLA is inferior in respect to mechanical properties, specifically tensile properties.

In addition, it is concluded that it seems possible to substitute PA 6 with PA 410.

However, it is necessary to confirm this by conducting further tests, *eg.* melt flow index and size exclusion chromatography in addition to mechanical tests like tensile tests and impact strength before reaching a conclusion. These tests are planned within the current project.

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