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SURFACE CHARACTERIZATION OF RECYCLED PLA AND ITS NANOCOMPOSITE

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The impact of recycling on selected properties of polylactic acid (PLA) neat polymer and its composite with montmorillonite was investigated. The changes occurring at the material's surface were discussed in terms of gloss, colour and surface free energy. The materials were recycled and samples after the 1st, 5th and 10th cycle of processing were investigated. The unprocessed material was treated as a reference one (0 cycle). The results have been related to the physicochemical changes occurring in the materials during recycling.

Keywords: polylactic acid, organoclay, surface free energy, gloss, colour

INTRODUCTION

A product's quality is not the only factor that determines its popularity on the market – for most people, product appearance plays a decisive role in the process of product selection. Thus, it needs a catchy design to attract consumer's attention. This is the reason why producers, advertisers and sellers invest much effort and money into product appearance. Therefore, the selection of colour and the quality of the dyes are of a major importance for every commercial article.

Gloss factor is the second most important surface feature that has to be taken into consideration.[1] The other two, translucency and surface texture, complement the set of four determinants in the process of product recognition in terms of the sight sense.[2]

Gloss is a feature of a particular surface, which can be influenced by several factors starting from the production line (processing conditions), storage conditions (thermal insulation, humidity) to further usage.[3] According to the work of Leloup *et al.*,[3] gloss is generally associated with specular reflection giving the mirror-like appearance of the observed surface. Since gloss is a very important factor in surface appearance, the way it can be measured was standardized by both American Society for Testing Materials (ASTM D 532)[4] and International Organization for Standards.[5] The quality of the coating layer depends on the interaction forces between the covering layer and the substrate. The forces at the interface may be described by means of the surface free energy parameter, commonly used in the surface science. The surface free energy measurements have been particularly well developed in the composite science, because adhesion in the polymer matrix–filler interface plays a crucial role. Surface free energy measured as wettability,[6] is influenced by numerous factors, starting from the material chemical composition (chemical nature) and ending with the surface treatment during processing or product storage (the physical aspect).[7-10] During processing, temperature and shear stress markedly influence the material properties, causing polymer degradation.[11,12] The process runs according to the radical or hydrolytic mechanisms, supported by the presence of a catalyst promoting the intermolecular transesterification.[13] A reduction of the polymer chain length results in the deterioration of the material's mechanical properties.

Although the mechanical and thermal behaviour of polylactide has been well described in several papers,[14-19] the authors have focused mainly on the influence of mechanical recycling on the surface properties. In this paper, material properties have been reported in terms of surface

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morphology and appearance.

EXPERIMENTAL

Materials

The tested materials were polylactic acid 3051 D (Nature Works) (PLA) and its composite containing 5 wt% montmorillonite (PLA-MMT). The nano-filler was supplied by Nanocor and is available under the commercial name Nanomer® I.44P. This preintercalated montmorillonite contains 35-45% dimethyl octadecyl tetradecylamine.

Sample preparation

The neat polymer and its nanocomposite were extruded once and press moulded to provide the reference samples (PLA-0 cycle and PLA-MMT-0 cycle). Additional processing was performed to simulate the recycling process – PLA and PLA-MMT composite were recycled for 1, 5 and 10 times by means of extrusion (the number of cycles was noted in the sample code). For the gloss, colour and surface free energy measurements, thin plates (0.15 mm) of each material were produced by press moulding.

Gloss measurements

Gloss measurements were performed using a Konica Minolta Multigloss meter (GM-268) at three geometry regimes: 20º, 60º and 85º. The results were expressed in Gloss Units (GU), simplified to "gloss" further in the paper. According to ISO measuring standards,[5] only the results obtained for 60º have been presented.

Colorimetry

The colorimetric study was performed with an HP-200 apparatus (Nanjing T-Bota Scietech Instruments & Equipment Co., Ltd.). The measurements deal with Hunter *L*, *a*, *b* colour scale,[20] which was formally normalized in 1976 by an International Commision of Illumination (Comission Internationale de l'Eclairage) under the abbreviation: CIELAB or CIE 1976.[21] The a, b and L components reflect the saturation of opposing colours: yellow – blue, red – green and white – black, respectively.

Surface free energy measurements

The surface free energy (SFE) measurements have been performed by means of the drop geometry method with a Surface Energy Evaluation apparatus (Czech Republic). For wetting characterization purposes, three liquids were used: water, formamide and diiodomethane (all at least of analytical grade). SFE was calculated using the van Oss-Chaudhurry-Good model.[6,22,23]

Infrared spectroscopy

The FT-IR analysis was performed using a Bruker Tensor™ series infrared apparatus. The measuring range was set to 4000-600 cm^{-1} with a 2 cm^{-1} step.

RESULTS AND DISCUSSION

PLA and PLA-MMT composite were recycled up to 10 times in the extruder (HAAKE RHEOMEX CTW 100). The samples were withdrawn after the 1st, 5th and 10th cycle, and then characterized and compared to the reference (0 cycle). Error values calculated for the SFE experiment are listed in Table 1.

Starting with the PLA sample (Fig. 1), one can observe that the total SFE value decreased simultaneously with the cycle number. The total difference between the null and last cycle is of about 10%. The acid-base (γ^{AB}) contribution was reduced for 2.5 times simultaneously with the dispersion part of total SFE (from 41 mJ/m^2 for 0 cycle to 37 mJ/m^2 for the last two samples).

Table 1
Calculated experimental errors - SFE measurement

	PLA		PLA-MMT	
	gamma LW	gamma AB	gamma LW	gamma AB
0 cycle	41.1	3.2	36	1.8
STD	0.7	0.8	0.7	0.8
1st cycle	40.1	2.4	36.7	1.5
STD	0.6	0.9	1.2	1.5
5th cycle	37.6	1.0	35.6	2.2
STD	0.9	1.0	1.1	0.8
10th cycle	37.4	1.1	39.8	1.8
STD	1.0	0.4	0.6	0.9

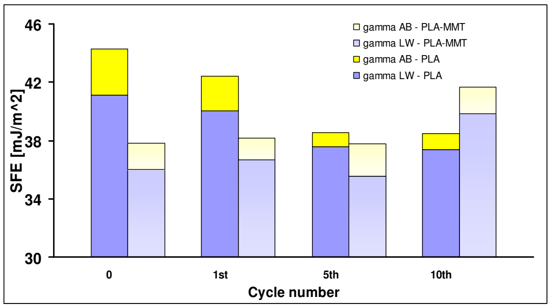

Figure 1: Recycling impact on surface free energy in recycled PLA and PLA-MMT samples

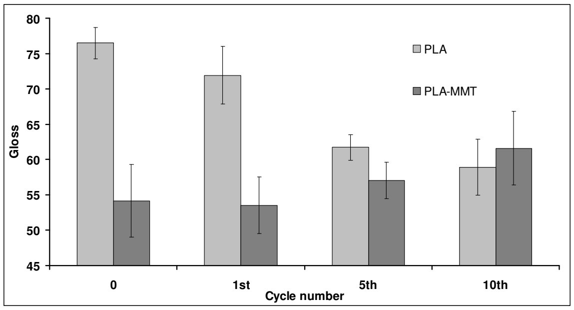

Figure 2: Recycling impact on gloss in recycled PLA and PLA-MMT samples

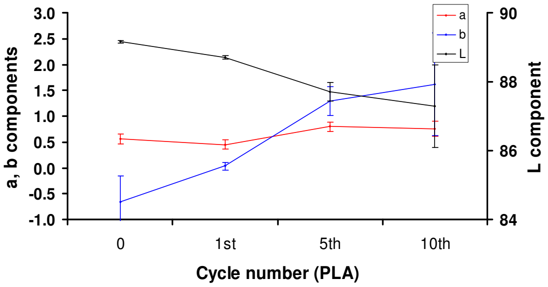

Figure 3: Recycling impact on colour in PLA samples

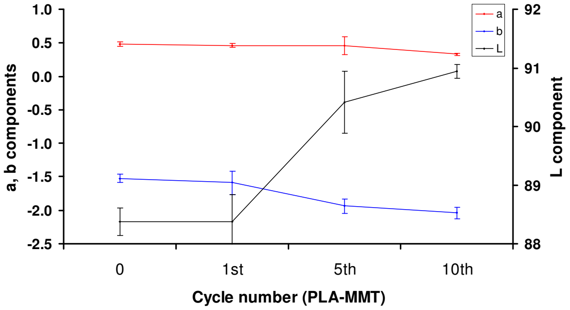

Figure 4: Recycling impact on colour in PLA-MMT samples

That is consistent with a reduction of material's gloss (Fig. 2), which decreased progressively from 76 units (72 for the 1st cycle) to 62 and finally 58 units (the 5th and 10th cycles, respectively). Simultaneously, a change in the colour (Fig. 3) was observed, e.g. a remarkable increase of "b" contribution (the balance shifted to a red shade) and decrease of the "L" parameter (darker colour). The "a" factor, reflecting the changes in the yellow–blue colour balance, remained almost unchanged.

In the PLA-MMT composite, a consistency in the evolution trends of gloss, colour and SFE is also visible (compare Figs. 1, 2, 4). An increase in gloss and SFE with an increasing number of recycling cycles has been noted (Fig. 1).

The total surface free energy increased from 38 mJ/m^2 for PLA-MMT (unprocessed and after the 1st cycle) to 42 mJ/m^2 after 10 cycles, mostly due to differences in the Lifshitz-van der Waals (γ^{LW}) contribution. This value increased from 36.5 mJ/m^2 to almost 40 mJ/m^2 over the whole course of recycling. Simultaneously, the gloss increased by 15%, which is opposite to the tendency observed for PLA without filler. Similarly, the "L" and "b" colour contributions have opposite trends compared to those of recycled neat PLA.

Recycling caused the most significant changes in polylactide after the 1st and 5th cycles, whereas for PLA–MMT composite after the 5th and 10th cycles. Additionally, some differences for the PLA samples between 0 and 1st cycle are also visible, contrary to the PLA-MMT composite, where the values are comparable for the respective cycles (Figs. 1-4).

As a rule, processing causes the degradation of polymers,[14,24,25] its extent depending on the thermomechanical history: the temperature and stress applied, as a function of technological implementation. Multiple processing – recycling – makes the probability of degradation higher. As the polar contribution of total SFE in the PLA samples has not increased after recycling, it can be assumed that no chemical species (groups) of polar character were created. Hence, the recycling process induced chain breakage more likely than oxidative degradation. Additionally, a decrease of the total SFE after 10 cycles of processing may suggest changes in polymer morphology.

The character of the observed changes, i.e. a substantial decrease of PLA after the 1st and 5th cycles, followed by a smooth, hyperbolical course (the 5th and 10th cycles), is consistent with the findings of other authors on the changes in the mechanical properties of PLA. According to the work of Pillin *et al.*,[14] most changes in viscosity and elongation at break were observed for the samples originating from the initial cycles (1–4), then the properties seemed to be constant. A similar observation was made by Kozłowski and Macyszyn.[26] Considering this, it may be concluded that the simultaneous decrease of gloss and SFE noted in our study may be assigned mainly to chain scission and changes in crystallinity.

The opposite tendency observed for PLA–MMT (increase of SFE and gloss with recycling) should be assigned to the presence of the filler phase. The presence of preintercalated (with alkyl amine) aluminium silicate caused the lowering of the total value of SFE nanocomposite, compared to neat PLA. Even though the filler content was equal to 5%, its impact on the surface properties of the composite is clearly visible. That may be related to isotropic migration and spatial orientation of intercalated clay plates. According to the authors' best knowledge, there is no chemical reaction resulting in the formation of new chemical bonds between the polymer matrix and modified organoclay nanocomposite. At least, this situation is valid before recycling. Due to the terminal hydroxyl groups at montmorillonite plate edges[27] or the presence of ammonium alkyl tertiary amines,[28-30] the aluminium silicate filler may impact on the degradation of the polymer matrix. It is common knowledge that ammonium species used as a preintercalating agent may act as a polymer degradation promoter during mechanical processing. Infrared investigation revealed no significant changes in the spectra (Figs. 5 and 6) of the produced samples. Thus, the changes in total SFE should be associated only with the physical modifications of the sample surface, i.e.: migration of montmorillonite to the nanocomposite's top layer due to flow induced forces.[31-33]

Recycling of the polylactic acid – montmorillonite nanocomposite affects the polymer matrix in the same manner as in the case of the neat polymer. Shear forces occurring in consecutive extrusions also influence the organoclay. As in the initial nanocomposite, an intercalation is likely to occur. One can expect exfoliation of platelets to occur in the course of recycling. This in turn may dramatically increase the number of single silicate plates and their dispersion rate.[34] The exfoliated and intercalated modified clay structures can coexist in the polymer nanocomposite.[34-36]

Considering the forces induced during the melt flow while conducting the press moulding process, one may expect orientation of clay platelets on the plane normal to the pressing force area. This may influence the macroscopic properties of the composite. The newly formed flat surface of aluminium silicates embedded within the polymer matrix reflects differently the incident light beam, compared to the pristine polymer sample. Therefore, the gloss of the composites is frequently higher than that of unmodified polymers. Such a "mirror-like" structure is commonly reported in composites filled with plates or flakes.[37]

Mechanical degradation resulted in a decrease of the polymer's mean molecular weight, contrary to the number of carboxyl terminal groups.[27-30,38] However, in the investigated material, there were reported no disturbances related to the number of polar species, in particular carboxyl groups, which was demonstrated by the IR investigation (see Figs. 5 and 6). The changes in the apolar contribution of SFE may be then reflected only by the physical changes occurring on the surface of PLA and PLA–MMT composites.

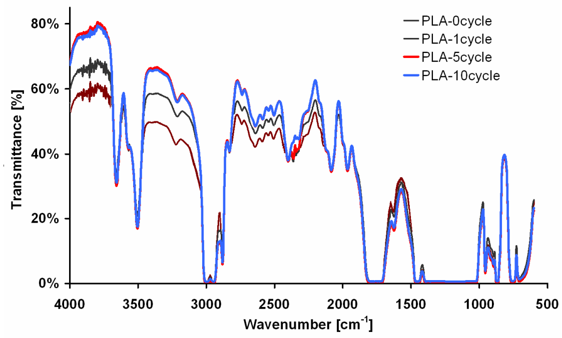

Figure 5: FT-IR investigation of PLA samples

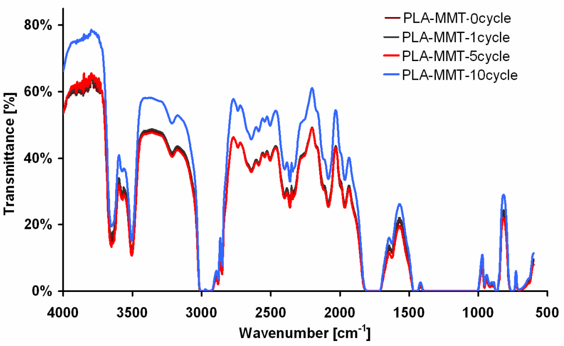

Figure 6: FT-IR investigation of PLA–MMT composites

CONCLUSION

PLA and PLA–MMT composite samples were investigated in terms of their surface changes during recycling. The investigation revealed subsequent morphological changes related to recycling. For the PLA sample, the surface free energy, colour and gloss subsequently decreased, which was interpreted in terms of polymer chain scission. For PLA–MMT, a reverse relation was observed, which was explained by the creation of mirror-like structures in the exfoliated or partially exfoliated composite. The degradation of polymer chains did not lead to the creation of polar species.

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