The method of obtaining polymer masterbatches based on polylactide with carbon filler

D Kaczor1, K Bajer2, G Domek3, A Raszkowska-Kaczor2, P Szroeder4

1 Kazimierz Wielki University, J.K. Chodkiewicza 30, 85-064 Bydgoszcz, Poland
2 Łukasiewicz Research Network – Institute for Engineering of Polymer Materials and Dyes, Marii Skłodowskiej-Curie 55, 87-100 Toruń, Poland
3 Faculty of Mechatronics, Kazimierz Wielki University, Kopernika 1, 85-074 Bydgoszcz, Poland
4 Institute of Physics, Kazimierz Wielki University, Powańców Wielkopolskich 2, 85-090 Bydgoszcz, Poland
daniel.kaczor@impib.lukasiewicz.gov.pl

Abstract. The method of obtaining polymer composites with a graphite filler using a kneading mixer was presented. The best mixing parameters (rotational speed and temperature) were determined, allowing to obtain composites with the best filler dispersion in the polymer matrix. A series of graphite/polylactide (PLA) masterbatches were made. The following composites tests were performed: scanning electron microscopy (SEM), infrared spectroscopy (FTIR-ATR), and differential scanning calorimetry (DSC). The value of the mass melt flow rate (MFR) was also determined. It was observed that the best homogenization were obtained for samples mixed at a speed of 40-50 rpm and at a temperature of 180-190°C.

1. Introduction
Polylactide, also known as poly(lactic acid), is one of the compostable, thermoplastic polyesters. Due to the possibility to obtaining this polymer from renewable sources, it has become popular in recent years. It can be used to produce durable, water-resistant materials. Properties of polylactide are similar to polypropylene, polyethylene or polystyrene [1]. Pure PLA is stiff and brittle. The use of this polymer in the automotive, electronics and electrical industries requires modification of its properties with various types of additives [2]. The addition of graphene oxide increases the value of Young's modulus [3]. Graphene/PLA composites with improved mechanical properties and electrical conductivity are used as filaments for 3D printing [4]. The use of nano carbons is limited by their high cost. An alternative approach is to replace graphene and carbon nanotubes with graphite micropowders, which combine low price and excellent thermal and electrical properties of graphene [5].

In literature there is several methods of obtaining polylactide composites with carbon fillers. The physical method using a masterbatch made on a twin-screw extruder [6]–[8]. The chemical method is a preparation of composites from THF solution, methanol or chloroform [9], [10]. Each of the above methods has advantages and disadvantages. The methods using a twin-screw extruder require a large amount of carbon filler and the resulting composite can be characterized by insufficient dispersion of the filler in the polymer matrix. The advantage is the high yield of composites. Solvent methods are inefficient and complicated.

In this article, there is propose a method of obtaining graphite/polylactide concentrates using a kneading mixer. The aim of this study is to create a method of determining the optimal mixing parameters of polymer composites obtained with the use of a laboratory mixer. This device is used in the production of homogeneous polymers, elastomeric, ceramic or other blends. It can be used to produce polymer masterbatches for laboratory purposes.

A series of two-component blends of polylactide with the addition of a constant amount of carbon filler was obtained. The influence of the rotational speed and temperature changes on the stirrer torque...
was discussed. The structures of the concentrates as well as their physical and thermal properties were also compared.

2. Materials and sample preparation

2.1. Materials
Graphite micropowder of industrial grade, MG3096 (3000 mesh), was purchased from Sinograf S.A. The polylactide (PLA) produced by Total-Corbion, available under the trade name Luminy® LX175, was used as a matrix in the obtained polymer masterbatches. Typical properties of used PLA are show in Table 1.

| Properties                   | Method                        | Typical value         |
|------------------------------|-------------------------------|-----------------------|
| Density                      | Literature value              | 1.24 g/cm³            |
| Stereocchemical purity       | Total Corbion PLA method      | 96% (L-isomer)        |
| Residual monomer             | Total Corbion PLA method      | ≤ 0.3%                |
| Melting temperature          | DSC                           | 155°C                 |
| Glass transition temperature | DSC                           | 60°C                  |

2.2. Composite preparation
Composites with carbon fillers (marked as G/PLA) were prepared by mixing 30 g of PLA with 10 g of graphite powder by Brabender Plasti-Corder® Lab-Station, equipped with measuring mixer 50 EHT and roller blades, at different temperature and mixing speed. Samples without graphite (marked as NG/PLA) were prepared by mixing 40 g of polylactide. Before the mixing process, polylactide (PLA) was dried in the temperature of 80°C for 8 hours. The mixture was stirred for 4 minutes. As a result, two types of masterbatches containing 25% of graphite were obtained. The first type of composites was make by mixing PLA with graphite at the temperature of 190°C and variable speed from 30 to 70 rpm. The second type was make by mixing in a temperature range from 170 to 210°C and a constant speed of 50 rpm. Samples are listed in the Table 2.
Table 2. Designation of the graphite/PLA masterbatches with their preparation conditions.

| Sample       | Graphite content [%] | Mixing temperature [°C] | Mixing speed [rpm] |
|--------------|----------------------|-------------------------|-------------------|
| PLA          | -                    | -                       | -                 |
| NG/PLA30rpm  | -                    | 190                     | 30                |
| NG/PLA40rpm  | -                    | 190                     | 40                |
| NG/PLA50rpm  | -                    | 190                     | 50                |
| NG/PLA60rpm  | -                    | 190                     | 60                |
| NG/PLA70rpm  | -                    | 190                     | 70                |
| G/PLA30rpm   | 25                   | 190                     | 30                |
| G/PLA40rpm   | 25                   | 190                     | 40                |
| G/PLA50rpm   | 25                   | 190                     | 50                |
| G/PLA60rpm   | 25                   | 190                     | 60                |
| G/PLA70rpm   | 25                   | 190                     | 70                |
| NG/PLA170C   | -                    | 170                     | 50                |
| NG/PLA180C   | -                    | 180                     | 50                |
| NG/PLA190C   | -                    | 190                     | 50                |
| NG/PLA200C   | -                    | 200                     | 50                |
| NG/PLA210C   | -                    | 210                     | 50                |
| G/PLA170C    | 25                   | 170                     | 50                |
| G/PLA180C    | 25                   | 180                     | 50                |
| G/PLA190C    | 25                   | 190                     | 50                |
| G/PLA200C    | 25                   | 200                     | 50                |
| G/PLA210C    | 25                   | 210                     | 50                |

3. Process and material characterization

3.1. Mixing behavior analysis
During the mixing process, changes of the stirrer torque were recorded by Lab Station system, Brabender.

3.2. Morphology structure analysis
Scanning electron microscopy (SEM, SU8010, Hitachi, Japan) was used for studying the morphology of graphite/PLA composites. For recording high resolution surface topography, the samples were coated with thin conductive layer of gold deposited by evaporation in vacuum. The structure of the samples from cross-section were observed.

3.3. Chemical structure analysis
FTIR-ATR spectra were measured using the Agilent Technologies Cary 630 FTIR-ATR spectrometer. Parameters used in measurements were: spectral range 400–4000 cm⁻¹, spectral resolution <2 cm⁻¹, wavelength accuracy 0.05 cm⁻¹, signal to noise ratio (1 min, RMS) > 30000:1. The FTIR-ATR spectra were acquired at ambient temperatures from the sample surface.
3.4. **Thermal behavior and stability analysis**

Differential scanning calorimetry (DSC) was performed with a METTLER TOLEDO DSC1 Star System calibrated with pure indium and zinc standards, under nitrogen atmosphere, at gas flow rate 50 cm$^3$/min. Samples of about 5 - 7 mg, sealed in aluminum crucible, were used. The DSC test method consisted of five stages. In the first stage (heating 1), the samples were heated at a constant rate of 10°C/min from 0°C to 300°C. Next was isothermal stage lasting 3 minutes. After this time, the samples were cooled at a rate of 10°C/min to 0°C and remained at this temperature for 3 minutes. This isothermal stage was followed by heating (heating 2) at a rate of 10°C/min to 300°C. The room temperature crystallinity, $X_c$, of PLA composites was evaluated using the following expression:

$$X_c = \left( \frac{\Delta H_m - \Delta H_{cc}}{w \Delta H_m^0} \right) \cdot 100\%$$

where $\Delta H_m$ is the melting enthalpy (J/g), $\Delta H_{cc}$ is the cold crystallization enthalpy (J/g), $\Delta H_m^0$, is the melting enthalpy of 100% crystalline PLA (93 J/g) and $w$ is the fraction of the polymer in the composite materials [11]. The experiment was performed in accordance with the ISO 11357-(1-3): 2009 standard.

3.5. **Melt flow rate properties**

The melt flow rate (MFR) of the composites was determined according to the ISO 1133:2011 standard with a Dynisco LMI 4003 capillary plastometer. The measurements were carried out under the piston loading of 2.16 kg at 190°C.

4. **Results**

4.1. **Mixing behavior analysis**

Changes in the mixer torque are show in Table 3. Loading peak, minimum and end torque during mixing where recorded. No correlation was found between the speed of rotation of the mixer and the loading peak torque. In pure PLA samples, an increase in the speed of rotation of the mixer increases the minimal torque exerted on the blades of the mixer. Minimal torques recorded when mixing PLA with graphite filler are one-third higher. It is worth noting that the final torque measured when mixing pure PLA is higher than the minimum torque. In the presence of filling, no changes were observed. For samples mixed with the speed of 50 rpm and at the temperature from 170 to 210°C, a decrease in the minimum and end torque values was noticed along with the increase in mixing temperature. This effect may be related to the reduction of the polymer viscosity at higher temperatures [12]. This effect is show in Figure 1a and 1b. The decrease in torque as a function of temperature increase is similar to a linear one.
Table 3. Changes in mixer torque.

| Sample       | Loading peak [Nm] | Minimum [Nm] | End [Nm] | Stock temperature [°C] |
|--------------|-------------------|--------------|----------|------------------------|
| PLA          | -                 | -            | -        | -                      |
| NG/PLA30rpm  | 33.8              | 6.4          | 6.5      | 191                    |
| NG/PLA40rpm  | 34.1              | 6.2          | 10.7     | 191                    |
| NG/PLA50rpm  | 30.0              | 7.1          | 9.5      | 192                    |
| NG/PLA60rpm  | 26.2              | 7.5          | 11.9     | 193                    |
| NG/PLA70rpm  | 36.9              | 7.6          | 14.5     | 193                    |
| G/PLA30rpm   | 33.5              | 10.9         | 11.2     | 191                    |
| G/PLA40rpm   | 31.4              | 11.4         | 11.6     | 193                    |
| G/PLA50rpm   | 37.2              | 10.0         | 10.2     | 193                    |
| G/PLA60rpm   | 34.8              | 11.1         | 11.2     | 195                    |
| G/PLA70rpm   | 38.7              | 11.1         | 11.2     | 195                    |
| NG/PLA170C   | 40.5              | 12.2         | 14.7     | 171                    |
| NG/PLA180C   | 38.2              | 11.2         | 11.3     | 183                    |
| NG/PLA190C   | 30.0              | 7.1          | 9.5      | 192                    |
| NG/PLA200C   | 36.7              | 6.0          | 6.0      | 200                    |
| NG/PLA210C   | 26.6              | 4.4          | 4.6      | 210                    |
| G/PLA170C    | 39.0              | 13.7         | 14.1     | 175                    |
| G/PLA180C    | 43.3              | 12.2         | 12.3     | 184                    |
| G/PLA190C    | 37.2              | 10.0         | 10.2     | 193                    |
| G/PLA200C    | 30.3              | 9.5          | 11.3     | 202                    |
| G/PLA210C    | 27.8              | 7.1          | 7.2      | 211                    |

Figure 1. Correlation between minimum/end torque and mixing temperature for non-graphite (a) and graphite containing (b) composites.
4.2. Phase morphology analysis
Figure 2 shows SEM images of PLA and graphite/PLA composites after mixing at 190°C and different mixing speed. Figure 3 shows SEM images of mixed samples with a constant speed of 50 rpm and in the temperature range from 170 to 210°C and graphite filler. The size of the graphite MG3096 flakes was found to be 6 ± 2 µm, respectively. The best dispersion of graphite filler in the matrix seems to be obtained for samples mixed at 40, 50 rpm and in temperature 180-190°C. For this samples the distribution of graphite flakes in the matrix was most homogeneous. No graphite agglomerates or changes in its structure were observed in all sample. Which may indicate a good mixing of the composite.

4.3. Chemical structure analysis
Figures 4 and 5 shows FTIR-ATR spectra of graphite/PLA composites compared with neat PLA sample. The infrared absorption spectra graphite/PLA composites contain the bands that are assigned to the PLA-based polymer [13]. Two bands at 755 and 869 cm\(^{-1}\) are attributed to the crystalline and amorphous phases of the polymer. The stretching modes of the C-CH\(_3\) group appear at 1041 cm\(^{-1}\) while the symmetric and asymmetric stretching modes of the C-O-C group appear at 1081 (symm.), 1180 and 1266 cm\(^{-1}\) (asymm.), respectively. The band at 1128 cm\(^{-1}\) is assigned to the rocking modes of the CH\(_3\) group. Characteristic of the CH and CH\(_3\) symmetric bending modes appear at 1357 and 1382 cm\(^{-1}\) while the band corresponding to the asymmetric bending modes is found at 1452 cm\(^{-1}\). Then, the C=O stretching modes of the ester group appear at 1746 cm\(^{-1}\). There are also weak bands at 2945 and 2994
attributed to the asymmetric stretching modes of the CH$_3$ group. The presence of graphite fillers does not affect the position and relative intensities of the characteristic PLA bands. However, due to the presence of the delocalized $\pi$-electrons that affect the optical properties of graphite, there is a strong correlation between the graphite content and the intensity of the absorption background [14]. When the size of the graphite grains are comparable with the wavelength of IR radiation (4 – 20 µm), the strong absorption background from the graphite fillers partially obscures the characteristic bands from PLA matrix.

![Figure 4](image1.png)

**Figure 4.** FTIR-ATR spectra of PLA, G/PLA30rpm, G/PLA40rpm, G/PLA50rpm, G/PLA60rpm, G/PLA70rpm.

![Figure 5](image2.png)

**Figure 5.** FTIR-ATR spectra of PLA, G/PLA170C, G/PLA180C, G/PLA190C, G/PLA200C, G/PLA210C.
4.4. Thermal behavior and stability analysis

Figures 6 and 7 show the DSC curves of PLA masterbatches recorded during the first heating. Thermal data such as the glass transition temperature ($T_g$), crystallization temperature ($T_c$), cold crystallization temperature ($T_{cc}$), melting temperature ($T_m$), crystallization enthalpy ($\Delta H_c$), cold crystallization enthalpy ($\Delta H_{cc}$), melting enthalpy ($\Delta H_m$) and polymer crystallinity ($X_c$) are summarized in the Table 4. Around 58-64°C (heating 1 and 2) was seen endothermic, glass transition of PLA peak. Graphite addition does not change the $T_g$ of PLA. This may prove the lack of influence of the carbon filler used on limiting the mobility of the polymer chains due to the weak interaction between graphite grains and PLA matrix [11]. During heating 1, cold crystallization peak of PLA appears between 110 to 116°C for samples without graphite and between 95 to 114°C for samples with graphite. The lower $T_{cc}$ temperature was observed for the samples mixed at 40-70 rpm and at a temperature between 190 and 210°C. Differences in cold crystallization enthalpy, $\Delta H_{cc}$, are clearly seen. The cold crystallization enthalpy of samples containing graphite is lower than for NG/PLA samples. The lower crystallization enthalpy and its temperature favor less perfect crystallites [11]. The melting point, $T_m$, of all samples is comparable. The melting enthalpy, $\Delta H_m$, of the NG/PLA sample is similar to the PLA, about 25-29 J/g, and higher than the melting enthalpy of the graphite containing samples, 6.5 - 30 J/g. For samples mixed in speed 70 rpm and in temperature 200 and 210°C, higher melting enthalpy was saw. Since the degree of crystallinity of samples containing graphite and NG/PLA samples is at a similar level it can be assumed that the quality of the formed crystallites is responsible for the change of the melting enthalpy. In the first and second heating for samples noncontaining graphite bimodal, endothermic process (approx. 150-160°C) has been registered. The presence of two melting peaks (overlapping) indicates the reorganization of classic crystals after melting into spherulites of a greater lamellar thickness, melting at a higher temperature. The source of double peaks may also be the presence of two species of crystallites of different size, disorder, or type [15]. The first, lower melting peak (approx. 150°C) is attributed to the melting and recrystallization of the primary crystals into a more stable form. The second, higher (approx. 160°C) corresponds to the melting of the newly formed crystals [16]. This effect was not observed for samples containing graphite. There were no crystallization peaks during cooling recorded for all samples.

Crystallinity of $X_c$ at room temperature in pure polymer (PLA) decreased after each heating cycle. $X_c$ estimated on the basis of the first heating curve was 29%. After the melting process (NG/PLA sample), $X_c$ had dropped to almost 0%. The second heating caused the crystallinity to drop to almost zero in the samples containing PLA, NG/PLA and graphite. The presence of graphite admixture causes a slight increase in crystallinity during the first heating cycle for samples G/PLA70rpm (35%), G/PLA200C (20%) and G/PLA210C (13%). In the second heat all samples showed amorphic structure.
### Table 4. Thermal data obtained by DSC for PLA and graphite/PLA composites.

| Code          | Heating 1 | Heating 2 |
|---------------|-----------|-----------|
|               | $T_m^1$ | $\Delta H_m^1$ | $T_g^1$ | $T_{cc}^1$ | $\Delta H_{cc}^1$ | $X_c^1$ | $T_m^2$ | $\Delta H_m^2$ | $T_g^2$ | $T_{cc}^2$ | $\Delta H_{cc}^2$ | $X_c^2$ |
| PLA           | 145.2 | 29.4 | 64 | 116.6 | 2.11 | 29 | 151.5 | 0.6 | 58.5 | - | - | 1 |
| NG/PLA30rpm   | 151.9 | 26.3 | 58.4 | 112.9 | 26.3 | 0 | 151.2 | 11.5 | 59.0 | 128.3 | 10.4 | 1 |
| NG/PLA40rpm   | 152.1 | 28.3 | 59.4 | 112.1 | 28.2 | 0 | 150.6 | 22.6 | 59.0 | 125.9 | 22.1 | 1 |
| NG/PLA50rpm   | 152.1 | 24.7 | 59.2 | 112.0 | 25.0 | 0 | 151.1 | 14.3 | 58.7 | 128.1 | 13.6 | 1 |
| NG/PLA60rpm   | 151.6 | 26.6 | 58.0 | 112.1 | 26.6 | 0 | 150.8 | 15.0 | 59.8 | 127.9 | 15.2 | 0 |
| NG/PLA70rpm   | 151.8 | 28.1 | 59.3 | 110.9 | 28.3 | 0 | 151.0 | 11.1 | 59.2 | 128.9 | 11.3 | 0 |
| G/PLA30rpm    | 154.4 | 6.5 | 60.1 | 128.8 | 6.8 | 0 | 149.2 | 14.9 | 58.5 | 125.0 | 14.9 | 0 |
| G/PLA40rpm    | 154.5 | 20.7 | 58.7 | 101.5 | 16.7 | 6 | 150.0 | 12.1 | 58.9 | 126.8 | 11.6 | 1 |
| G/PLA50rpm    | 151.9 | 18.2 | 59.2 | 101.5 | 17.6 | 1 | 150.0 | 12.9 | 59.4 | 127.1 | 12.1 | 1 |
| G/PLA60rpm    | 152.6 | 20.2 | 58.3 | 114.1 | 20.1 | 0 | 149.5 | 12.9 | 58.6 | 126.6 | 12.3 | 1 |
| G/PLA70rpm    | 153.2 | 30.6 | 59.5 | 95.3 | 6.5 | 35 | 149.6 | 13.8 | 58.7 | 126.4 | 13.0 | 1 |
| NG/PLA170C    | 150.3 | 25.7 | 58.1 | 111.1 | 25.4 | 0 | 150.8 | 17.8 | 58.3 | 126.8 | 17.2 | 1 |
| NG/PLA180C    | 150.0 | 28.7 | 57.8 | 109.9 | 27.2 | 2 | 150.6 | 16.4 | 58.7 | 127.0 | 15.8 | 1 |
| NG/PLA190C    | 152.1 | 24.7 | 59.2 | 112.0 | 25.0 | 0 | 151.1 | 14.3 | 58.7 | 128.1 | 13.6 | 1 |
| NG/PLA200C    | 151.0 | 27.7 | 59.4 | 110.4 | 26.7 | 1 | 150.8 | 16.7 | 59.2 | 128.0 | 16.8 | 0 |
| NG/PLA210C    | 150.9 | 28.7 | 58.8 | 110.2 | 28.6 | 0 | 151.1 | 12.8 | 58.9 | 128.3 | 12.8 | 0 |
| G/PLA170C     | 151.1 | 19.5 | 57.8 | 113.2 | 19.2 | 0 | 149.7 | 17.2 | 59.6 | 124.8 | 15.8 | 2 |
| G/PLA180C     | 153.3 | 20.0 | 59.1 | 114.0 | 19.9 | 0 | 150.7 | 12.3 | 59.6 | 127.3 | 12.4 | 0 |
| G/PLA190C     | 151.9 | 18.2 | 59.2 | 101.5 | 17.6 | 1 | 150.0 | 12.9 | 59.4 | 127.1 | 12.1 | 1 |
| G/PLA200C     | 154.3 | 24.3 | 57.3 | 98.3 | 10.6 | 20 | 149.6 | 14.3 | 59.1 | 126.3 | 14.2 | 0 |
| G/PLA210C     | 150.0 | 25.8 | 58.4 | 101.8 | 16.5 | 13 | 148.4 | 14.5 | 58.2 | 124.7 | 14.3 | 0 |
Figure 6. DSC thermograms for samples prepared at the temperature of 190°C and different mixing speed – heating 1.

Figure 7. DSC thermograms for samples prepared at mixing speed of 50 rpm and different temperatures – heating 1.
4.5. Melt flow rate properties
Table 5 and Figures 8, 9 summarize the MFR results for individual samples.

| Sample          | MFR [g/10min] |
|-----------------|---------------|
| PLA             | 11.6          |
| NG/PLA30rpm     | 12.6          |
| NG/PLA40rpm     | 18.3          |
| NG/PLA50rpm     | 25.1          |
| NG/PLA60rpm     | 25.3          |
| NG/PLA70rpm     | 27.7          |
| G/PLA30rpm      | 4.7           |
| G/PLA40rpm      | 5.9           |
| G/PLA50rpm      | 5.7           |
| G/PLA60rpm      | 6.5           |
| G/PLA70rpm      | 8.9           |
| NG/PLA170C      | 15.5          |
| NG/PLA180C      | 24.0          |
| NG/PLA190C      | 25.1          |
| NG/PLA200C      | 26.6          |
| NG/PLA210C      | 31.3          |
| G/PLA170C       | 7.4           |
| G/PLA180C       | 7.8           |
| G/PLA190C       | 8.3           |
| G/PLA200C       | 10.1          |
| G/PLA210C       | 22.1          |

For samples obtained at the same temperature and at different stirring speeds without graphite, a significant increase in the MFR value (from 12.6 to 25.1 g/10min) in the range from 30 to 50 rpm was observed. In the range from 50 to 70 rpm, the increase in the MFR value also occurs, but it is much smoother. The dependence of the increase in the MFR value on the mixing speed also occurs for the samples with graphite. However, the MFR increments for these samples are much smaller than for the nongraphite samples. The samples obtained at the same speed but at different mixing temperatures also show changes in the course of the MFR value increase, depending on the presence or absence of graphite in the composition. For samples without graphite, the greatest increase in the MFR value occurs at a temperature between 170 and 180°C. For samples with graphite, the greatest increase in the value was observed between 200 and 210°C. The MFR values of all samples with the addition of graphite, except for sample obtained at the highest temperature G/PLA210C, are lower than the original PLA. This may be due to an increase in flow resistance associated with the use of solid filler [17], [18]. During thermal processing, polylactide is partially degraded. Based on the obtained results, it can be assumed that the addition of graphite shifted the polymer degradation to higher mixing speed and temperature [19]. However, this discovery requires further research.
5. Conclusions
The correct distribution of the additive in the polymer matrix is most important in the preparation of polymer masterbatches. The proposed method, using a kneading mixer, is characterized by good homogenization. Introduction of graphite fillers into PLA matrix resulted in the modification of the thermal and rheological properties of the composites without changes in the chemical structure of the polymer. The lack of changes is confirmed by the results of the FTIR-ATR analysis and the lack of major differences in the glass transition temperature and melting temperature between the powdered polymer (PLA) and mixed samples. The addition of graphite lowered the cold crystallization temperature without changes in other thermal properties of the sample. Based on the results of the melt flow rate (MFR) analysis, it can be assumed that the addition of graphite shifted the polylactide degradation conditions to higher temperatures and rotation mixing speeds. However, confirmation of this observation requires further work involving the measurement of the intrinsic viscosity of polymer solutions. It seems that the best properties (best homogenization, without deterioration of other parameters) were obtained for samples mixed at a speed of 40-50 rpm and at a temperature of 180-190°C. The biggest disadvantage of the proposed method is its efficiency, which is worsened by the small mass of the obtained sample and the time needed to clean the mixer before re-use. The low demand for raw materials, compared to the method of obtaining masterbatches with the use of extruders, may be an advantage in laboratory/scientific applications.

References
[1] Ahmed J, Mulla M Z, Vahora A, Bher A, Auras R 2021 Polylactide/graphene nanoplatelets composite films: Impact of high-pressure on topography, barrier, thermal, and mechanical properties Polym. Compos 42 2898–2909
[2] Arriagada P, Palza H, Palma P, Flores M, Caviedes P 2018 Poly(lactic acid) composites based on graphene oxide particles with antibacterial behavior enhanced by electrical stimulus and biocompatibility J. Biomed. Mater. Res. A 106 1051–1060
[3] Bartczak Z, Galeski A, Kowalczyk M, Sobota M, Malinowski R 2013 Tough blends of poly(lactic acid) and amorphous poly([R,S]-3-hydroxy butyrate) – morphology and properties Eur. Polym. J. 49 3630–3641
[4] Batakliev T, Georgiev V, Kalupgian C, Muñoz P A R, Ribeiro H, Fechine G J M, Andrade R J E, Ivanov E, Kotsilkova R 2021 Physico-chemical Characterization of PLA-based Composites Holding Carbon Nanofillers Appl. Compos. Mater. 28 1175–1192
[5] Bieliński M, Kotewicz P 2010 Technologiczne aspekty recyklingu tworzyw porowatych Inż. Apar. Chem. 20–21
[6] Botta L, Scaffaro R, Sutera F, Mistretta M C 2018 Reprocessing of PLA/Graphene Nanoplatelets Nanocomposites Polymers 10 18
[7] Chakraborty G, Valapa R B, Pugazhenthi G, Katiyar V 2018 Investigating the properties of poly (lactic acid)/exfoliated graphene based nanocomposites fabricated by versatile coating approach Int. J. Biol. Macromol. 113 1080–1091
[8] Gao Y, Picot O T, Tu W, Bilotti E, Peijs T 2018 Multilayer coextrusion of graphene polymer nanocomposites with enhanced structural organization and properties J. Appl. Polym. Sci. 135 46041
[9] Gurunathan T, Mohanty S, Nayak S K 2015 A review of the recent developments in biocomposites based on natural fibres and their application perspectives Compos. Part Appl. Sci. Manuf. 77 1–25
[10] Kim M, Jeong J H, Lee J Y, Capasso A, Bonaccorso F, Kang S H, Lee Y K, Lee G H 2019 Electrically Conducting and Mechanically Strong Graphene–Polylactic Acid Composites for 3D Printing ACS Appl. Mater. Interfaces 11 11841–11848
[11] Kister G, Cassanas G, Vert M 1998 Effects of morphology, conformation and configuration on the IR and Raman spectra of various poly(lactic acid)s Polymer 39 267–273
[12] Kotsilkova R, Angelova P, Batakliev T, Angelov V, Di Maio R, Silvestre C 2019 Study on Aging and Recover of Poly (Lactic) Acid Composite Films with Graphene and Carbon Nanotubes Produced by Solution Blending and Extrusion Coatings 9 359

[13] Kuzmenko A B, van Heumen E, Carbone F, van der Marel D 2008. Universal Optical Conductance of Graphite Phys. Rev. Lett. 100 117401

[14] Li M X, Kim S H, Choi S W, Goda K, Lee W I 2016 Effect of reinforcing particles on hydrolytic degradation behavior of poly (lactic acid) composites Compos. Part B Eng. 96 248–254

[15] Murariu M, Dechief A L, Bonnaud L, Paint Y, Gallos A, Fontaine G, Bourbigot S, Dubois P 2010 The production and properties of polylactide composites filled with expanded graphite Polym. Degrad. Stab. 95 889–900

[16] Passaglia E, Coiai S, Augier S 2009 Control of macromolecular architecture during the reactive functionalization in the melt of olefin polymers Prog. Polym. Sci. 34 911–947

[17] Przekop R E, Kujawa M, Pawlak W, Dobrosielska M, Sztorch B, Wieleba W 2020 Graphite Modified Polylactide (PLA) for 3D Printed (FDM/FFF) Sliding Elements Polymers 12 1250

[18] Raquez J M, Habibi Y, Murariu M, Dubois P 2013 Polylactide (PLA)-based nanocomposites Prog. Polym. Sci. Progress in Bionanocomposites: from green plastics to biomedical applications 38 1504–1542

[19] Speranza V, De Meo A, Pantani R 2014 Thermal and hydrolytic degradation kinetics of PLA in the molten state Polym. Degrad. Stab. 100 37–41