This accepted author manuscript is copyrighted and published by 1 Elsevier. It is posted here by agreement between Elsevier and 2 MTA. The definitive version of the text was subsequently 3 published in Waste Management, 76, 2018, DOI: 4 10.1016/j.wasman.2018.02.045 Available under license CC-BY-5 NC-ND. 6 7 8 Rheological and mechanical properties of recycled polyethylene films contaminated by 9 biopolymer 10 11 D. Gere<sup>a</sup>, T. Czigany<sup>a,b,\*</sup> 12 13 <sup>a</sup> Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, H-1111 Budapest, Muegyetem rkp. 3, Hungary 14 <sup>b</sup> MTA-BME Research Group for Composite Science and Technology, H-1111 Budapest, 15 16 Muegyetem rkp. 3., Hungary \* corresponding author: czigany@eik.bme.hu 17 18 19 **Abstract.** Nowadays, with the increasing amount of biopolymers used, it can be expected that 20 biodegradable polymers (e. g. PLA, PBAT) may appear in the petrol-based polymer waste 21 stream. However, their impact on the recycling processes is not known yet; moreover, the 22 properties of the products made from contaminated polymer blends are not easily predictable. 23 Therefore, our goal was to investigate the rheological and mechanical properties of synthetic 24 and biopolymer compounds. We made different compounds from regranulates of mixed 25 polyethylene film waste and original polylactic acid (PLA) by extruison, and injection molded 26 specimens from the compounds. We investigated the rheological properties of the regranulates, 27 and the mechanical properties of the samples. When PLA was added, the viscosity and specific 28 volume of all the blends decreased, and mechanical properties (tensile strength, modulus, and 29 impact strength) changed significantly. Young's modulus increased, while elongation at break 30 and impact strength decreased with the increase of the weight fraction of PLA. 31 32 Keywords: recycled polyethylene; polylactic acid; viscosity; pvT diagrams; mechanical 33 properties 34

#### 1. Introduction

- 3 Nowadays most plastic (about 40% of all plastic) is processed by the packaging sector (Gilbert,
- 4 2017). The polymers most commonly used for packaging are low density polyethylene (LDPE),
- 5 linear low density polyethylene (LLDPE), high density polyethylene (HDPE), polypropylene
- 6 (PP), poly(ethylene terephthalate) (PET), polystyrene (PS) and polyvinyl chloride (PVC)
- 7 (Gilbert, 2017). The main fields of application of LDPE and LLDPE are reusable bags, trays
- 8 and containers, agricultural films and food packaging films (Andreoni et al., 2015). According
- 9 to Plastics News, PET (60%) and PE (35%) accounted for most recycled plastic, due to the
- short lifetime of packaging materials (Biron, 2017). A wide variety of new products can be
- produced from plastic waste, therefore it has to be collected and recycled (Andreoni et al., 2015,
- 12 Sharma and Bansal, 2016).
- However, lately there has been great demand for packaging made from bioplastics. In 2015, the
- 14 global production of petroleum-based plastics exceeded 300 million tonnes (Emadian et al.,
- 15 2017). Nevertheless, in 2014, 1.7 million tonnes of bioplastics were manufactured in the world
- with almost 75% of the volume destined for the packaging market (Biron, 2017; Emadian et
- al., 2017). According to European Bioplastics, bioplastics have three main groups: biobased,
- non-biodegradable materials (bio-PE, bio-PET); biobased and biodegradable materials (PLA,
- 19 starch blends); and fossil-based and biodegradable materials (poly(buthylene-adipate-co-
- terephthalate) (PBAT)). Shopping bags, mulch films, and yoghurt cans can be made from PLA
- 21 (Tábi et al., 2010). However, PLA (4.75 \$/kg) is more expensive than PE (1.9 \$/kg) or PET (1.6
- 22 \$/kg) (Biron, 2017; Emadian et al., 2017).
- 23 The potential risk of contamination of the collected conventional plastics and the cost of
- separation have an impact on the quality and processing of recycled materials. For example,
- 25 PLA and PET cannot be easily or cheaply sorted by sight or by separation methods based on
- density because their densities are similar (Gent et al., 2009). Therefore, hybrid bioplastics
- 27 (blends of bio-based and petroleum-based polymers) appeared. While some biopolymers may
- 28 have little effect on recycled HDPE, the presence of biopolymers can significantly modify the
- 29 properties of PET (Cornell, 2007; La Mantia et al., 2012). The presence of biopolymers in post-
- 30 consumer plastic waste makes the recycling of bioplastic blends complicated (Soroudi and
- 31 Jakubowicz, 2013).
- 32 Yarahmadi et al., 2016 investigated the effects of reprocessing and recycling on PLA and a
- 33 PLA/HDPE blend. They used a commercially available (RTP Company) PLA/HDPE blend
- 34 which contained 39% PLA. To reduce compatibility problems, they used glycidyl methacrylate-

1 grafted PE as compatibilizer. The materials were evaluated after a varying number of processing 2 steps (up to 6 consecutive extrusions). Multiple processing of the blend did not significantly 3 change the elastic modulus, but elongation at break was significantly affected by the number of 4 extrusions. Two basic mechanisms can affect elongation at break. One is the degradation of one 5 or both polymers, which decreases elongation at break (La Mantia, 1996). The second is the 6 increased dispersion of the dispersed phase, which means smaller domain size and lower 7 interfacial tension, which causes an increase in elongation at break (Fortelný et al., 2011). The 8 results of Yarahmadi et al., 2016 indicated that multiple processing of a PLA/HDPE blend 9 caused increased dispersion of the PLA in the HDPE, and thus increased elongation at break. Using SEM, they observed the cryofractured surfaces of the samples and found that the size of 10 11 the particles and holes in the blend extruded once were in the range of 1.0-1.4 µm, whereas in 12 the blend extruded six times, the range was 0.5-0.9 µm. The DSC thermograms of the blends 13 showed that the components of the blend were not miscible. The blending of PLA with HDPE 14 not only caused the crystallization of the PLA, but also led to a significant decrease in its cold 15 crystallization temperature and a significant increase in its melting peak temperature. HDPE 16 acted as a nucleating agent and lowered the surface free energy barrier toward nucleation and 17 thus initiated crystallization. 18 PLA has several advantages: it is recyclable, compostable and can be produced from renewable 19 resources. In addition, it has good stiffness and strength, but it has some disadvantages too, such 20 as moisture sensitivity, poor impact resistance and low heat deflection temperature. There are 21 numerous methods to modify its properties, such as plasticization, copolymerization, blending, 22 or producing composites (As'habi et al., 2013; Chow et al., 2016; Graupner et al., 2016; Imre 23 et al., 2014; Tábi et al., 2016). 24 Abdolrasouli et al., 2015 studied virgin PLA and PLA/PE blends which contained 10%, 20% 25 and 30% PE. They investigated the effects of PE content on morphology and the linear 26 viscoelastic properties of the melt. The minor phase was a linear low density polyethylene co-27 polymer (PE) with butane as co-monomer. The samples were prepared with an internal mixer 28 (Brabender Plasticorder W50) at a temperature of 180°C. They studied the linear viscoelastic 29 behavior of the samples in the melt with a rheometric mechanical spectrometer (Paar Physica 30 UDS 200). They performed all the measurements at 180°C in a parallel plate fixture. When the 31 concentration of PE increased from 10% to 20%, the diameter of the dispersed phase increased 32 and the relaxation process became longer, leading to an increase in the storage modulus. The 33 blend containing 30% of PE showed higher elasticity than both PLA and the PE homo-polymer

- in the low frequencies. Complex viscosity increased with the increase of the weight fraction of
- 2 PE, even if this effect was not significant in the higher (100-1000 1/s) shear rate range.
- 3 Only a few publications examine how the presence of biopolymers affects the properties of
- 4 conventional petrol-based polymers in their blends. However, according to a recent study of
- 5 Plastics Recyclers Europe, 2017 it is a considerable problem in Southern Europe because there,
- 6 in mixed film waste, the share of biodegradable plastics (e.g. starch, PLA, polybutylene adipate
- 7 terephthalate (PBAT)) is higher than in Northern Europe. Film production with recycled
- 8 plastics from Northern Europe worked normally, but holes and peaks occurred regularly when
- 9 recycled plastics from Southern Europe were used. The laboratory tests showed that most of
- 10 the degradation is caused by substances which are used for the production of biodegradable
- 11 polymers.
- Nowadays, when mixed polyethylene film waste is recycled, it is a great problem that small
- amounts (0.5-1.5%) of bioplastics are often mixed into synthetic polymers. The changes in the
- properties of a product are not easily predictable, but they are very important to know for the
- manufacturing of products. The novelty of this manuscript, compared to other publications, is
- that our goal is not to develop a new blend to improve the properties of PLA or PE, but to
- analyze the influence of bioplastic contamination in the petrol-based polymer waste stream on
- the recycling process. Therefore, our goal was to investigate the rheological and mechanical
- 19 properties of synthetic and biopolymer compounds.

# 21 **2. Experimental**

# **22 2.1. Materials**

- 23 LDPE, PP, HDPE and PET are the most common types of plastic processed by the packaging
- 24 industry and the composition of the plastic fraction of municipal solid waste by polymer type
- 25 was LDPE (27.9%), HDPE (14%), PP (17.5%) and PET (11.9%) in Europe (Dahlbo et al., 2018;
- PlasticsEurope, 2016). According to Biron, 2017, PET (60%) and PE (35%) account for most
- 27 recycled plastic, PP accounting for only 2%. In 2014, PLA was the most used biodegradable
- bioplastic (Emadian et al., 2017), therefore there is a chance that PE and PLA are mixed in the
- 29 polymer waste stream.
- We used regranulates of mixed polyethylene film waste (MPE) (MFR (190°C, 2.16 kg): 0.56
- 31 g/10 min, density: 0.932 g/cm<sup>3</sup>), supplied by Jász-Plasztik Ltd. (Hungary). It is a post-industrial
- mixed film waste, which typically contains 50% HDPE and 50% LDPE. We also used virgin
- 33 PLA type Ingeo 3100HP (MFR (210°C, 2.16 kg): 24 g/10 min, density: 1.24 g/cm<sup>3</sup>), supplied
  - type ingeo 3100111 (WITK (210 C, 2.10 kg). 24 g/10 mm, density. 1.24 g/cm/), supplied
- 34 by NatureWorks LLC. (USA).

2

# 2.2. Material preparation and processing

- 3 Six different MPE-PLA compounds (regranulates) (100/0, 98/2, 90/10, 75/25, 50/50, 0/100
- 4 wt/wt%) were produced with a Labtech Scientific LTE 26-48 co-rotating twin-screw extruder.
- 5 Before extrusion, PLA was dried at 100°C in a Memmert UF1060 hot air drying oven for 90
- 6 minutes. The screw diameter of the extruder was 26 mm and the length/diameter (L/D) ratio
- 7 was 48. The temperature profile of the extruder (from intake zone to die) was 190-195-195-
- 8 200-200-205-210-215-215-220-220-215°C. The melt pressure was 50-55 bar and the
- 9 throughput was 8 kg/h.
- Before injection molding, the compounds were dried at 100°C in a Memmert UF1060 hot air
- drying oven for 3 hours. The injection molded samples were made with an Engel ES 200/45
- 12 HL-V injection molding machine. Injection rate was 40 cm<sup>3</sup>/s, holding pressure was 800 bar,
- holding time was 20 s, residual cooling time was 30 s, and melt and mold temperature were
- 14 225°C and 25°C, respectively. The mechanical tests were carried out on ISO standard dumbbell
- shaped tensile specimens.

# 16

17

### 2.3. Methods

- Before the rheological tests, the samples were dried at 100°C in a Memmert UNE 200 hot air
- drying oven for 3 hours. The shear viscosity of the regranulates was measured with an Instron
- 20 Ceast SR20 capillary rheometer. The testing temperature in the capillary rheometer was set to
- 21 190°C. We carried out the measurements in the 100-20000 1/s shear rate range, using four
- 22 different capillaries:  $L_1 = 5$  mm,  $D_1 = 1$  mm;  $L_2 = 10$  mm,  $D_2 = 1$  mm;  $L_3 = 20$  mm,  $D_3 = 1$  mm;
- $L_4 = 30$  mm,  $D_4 = 1$  mm. We used Bagley correction to calculate true shear stress and the
- 24 Rabinowitsch analysis to calculate true shear rate. The specific volume (pvT diagram) of the
- 25 regranulates was measured with an Instron Ceast SR20 capillary rheometer. We determined the
- specific volume with the direct method at 6 different pressures (50-1000 bar) and at 22 different
- temperatures ranging from 230°C to 50°C (Carreau et al., 1997). We tested all the samples at
- least 8 times; in every sample standard deviation was within 5% (therefore error bars are not
- visible on the figures).
- 30 Tensile tests were carried out on an Instron 3369 universal testing machine. We calculated the
- tensile modulus between 0.05% and 0.25% strain with a crosshead speed of 1 mm/min, and
- determined tensile strength and elongation at break with a crosshead speed of 10 mm/min. The
- measurements were performed on ISO 527-2/1B dumbbell shaped specimens with an overall

- length of 150 mm and a cross-section of 4 mm × 10 mm. In every measurement, we tested at
- 2 least 5 specimens, and calculated the average value and standard deviation.
- 3 Impact strength was determined with the Izod impact test on a Zwick 5113.100/01 impact tester,
- 4 with pendulums of 2.75 J and 22 J. The measurements were performed on 2 mm notched ISO
- 5 180/A dumbbell shaped specimens with a length of 80 mm and a cross-section of 4 mm  $\times$  10
- 6 mm. The tests were performed at room temperature and at a relative humidity of 50%. In every
- 7 measurement we tested at least 10 specimens, and calculated the average and standard
- 8 deviation.
- 9 After drying the samples, we measured the residual moisture content with an aboni Hydrotracer
- 10 FLV water content analyzer. The absolute water content of the material was determined with a
- 11 chemical method, not based on weight loss during heating. The instrument warmed the PLA
- granules to 140°C, therefore the water evaporated. The gaseous water reacted with the calcium
- hydride reagent in a cooled area and hydrogen was formed. A gas sensor detected the hydrogen
- 14 concentration within the reactor and separate sensors detected the moisture of the ambient air,
- which came into the reactor at the beginning of the measurement. The software considered these
- in the calculation of the water content of the PLA granules.
- 17 The morphology of the blends was studied with a light microscope (Zeiss AXIO Imager M2m)
- and a scanning electron microscope (Zeiss EVO MA 10). The SEM micrographs were taken
- 19 from cryo-fractured surfaces.
- 20 The core and the skin layer of the injection molded samples were investigated with a Bruker
- 21 Tensor 37 Fourier Transform Infrared Spectroscopy (FTIR) equipment (the resolution of the
- 22 instrument is better than 0.6 cm<sup>-1</sup>).

# 2.4. Processing experiments

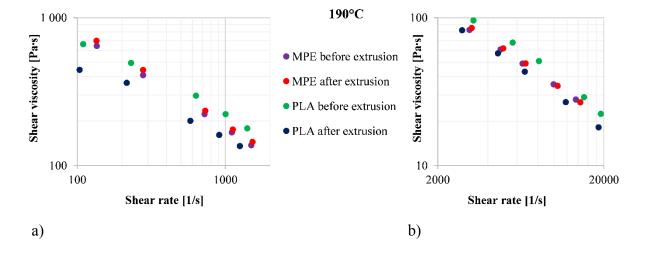
- 25 In the experiments, MPE was mixed with original PLA (instead of PLA waste), because we did
- 26 not want to increase the number of influencing factors, we just wanted to discover the effect of
- 27 biodegradable polymer "contamination".
- 28 In the case of PLA, according of the technical data sheet, a moisture content of less than 250
- 29 ppm (0.025%) is recommended before processing, to prevent hydrolytic degradation. In order
- 30 to model industrial conditions (PE flakes are usually dried for a short time after the
- 31 washing/cleaning process), we dried PLA for a shorter time and it had a moisture content of
- 32 457 ppm before extrusion. Modern film recycling systems (Erema, Starlinger) can process
- materials (PE, PP) with up to 12% residual moisture. Therefore, drying temperature and/or time
- can be reduced, and energy consumption, as well as production costs and CO<sub>2</sub> emission can be

decreased. However, in the case of hydrophilic biopolymer (PLA) contaminants mixed in synthetic polymers, hydrolytic degradation probably occurs. Melt temperature was 20°C higher than the recommended value for PLA because of the processing melt temperature of MPE, therefore thermal degradation probably occurred. After extrusion the different regranulates looked like typical regranulates.

#### 3. Results and discussion

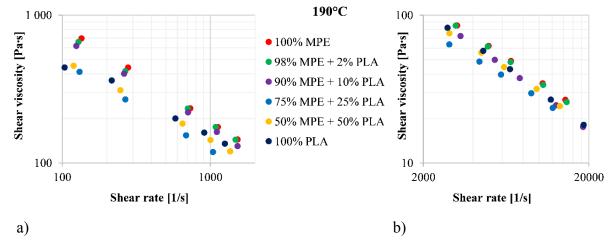
### 3.1. Rheological properties of the regranulates

Figure 1 shows the shear viscosity curves of MPE and PLA before and after extrusion at 190°C. Extrusion did not affect the viscosity of MPE, but after extrusion, the viscosity of PLA decreased. In the case of PLA, this decrease was due to degradation reactions such as thermal unzipping degradation, oxidative chain scission, inter- or intramolecular transesterification and hydrolysis in the presence of moisture. Residual moisture after the drying process attacks the ester linkages, causing chain scission and a decrease in molecular weight, and as a result, viscosity decreases. Several researchers (Harris and Lee, 2012; Jamshidi et al., 1988; Yarahmadi et al., 2016) came to similar conclusions about the degradation of PLA. Degradation under processing takes place not only in sensitive polymers, such as PET or PLA, but also in polymers that are relatively resistant to degradation, for example PE. In the case of PE, both degradation and cross-linking occur after multiple processing, which can increase melt viscosity. This is also supported by the results of Cornell, 2007.



**Figure 1.** Viscosity curves of MPE and PLA before and after extrusion in the 100-2000 1/s (a) and the 2000-20000 1/s (b) shear rate range

Figure 2 shows the shear viscosity curves of the six different regranulates in the 100-20000 1/s shear rate range at 190°C. The results indicated that the presence of PLA can significantly affect viscosity. The viscosity curves of all the blends showed a decrease in viscosity when PLA was added but this effect was not significant in the 98/2 blend. The melt viscosities of MPE (100/0) and PLA (0/100) were similar in the higher shear rate range (> 2000 1/s), but the viscosities of the blends did not change according to the linear rule of mixtures. Incompatible blends usually show negative deviation in rheological properties (e.g. viscosity, die swell). Therefore, the two components were probably incompatible in the melt at least in the concentrations investigated here. Hamad et al., 2012 found similar results for PLA/LDPE blends in the 0.1-200 1/s shear rate range. They also observed that the viscosity of the blends indicates negative deviation according to the linear rule of mixtures.



**Figure 2.** Viscosity curves of the different MPE-PLA regranulates in the 100-2000 1/s (a) and the 2000-20000 1/s (b) shear rate range

Figure 3 shows the pvT curves of the extruded MPE and PLA at 5 different pressures. The specific volume decreased with the increase of pressure. The crystallization of MPE started at ~125°C, whereas the crystallization of PLA started at ~135°C. Shrinkage (the decrease of specific volume) was 17% for MPE and 15% for PLA between 230 °C and 50 °C at 50 bar.

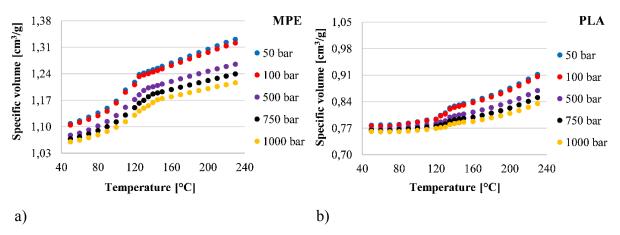


Figure 3. pvT curves of the extruded MPE (a) and PLA (b) at different pressures

Figure 4 shows the pvT curves of the different regranulates. The melt pressure for film blowing is about 200-300 bar in industrial extruders, therefore we analyzed the pvT curves at 250 bar. Specific volume decreased with the increase of the weight fraction of PLA but this effect was not significant in the 98/2 blend. This decrease was due to the higher density of PLA. The pvT curve of blends can be estimated based on the rule of mixtures if the pvT curves of the components are known.

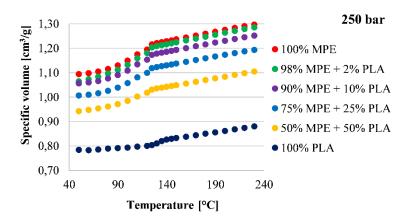


Figure 4. pvT curves of the different MPE-PLA regranulates at 250 bar

# 3.2. Mechanical properties of the injection molded samples

Figure 5 shows the tensile stress-strain curves of the six different samples. The curves show that MPE was flexible and PLA was rigid. The stress-strain curves of all the blends showed a decrease in elongation, but an increase in tensile strength when PLA was added, but this effect was not significant in the 98/2 blend.

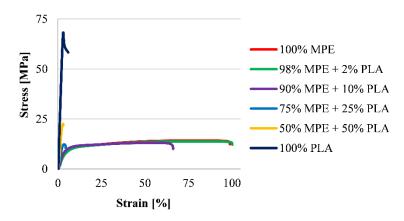


Figure 5. Tensile stress-strain curves of MPE-PLA samples with different weight fractions

3

4

5

6

7

8

9

10

11

1213

14

15

16

17

18

19

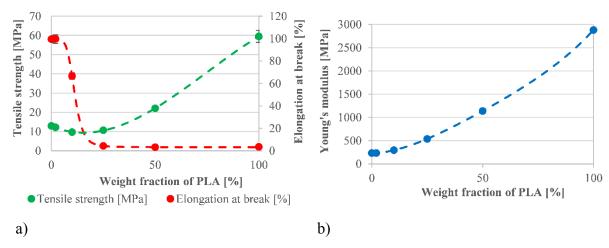
20

21

22

23

Figure 6 and Table 1 show the mechanical properties of the injection molded samples. The 100/0 and the 98/2 blend had similar mechanical properties. Tensile strength decreased when 10 and 25 wt% PLA was added, but doubled when 50 wt% PLA was added. As the weight fraction of PLA was increased from 0% to 50%, the Young's modulus increased from 232 MPa to 1137 MPa, while elongation at break decreased from 99.53 % to 3.08 %. In addition to the presence of a rigid component (PLA), the degradation of PLA and the increased droplet size (see Figure 9e-h) could also lead to a decrease in elongation at break when the weight fraction of PLA was increased. The impact strength of the samples greatly decreased when 25 and 50 wt% PLA was added, but the 100/0, 98/2, 90/0 samples were not broken, even when the 22 J pendulum was used. As the weight fraction of PLA was increased, tensile strength and the Young's modulus seemed to change along a parabola, while elongation at break decreased sharply and stayed low, and no tendency could be observed for impact strength. These mechanical properties of the blends did not change according to the linear rule of mixtures. Similarly to rheological properties, the polymer blends are typically incompatible if the values of Young's modulus, elongation at break and stress at break are below the line of linear rule of mixtures (negative deviation). These results show that PLA and MPE compose an incompatible blend, which is confirmed by the rheological results. The trend of increasing Young's modulus and decreasing elongation at break well matched the results of Hamad et al., 2012, who studied a PLA/LDPE blend.



**Figure 6.** Tensile strength and elongation at break (a) and Young's modulus (b) of the different injection molded MPE-PLA samples

Property	100% MPE	98% MPE + 2% PLA	90% MPE + 10% PLA	75% MPE + 25% PLA	50% MPE + 50% PLA	100% PLA
Impact						
Strength	not broken	not broken	not broken	$6.07 \pm 0.28$	$2.56 \pm 0.11$	$3.75 \pm 0.13$
– Izod						
$[kJ/m^2]$						

**Table 1.** Impact strength of the different injection molded MPE-PLA samples

### 3.3. Structure

After the tensile tests, it seemed that there was a core part which was flexible and a skin part which behaved more rigidly. To prove this, we analyzed the cross sections of the tensile bars with a light microscope (Figure 7) and an FTIR spectrometer (Figure 8). In the blends which contained 2 and 10 wt% PLA, the dispersed PLA phases were not visible. However, in the case of the 75/25 blend, the dispersed PLA component was visible in the MPE matrix, furthermore, the structure of the 50/50 blend was close to co-continuous. The micrographs were taken from the edge of the cross section, where both components could be found and the components were not clearly layered. The outer surface of the samples was investigated by FTIR. In this analysis the region between 800 and 1800 cm<sup>-1</sup> is interesting, where the active ester and methyl groups of PLA are located. A higher intensity in the –C=O ester carbonyl stretch region (~1720-1775 cm<sup>-1</sup>) was observed with the increase of the weight fraction of PLA. The peak maximum was a

wave number of 1752 cm<sup>-1</sup>; this peak is related to carboxylic end groups formed during the hydrolysis of the ester bonds, which can indicate the degradation of PLA. This is supported by Yarahmadi et al., 2016 and Badia et al., 2012, who observed the influence of multiple processing of neat PLA and PLA blends on degradation. In Figure 8, at the same time, an increase in signal intensity can be observed at the characteristic PLA peak at 1266 cm<sup>-1</sup> (-CO bend) and the peak of 1086 cm<sup>-1</sup> with the increase of the weight fraction of PLA, which was ascribed to symmetric stretching of the -C-O- band of ester groups. Figure 8 shows that the symmetric deformation of the methyl –CH<sub>3</sub> group occurred at 1381 cm<sup>-1</sup> and 1266 cm<sup>-1</sup>, when PLA content was increased from 10% to 50%. The changes in these peaks were also observed by Ndazi and Karlsson, 2011, when they investigated the hydrolytic degradation of PLA and by Vasile et al., 2017, when they studied PLA bionanocomposites for food packing. In Figure 8, the spectra demonstrated the presence of -CH<sub>3</sub>, -CH<sub>2</sub> and C-H groups of highly aliphatic components in the 2800-3000 cm<sup>-1</sup> wavenumber range, due to the MPE component. A decrease in signal intensity can be observed at the peak of 2848 cm<sup>-1</sup> and the peak of 2916 cm<sup>-1</sup> with the increase of the weight fraction of PLA, which was ascribed to the stretching of the -C-H bond of the alkanes. This is supported by Das and Tiwari, 2018 and Miandad et al., 2017, who observed the pyrolysis of plastic waste.

1

2

3

4

5

6

7

8 9

10

11

12

13

14

15

16

17

18

19

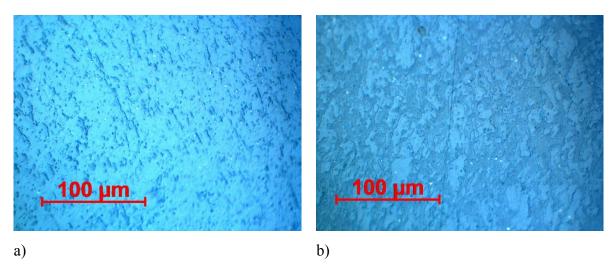
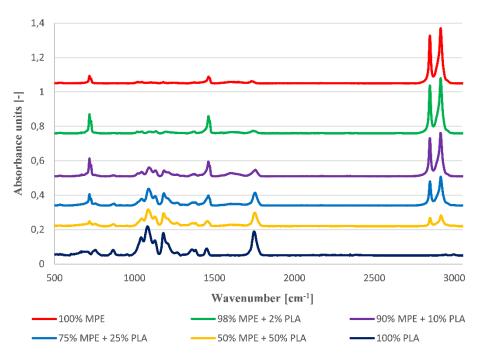
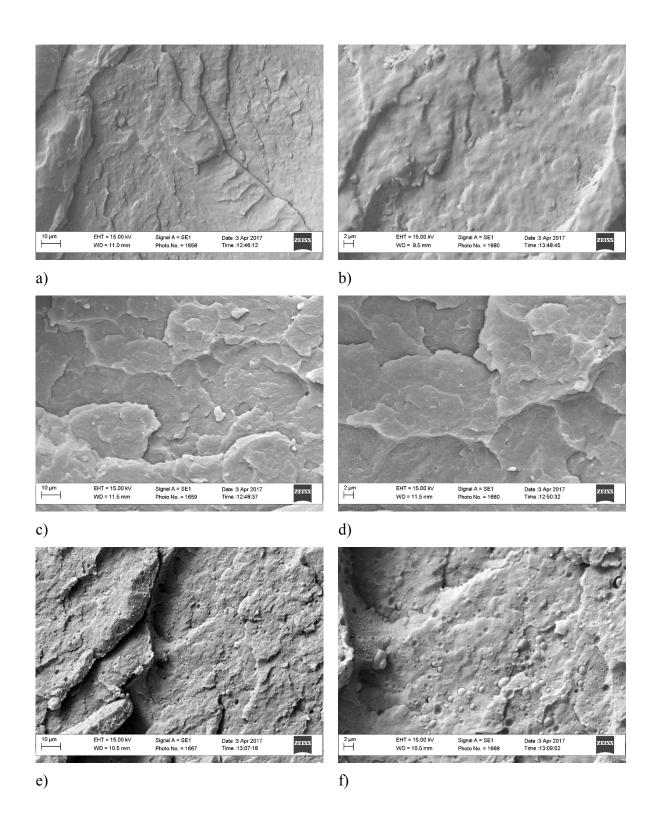


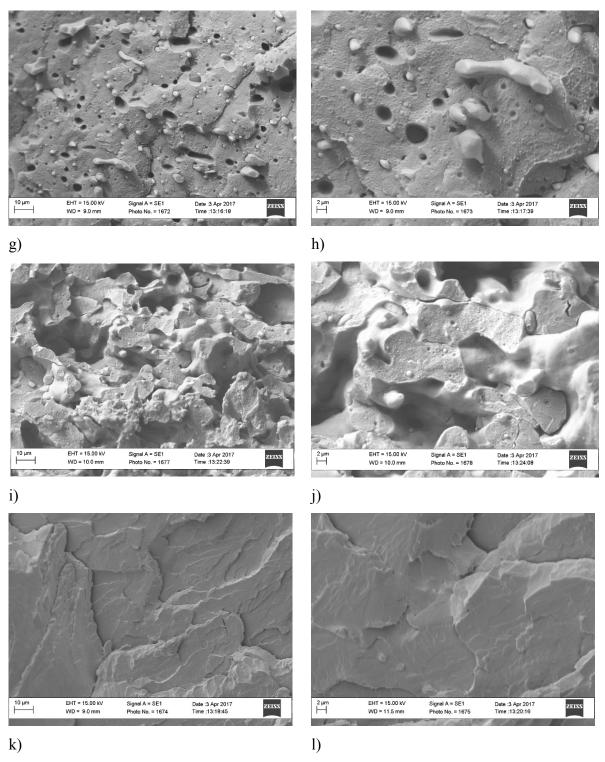
Figure 7. Changes in the morphology of MPE/PLA blends (a) 25 wt% PLA, b) 50 wt% PLA)



**Figure 8.** FTIR curves of the different MPE-PLA blends in the 500-3000 cm<sup>-1</sup> wavenumber range

We also studied the structure of the blends by SEM (Figure 9). The micrographs were taken from cryo-fractured surfaces. In the case of the 98/2 blend, the dispersed PLA phase formed only a few tenths of a micron droplets (droplet distribution) and then in the 90/10 blend the divided droplets grew a few microns in size. In the blend that contained 25 wt% PLA, the extended dispersed phases were deformed and the spherical droplets were converted to an elongated fibrous shape. Finally, in the 50/50 blend a co-continuous phase formed. These results are consistent with the results of light microscopy. In SEM micrographs, a typical morphology of immiscible polymer blends could be seen if one of the components had a well-defined spherical shape, very broad size distribution and a smooth fracture surface. These observations are also confirmed by rheological and mechanical test results. Kim et al., 2004 had similar results, when they investigated an 80/20 LDPE/PLA blend. Lu et al., 2016 also observed a cocontinuous phase morphology in PLA/HDPE blends (60/40 and 50/50) and a typical island-sea type morphology in PLA/HDPE (40/60 and 20/80) blends.





**Figure 9.** Changes in the morphology of MPE/PLA blends (a-b) 0 wt% PLA, c-d) 2 wt% PLA, e-f) 10 wt% PLA, g-h) 25 wt% PLA, i-j) 50 wt% PLA, k-l) 100 wt% PLA)

# 4. Conclusions

1 2

3

- 5 Nowadays, in the recycling of mixed polyethylene film waste, it is a considerable problem that
- 6 small amounts (0.5-1.5%) of bioplastic waste can contaminate synthetic polymer waste.

- 1 Developing a method of recycling this post-consumer waste of polymer blends is a major
- 2 challenge.
- 3 We investigated the rheological properties of regranulates and mechanical properties of
- 4 injection molded samples.
- 5 The viscosity curves of all the blends showed a decrease of viscosity when PLA was added.
- 6 The melt viscosities of MPE (100/0) and PLA (0/100) were similar, but the viscosities of the
- 7 blends did not change according to the linear rule of mixtures. Specific volume decreased with
- 8 the increase of the weight fraction of PLA, which is due to the higher density of PLA. The
- 9 stress-strain curves showed that MPE was flexible and PLA was rigid. Tensile strength
- decreased when 10 and 25 wt% PLA was added, but doubled when 50 wt% PLA was added.
- 11 As the weight fraction of PLA was increased from 0% to 50%, the Young's modulus increased
- from 232 MPa to 1137 MPa, while elongation at break decreased from 99.53 % to 3.08 %. The
- impact strength of the samples greatly decreased when 25 and 50 wt% PLA was added, but the
- 14 100/0, 98/2, 90/0 samples were not broken, even when a 22 J pendulum was used. In SEM
- micrographs, we observed a co-continuous phase morphology in the 50/50 blend, and a typical
- island-sea type morphology in the 98/2, 98/10 and 75/25 MPE/PLA blends. Therefore, the two
- components are incompatible, at least in the concentrations investigated.
- 18 Based on the results, it seems that the blend containing 2% PLA can still be used for film
- production, but the other blends are inappropriate for this purpose. The blends that contain more
- 20 than 2 % of PLA would probably result in a lot of faulty products, due to the immiscibility of
- 21 the components. These faulty products cannot be recycled, they just go to a landfill or are used
- 22 for energy production. The miscibility of the blends can probably be improved by adding
- compatibilizers, therefore products with a simple geometry and low mechanical loads (e. g.
- 24 flowerpot, speed bump etc.) can be produced from these contaminated blends. The applicability
- and cost-effectiveness of compatibilizers needs further research. Our opinion is that
- biodegradable plastics should be collected into a separate waste stream and then recycled (if
- possible) or composted.

### Acknowledgements

- 30 This work was supported by the National Research, Development and Innovation Office (grant
- number: NVKP 16-1-2016-0012). We are grateful for the assistance of Dr. Ferenc György
- 32 Ronkay and Béla Molnár in the preparation of the SEM micrographs and in the FTIR
- measurements. The infrastructure of the research project was supported by Jász-Plasztik Ltd.

28

### References

- 2 Abdolrasouli, M. H., Nazockdast, H., Sadeghi, G. M. M., Kaschta, J., 2015: Morphology
- development, melt linear viscoelastic properties and crystallinity of
- 4 polylactide/polyethylene/organoclay blend nanocomposites. J. Appl. Polym. Sci. 132,
- 5 41300.
- 6 Andreoni, V., Saveyn, H. G. M., Eder, P., 2015: Polyethylene recycling: Waste policy scenario
- 7 analysis for the EU-27. J. Environ. Manage. 158, 103-110.
- 8 As'habi, L., Jafari, S. H., Khonakdar, H. A., Boldt, R., Wagenknecht, U., Heinrich, G., 2013:
- 9 Tuning the processability, morphology and biodegradability of clay incorporated
- 10 PLA/LLDPE blends via selective localization of nanoclay induced by melt mixing
- sequence. Express Polym. Lett. 7, 21-39.
- Badia, J.D., Strömberg, E., Karlsson, S., Ribes-Greus, A., 2012: Material valorisation of
- amorphous polylactide. Influence of thermo-mechanical degradation on the morphology,
- segmental dynamics, thermal and mechanical performance. Polym. Degrad. Stabil. 97,
- 15 670-678.
- Biron, M., 2017: Industrial Applications of Renewable Plastics. Elsevier Ltd., Oxford.
- 17 Carreau, P. J., De Kee, D. C. R., Chhabra, R. P., 1997: Rheology of polymeric systems
- principles and applications. Hanser Publishers, Munich.
- 19 Chow, W. S., Leu, Y. Y., Ishak, Z. A. M., 2016: Mechanical, thermal and morphological
- properties of injection molded poly(lactic acid)/calcium carbonate nanocomposites.
- Period. Polytech. Mech. Eng. 60, 15-20.
- 22 Cornell, D. D., 2007: Biopolymers in the Existing Postconsumer Plastics recycling Stream. J.
- 23 Polym. Environ. 15, 295-299.
- Dahlbo, H., Poliakova, V., Mylläri, V., Sahimaa, O., Anderson, R., 2018: Recycling potential
- of post-consumer plastic packaging waste in Finland. Waste Manage. 71, 52-61.
- Das, P., Tiwari, P., 2018: Valorization of packaging plastic waste by slow pyrolysis. Resour.
- 27 Conserv. Recycl. 128, 69-77.
- 28 Emadian, S. M., Onay, T. T., Demirel, B., 2017: Biodegradation of bioplastics in natural
- environments. Waste Manage. 59, 526-536.
- Gent, M. R., Menendez, M., Torano, J., Diego I., 2009: Recycling of plastic waste by density
- separation: prospects for optimization. Waste Manage. Res. 27, 175-187.
- 32 Gilbert, M., 2017: Brydson's Plastics Materials. Elsevier Ltd., Oxford.
- Graupner, N., Albrecht, K., Ziegmann, G., Enzler, H., Müssig, J., 2016: Influence of
- reprocessing on fibre length distribution, tensile strength and impact strength of injection

- 1 moulded cellulose fibre-reinforced polylactide (PLA) composites. Express Polym. Lett.
- 2 10, 647-663.
- 3 Hamad, K., Kaseem, M., Deri, F., 2012: Poly(lactic acid)/low density polyethylene polymer
- blends: preparation and characterization. Asia-Pac. J. Chem. Eng. 7, 310-316.
- 5 Harris, A.M., Lee, E.C., 2012: Durability of polylactide-based polymer blends for injection-
- 6 molded applications. J. Appl. Polym. Sci. 128, 2136-2144.
- 7 Imre, B., Renner, K., Pukánszky, B., 2014: Interactions, structure and properties in poly(lactic
- 8 acid)/thermoplastic polymer blends. Express Polym. Lett. 8, 2-14.
- 9 Jamshidi, K., Hyon, S.-H., Ikada Y., 1988: Thermal characterization of polylactides. Polymer.
- 10 29, 2229-2234.
- 11 Kim, Y.F., Choi, C.N., Kim, Y.D., Lee, K.Y., Lee, M.S., 2004: Compatibilization of immiscible
- poly(l-lactide) and low density polyethylene blends. Fibers Polym. 5, 270–274.
- La Mantia, F. P., 1996: Basic concepts on the recycling of homogeneous and heterogeneous
- plastics, in: La Mantia, F. P. (Eds.), Recycling of PVC & mixed plastic waste. ChemTec
- Publisher, Toronto, pp. 63-76.
- La Mantia, F. P., Botta, L., Morreale, M., Scaffaro, R., 2012: Effect of small amounts of
- poly(lactic acid) on the recycling of poly(ethylene terephthalate) bottles. Polym. Degrad.
- 18 Stabil. 97, 21-24.
- Lu, X., Tang, L., Wang, L., Zhao, J., Li, D., Wu, Z., Xiao, P., 2016: Morphology and properties
- of bio-based poly (lactic acid)/high-density polyethylene blends and their glass fiber
- reinforced composites. Polym. Test. 54, 90–97.
- 22 Miandad, R., Barakat, M.A., Aburiazaiza, A.S., Rehan, M., Ismail, I.M.I., 2017: Effect of
- plastic waste types on pyrolysis liquid oil. Int. Biodeterior. Biodegradation 119, 239-252.
- Ndazi, B.S., Karlsson, S., 2011: Characterization of hydrolytic degradation of polylactic
- acid/rice hulls composites in water at different temperatures. Express Polym. Lett. 5, 119-
- 26 131.
- 27 PlasticsEurope, 2016: Plastics the Facts 2016. An analysis of European plastics production,
- demand and waste data.
- 29 Plastics Recyclers Europe, 2017: Recycled film quality negatively affected by degradable
- 30 plastics from Southern Europe, Press release.
- 31 <a href="http://www.plasticsrecyclers.eu/news/recycled-film-quality-negatively-affected-">http://www.plasticsrecyclers.eu/news/recycled-film-quality-negatively-affected-</a>
- degradable-plastics-southern-europe> (accessed 17.10.23).

- Fortelný, I., Hlavatá, D., Horák, Z., Kolařík, J., Sikora, A., 2011: Blending, in: Seidel, A. (Eds.),
- 2 Processing and finishing of polymeric materials. John Wiley & Sons, Inc., Hoboken, pp.
- 3 86-144.
- 4 Sharma, R., Bansal, P. P., 2016: Use of different forms of waste plastic in concrete a review.
- 5 J. Clean. Prod. 112, 473-482.
- 6 Soroudi, A., Jakubowicz, I., 2013: Recycling of bioplastics, their blends and biocomposites: A
- 7 review. Eur. Polym. J. 49, 2839-2858.
- 8 Tábi, T., Hajba, S., Kovács, J. G., 2016: Effect of crystalline forms (α' and α) of poly(lactic
- 9 acid) on its mechanical, thermo-mechanical, heat deflection temperature and creep
- 10 properties. Eur. Polym. J. 82, 232-243.
- 11 Tábi, T., Sajó, I. E., Szabó, F., Luyt, A. S., Kovács, J. G., 2010: Crystalline structure of annealed
- polylactic acid and its relation to processing. Express Polym. Lett. 4, 659-668.
- Vasile, C., Râpă, M., Ştefan, M., Stan, M., Macavei, S., Darie-Nită, R.N., Barbu-Tudoran, L.,
- Vodnar, D.C., Popa, E.E., Ştefan, R., Borodi, G., Brebu, M., 2017. New PLA/ZnO: Cu/Ag
- bionanocomposites for food packaging. Express Polym. Lett. 11, 531–544.
- 16 Yarahmadi, N., Jakubowicz, I., Enebro, J., 2016: Polylactic acid and its blends with petroleum-
- based resins: Effects of reprocessing and recycling on properties. J. Appl. Polym. Sci.
- 18 133, 43916.