INFLUENCE OF MECHANICAL RECYCLING ON PLA/MMT POLYMER NANOCOMPOSITES

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Abstract

Iimpact of reprocessing on polylactide (PLA) and PLA nanocomposites with montmorillonite (MMT) has been presented. The materials were extruded and properties of samples collected after 1, 5 and 10 cycle of processing were investigated. Mechanical properties of the materials were characterised by means of tensile testing, barrier properties were evaluated by the oxygen permeability, crystallinity and melting phenomena were estimated with DSC measurements. The changes occurring at the material surface were described by means of gloss, colour and surface free energy results.

The differences in the material properties have been discussed in terms of a filler nature in the polymer composites and compared to that of the polymer matrix. The changes have been related to the polymer degradation and the filler distribution within a matrix.

1 Introduction

Bio-based polymeric materials focus an interest of industry and research groups in respect of the oil shortages which frequently make a market instable not only for the economical but for political reasons as well. Therefore one should be aware of the properties of the bioplastics not only as the virgin materials, but also as recyclates is concerned. Most biobased polymers are derived of starch, either in a native, or post-fermented form. The most widely used bio-based polymer is polylactide (PLA), with mail application fields in the packaging and textile sectors. In this paper the impact of reprocessing on polylactide and PLA nanocomposites with montmorillonite (MMT) has been presented. The aim of the study was to compare the bulk and surface properties of the nanocomposite and polymer matrix. The differences in the material properties have been discussed in terms of a filler nature in the polymer composite and compared to properties of the polymer matrix.

2 Materials

Polylactic acid (PLA) 3051D (NatureWorks®, USA) has been used as the matrix polymer which was filled with 5 wt.% of montmorillonite (MMT) Nanomer I.30E (Nanocor, USA), which is an organically modified clay. The composites were prepared by melt mixing from a masterbatch prepared at our laboratory. PLA and PLA/MMT were extruded at 170ºC using a single screw extruder with mixing elements. Polymer samples were collected after 1, 5 and 10 cycle of processing, then their selected properties were tested. The samples for tensile testing were prepared by injection molding, whereas for the gloss and surface free energy (SFE) measurements thin plates (150 μm) were press molded.

3 Results

Mechanical properties of the materials were characterised by means of tensile testing. Young modulus and tensile strength for PLA has slightly decreased (Figs. 1 and 2). The filler influenced a stiffness of the material, but the tensile strength of PLA/MMT composite decreased in comparison to that of PLA. After reprocessing the tensile strength became higher which suggested a difference in the filler distribution. Most possibly the initial aggregates after reprocessing have been better distributed (exfoliated), thus enhancing the tensile strength of the composite.

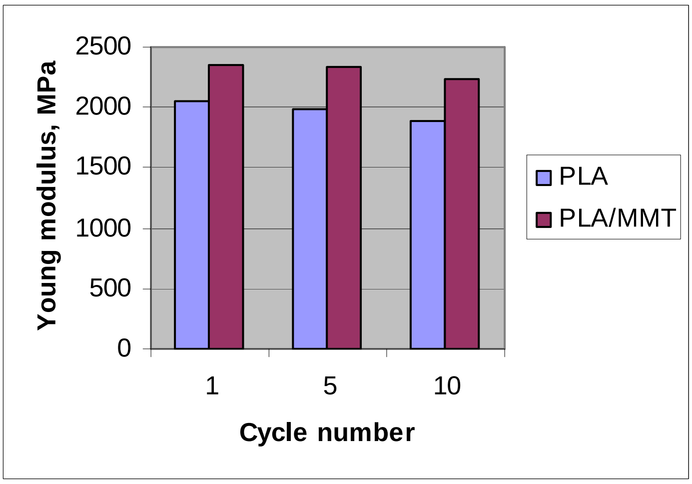

Figure 1. Tensile Young modulus for recycled PLA and PLA/MMT composite

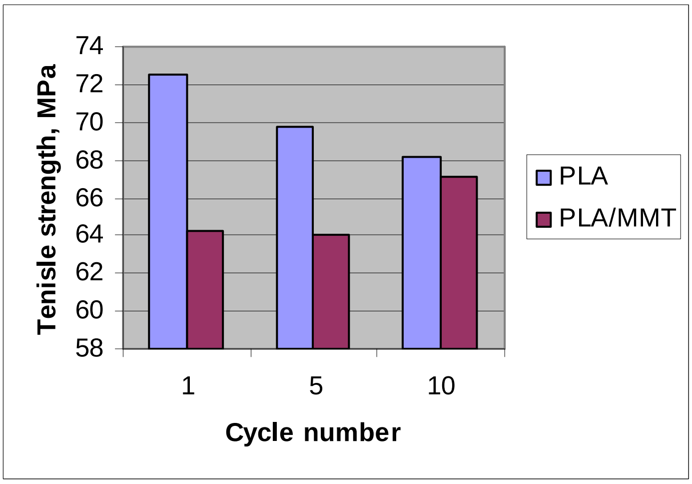

Figure 2. Tensile strength for recycled PLA and PLA/MMT composite

The crystallinity and melting phenomena of PLA and PLA/MMT composite were estimated by means of DSC measurements (Figs. 3 and 4). The materials were first heated above the melting temperature, then cooled and scanned again by a second heating. The first heating scan provides basic characteristics of PLA and PLA/MMT composite. From a dependency of the heat flow on temperature the second order transition (glass temperature) and the first order transition (cold crystallization temperature) were estimated. The crystallinity was evaluated by means of the enthalpy of melting, since the crystalline polymers exhibit a lower specific heat capacity due to their limited molecular mobility.

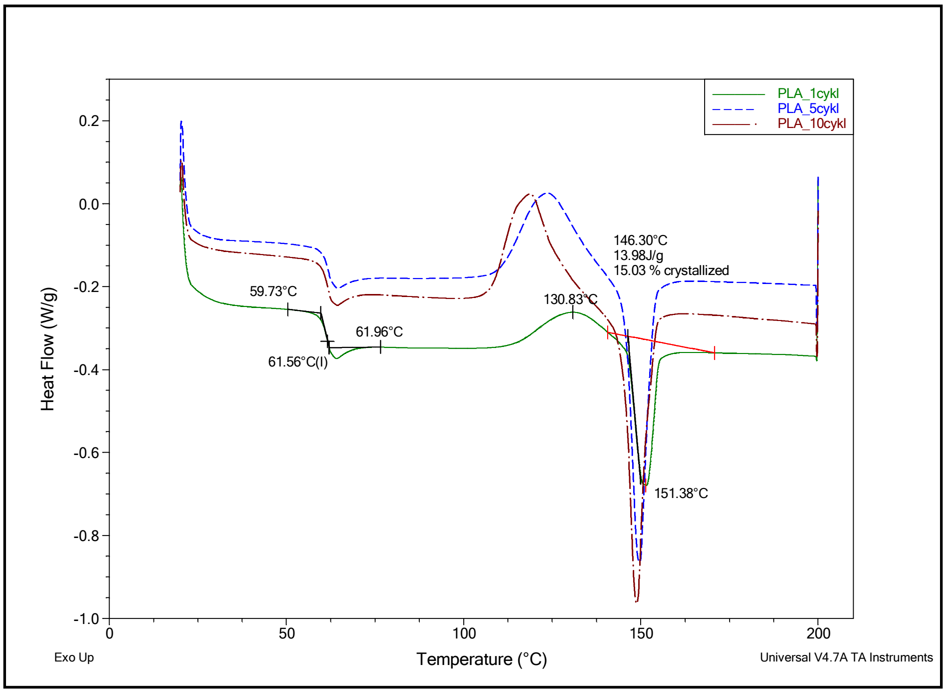

Figure 3. DSC results for recycled PLA

The change in the crystallinity and cold crystallization temperature has been observed in both materials as a function of reprocessing. The initial crystallinity of PLA and PLA/MMT composite accounted for 15%, whereas in PLA it increased to 28% and 29% after 5 and 10 cycles, respectively (Fig. 3). That has been explained by a progress in the polymer degradation, which facilitated arrangement of polylactide macromolecules.

The crystallinity of PLA/MMT composite increased after recycling up to 19% and 31%, respectively. After the oxygen permeability measurements one may suggest that the results should be related not only to PLA degradation, but also with the filler distribution in the polymer matrix.

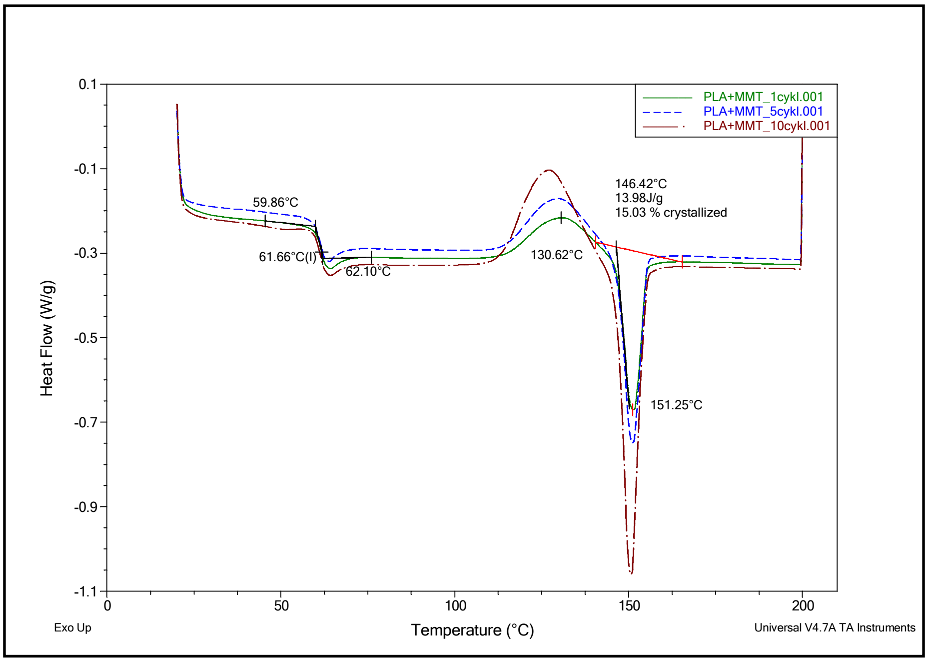

Figure 4. DSC results for recycled PLA/MMT composite

Possible degradation of polymeric materials after consecutive processing has been tested by means of melt flow rate (Fig. 5). It has been observed that in parallel with the extrusion cycles the viscosity was decreasing, thus suggesting a thermo-mechanical degradation. The influence of filler was the most distinct after 10th cycle, which suggests that not only the polymer matrix degradation occurred, but also the distribution mode of a filler within the polymer matrix may influence the processability.

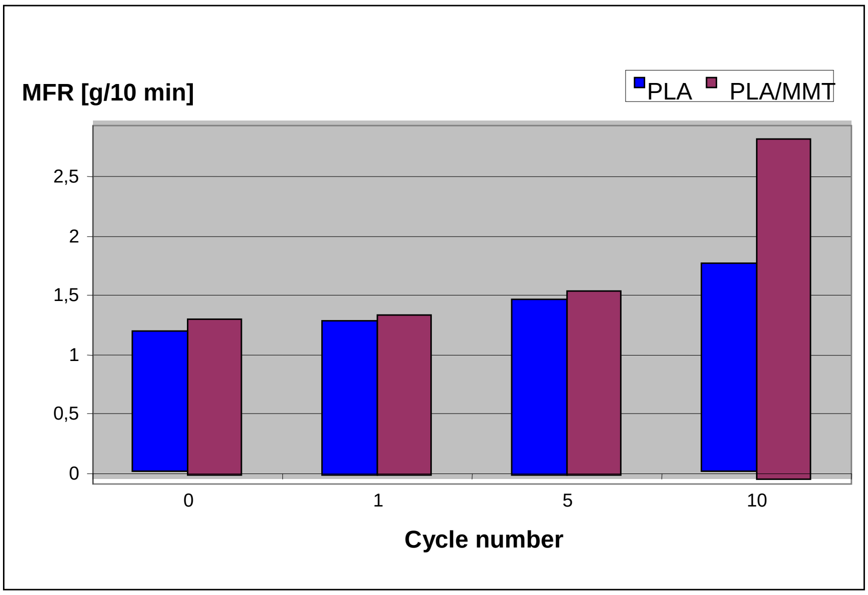

Figure 5. Melt flow rate for recycled PLA and PLA/MMT composite

The changes occurring at the material surface were described by means of the gloss and surface free energy results (Figs. 6 and 7).. The gloss measurements were performed at three angles of coincidence (20º, 60º and 85º) but only those obtained for 60º are presented. The results was given in Gloss Units (GU),

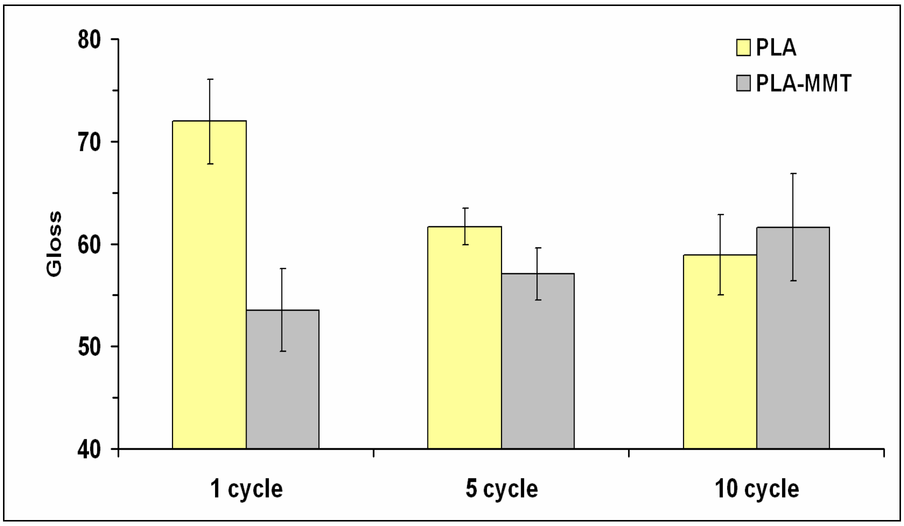

Figure 6. Surface gloss for recycled PLA and PLA/MMT composite

The surface free energy measurements were performed with a drop geometry evaluation method. Three liquids were used for these experiments: water, formamide and diiodomethane. Surface free energy was calculated with van Oss-Chaudhurry-Good model.

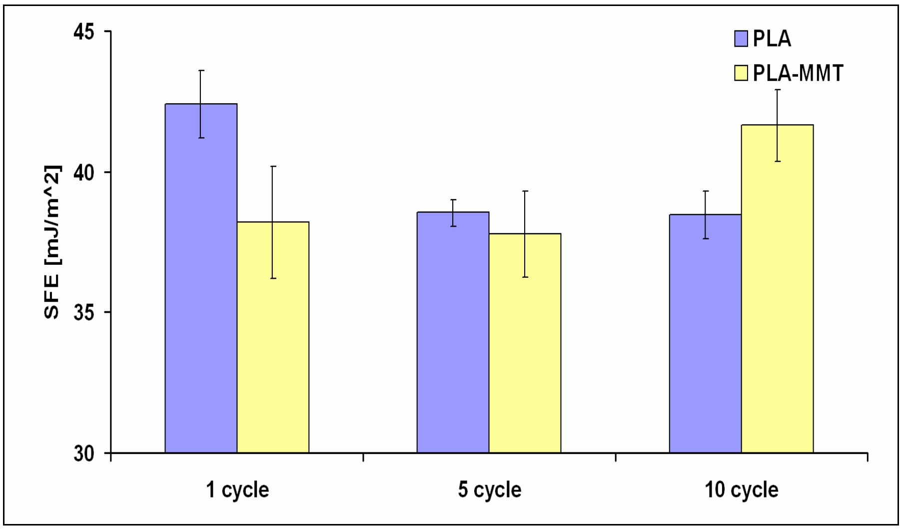

Figure 7. Total surface free energy for recycled PLA and PLA/MMT composite

For polylactide both the gloss and surface free energy decreased with reprocessing, which may reflect a stepwise degradation of the polymer.

The gloss and SFE increased with the recycling number for PLA/MMT composite. The total surface free energy changed from 38 mJ/m^2 after the first extrusion up to 42 mJ/m^2 after ten extrusion cycles. Simultaneously, the gloss increased frim 53 up to 62 gloss units. It has been supposed that higher gloss in PLA/MMT nanocomposite after several reprocessing cycles resulted from the exfoliated platelets distribution mode within the polymer matrix. Such arrangement of the two-dimensional nanosheets forms a surface that reflects light better than the aggregated/intercalated MMT plates in the undermixed nanocomposite.

4 Conclusions

1. The changes in PLA characteristics were related to the polymer degradation.
2. Properties of PLA/MMT nanocomposite resulted of a combined polymer degradation and the filler distribution within a matrix.
3. The difference in a gloss of PLA and PLA/MMT composite can be explained by a platelet nature of the filler and its mode of location in the matrix.

Acknowledgement

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