Influence of the parameters of the extrusion process on the properties of PLA composites with the addition of graphite

K Fiedurek¹, P Szroeder², M Macko³, A Raszkowska-Kaczor⁴ and N Puszczykowska⁴

E-mail: kacper.fiedurek@impib.lukasiewicz.gov.pl

¹ Kazimierz Wielki University, J.K. Chodkiewicza 30, 85-064 Bydgoszcz
² Institute of Physics, Kazimierz Wielki University, Powstańców Wielkopolskich 2, 85-090 Bydgoszcz, Poland; (P.S.)
³ Faculty of Mechatronics, Kazimierz Wielki University, Kopernika 1, 85-074 Bydgoszcz, Poland;
⁴ Łukasiewicz Research Network - Institute for Engineering of Polymer Materials and Dyes, Marii Skłodowskiej-Curie 55, 87-100 Toruń, Poland;

Abstract. The main purpose of the work is to determine the influence of the screw diameter on the parameters of the single screw extrusion process, such as power consumption, torque, throughput, the actual temperature of the melt on the extruder die, as well as phase s with the use of a laboratory single-screw extruder. The research was carried out with the use of various plasticizing systems. Two types of graphite: pre-expanded and normal grade with different grain sizes were used in the research. Flammability tests of the obtained composites were carried out using cone calorimeter.

1. Composite preparing in extrusion process – influence of plasticising unit and components particle size on extrudate’s dispersion quality

Extrusion process is a most common method for physical modification of thermoplastic polymers. Products of these modification are called composites, compounds or polymer compositions, and process name is often referred as compounding [1, 2].

Main advantages of compounding processes are connected with relative acceptable cost affordability, good efficiency and ease of production. Main drawback of process is connected with nature of physical modifications – their impact on material is a way lower than in chemical modifications [3].

Most common equipment used for preparing thermoplastic polymer composites for laboratory purposes, as well as in industrial and full scale production are various types of extruders and extrusion lines. Extrusion process can be described simply as continuous feeding, plasticizing, mixing and forming of composite’s stream. Extruding lines are composed with variety of units, such as dryers, dosing/feeding units, water baths, calibrating units, conveyors, cutting units, pelletizers and others, but most crucial element of extrusion line, as the name indicates, is the extruder [4].

Extruder comprises few systems, starting with plasticizing unit, consisted with two major parts: screw and barrel, where usually barrel is usually stocked-still, and the screw is rotating inside barrel by
drive system (motor and gearbox). Heating/cooling zones, located on the barrel, contains band, cartridge or induction heaters, fans or water chambers for air or liquid cooling respectively and thermocoupling sets – all elements are managed by digital controller to ensure constant temperatures sets of zones. Entrance of ingredients to barrel is provided through hopper and leaves device through dies on extruder head [5].

The extrusion process definition mentioned above can be used to describe any extruding operations, however, compounding is focused mostly on proper mixing of provided components. Most basic type of extruders with single-screw plasticizing units are used mainly for shaping polymers into usable details (films, sheets, profiles, pipes, filaments) in order to good compression-build abilities. Unfortunately, single-screw construction is unable to provide sufficient mixing and shearing forces – only place, where shear forces occur is between external edges of screw and barrel. Screw can be designed to provide more edge surface, while drastically decreasing pressure-buildup and throughput. For achieving great mixing and shearing, co-rotating twin screw extruders were developed. In this constructions, internal surface of barrel is increased, and new shear forces, especially between two screws occur and can be strengthened by special shaping and configuration of screws (backing, kneading, star-like mixing screw elements). Screws are usually made as segmental constructions to allow fast and cost-friendly changes of configurations in case of providing best processing parameters and proper mixing of various polymers and additives [5, 6]

However, twin-screw extruders bear some disadvantages, such as inability to build high, constant pressure needed to form dimensionally-stable details. To solve this problem, melt pumps, melt accumulators and cascade systems are used. While two first solutions are relatively cheap, they can affect on melt stability (burning leftovers on gearwheels of pumps and walls of devices), and cascade systems are nothing more than two separate lines (twin screw co-rotating as first extruder, single or twin counter-rotating as second), connected through melt adapter, while second, shaping extruder can be shorter in case of skipping plasticizing and mixing processes, already made in first extruder. It is highly effective, but expensive solution [7].

The biggest disadvantage of co-rotating screw solutions is the price – taking screw diameter as comparative parameter, price of twin screw extruder itself is from 5 to 10 times bigger than single screw. Costs are generated by sophisticated gearbox, set of screws with shafts, and shape of barrel.

As one of methods to provide better filler particle distribution in polymer matrix, especially with insufficient mixing and shearing properties of extruder, is pre-mixing of components before feeding. Pre-mixing is common for fragile poly(vinyl chloride) processing, due to provide stabilizers in whole mixture’ mass and to omit necessity of harsh mixing and shearing in extrusion temperatures, causing rapid degradation of PVC [8].

Pre-mixing process is restricted by grain size of components and their density – while similar components can be distributed evenly in mixture, 3-4 mm in diameter pellets with 50-100 μm powders are tend to separate and sediment from each other at transportation systems and feeder trays. As a result, obtained composite material can be very unequal.

PLA is the most common thermoplastic biodegradable polymer commercially available. Material found many applications in today’s use. PLA as neat resin bear many disadvantages, so usage of pure resin is limited and fitting properties to different requirements is obtained by compounding processes [9, 10].

Graphite is one of common additive used in compounding of various polymers, acting as colorant, nucleating agent, heat transfer promoter, processing additive and physico-mechanical modifier. Pre-expandable graphite, due to ability of expanding it’s structure in high temperatures (intumescent), what causes sealing other particles, as well as exude of inflammable CO₂ [11, 12, 13, 14, 15].

This work focuses on the mechanical parameters of the composite extrusion process at one of the cheapest methods – extruding pre-mixed components on laboratory single screw extruder. Obtained results show that the same geometry, but different diameter of screws result in change of the thermal and melt flow properties. We also consider processing influence on flammability of the composites. Research comprises two graphite types as fillers, unmodified and pre-expandable graphite flakes.
2. Equipment, materials, sample preparation and research methodology

2.1. Processing equipment
For research purposes, experimental single screw extruder with two changeable plasticizing units, produced by Research Network Lukasiewicz – Institute for Engineering of Polymer Material and Dyes was used. Both used units are alike and have the same shaping, length to diameter (L/D) ratio, height of shaft and coils ratio and compression rate (2,85:1), same number of coils and with coil pitches lengths exact with screw diameters. The difference are diameters (12 mm and 14 mm screw respectively). The temperatures of zones and screw speed were set even for every composition and plasticizing unit configuration. Initial parameters are listed in table 1.

| Parameter                  | Designation | Value |
|----------------------------|-------------|-------|
| L/D ratio                  | -           | 27    |
| Screw speed                | RPM         | 100   |
| Temperature – zone I       | °C          | 175   |
| Temperature – zone II      | °C          | 180   |
| Temperature – ext. head    | °C          | 185   |

Cone calorimeter samples were prepared on pneumatic press ARGENTA AW03 with 100x100x5 mm flat form, at temperature of liner heaters set to 190 °C.

2.2. Materials
Polylactide (PLA) in form of 80 µm medium and 90 µm maximum sized grains, melt flow ratio 10-30 g/10 min and density of 1,25 g/cm³ was supplied from AXALTA Coatings, Switzerland. Two grades of flake graphite (GR), normal and pre-expanded were kindly delivered by Institute of Carbon Technologies, Torun, Poland. Pre-expanded graphite with C4N E90 symbol, 400 µm approx. diameter of flakes, and normal graphite C4N M88 with 150 µm approx. diameter.

2.3. Sample Preparation
PLA/GR composites were made on single screw laboratory extruder mentioned in 2.1 paragraph. Components were weighted and pre-mixed in hand mixer to achieve homogenous mixture. After mixing, materials were fed by volumetric dosing unit to extruder hopper. Composite left device in the form of straws, transported on belt conveyor with air cooling (fans) to stand-alone pelletizer. Obtained pellets were ready to use in further research examinations.

Composites contents are listed below in table 2.
Table 2. Composites contents

| Code          | PLA(wt%) | Graphite(wt%)     |
|---------------|----------|------------------|
| PLA – Ø12     | 100      | -                |
| PLA/E90/1 – Ø12 | 99      | C4N E90(1)       |
| PLA/E90/5 – Ø12 | 95      | C4N E90(5)       |
| PLA/M88/1 – Ø12 | 99      | C4N M88(1)       |
| PLA/M88/5 – Ø12 | 95      | C4N M88(5)       |
| PLA – Ø14     | 100      | -                |
| PLA/E90/1 – Ø14 | 99      | C4N E90(1)       |
| PLA/E90/5 – Ø14 | 95      | C4N E90(5)       |
| PLA/M88/1 – Ø14 | 99      | C4N M88(1)       |
| PLA/M88/5 – Ø14 | 95      | C4N M88(5)       |

For cone calorimeter examination, pellets were melted and then pressed to form 100x100x5 mm sheet on pneumatic press mentioned in paragraph.

Other paragraphs are indented (BodytextIndented style).

2.4. Research methodology
PLA/GR composites were made on single screw laboratory extruder mentioned in 2.1 paragraph. Components were weighted and pre-mixed in hand mixer to achieve homogenous mixture.

2.4.1. Extrusion process parameter comparison
The temperatures of zones and screw speed were set even for every composition and plasticizing unit configuration. Initial parameters are listed in table 1, while actual measured processing parameters are shown below in table 3.

Table 3. actual measured parameters of process

| Parameter               | Designation |
|-------------------------|-------------|
| Torque on screw         | Nm          |
| Motor current           | A           |
| Temperature – zone I    | ºC          |
| Temperature – zone II   | ºC          |
| Temperature – ext. head | ºC          |
| Throughput              | kg/h        |
2.4.2. Phase morphology analysis
Scanning electron microscopy (SEM, SU8010, Hitachi, Japan) was used for studying the morphology of both the pure PLA resin and PLA/Graphite composites. For SEM imaging, composite straws were broken, and breakthrough surface was sputtered with gold.

2.4.3. Melt Flow Ratio (MFR) measurement
For research purposes, MFR measurement were conducted on LMI 4003 Plastometer (DYNISCO, USA), partially according to PN-EN ISO 1133:2011 standard. Due to too rapid flow of composites with E90 content, special method of measurement was developed – after 5 minutes of heating polymer inside device cylinder, piston and load were applied and one outflows from whole measurement section was gathered and weighted. Procedure was repeated five times for every composite. The measurements were carried out under the piston load of 2.16 kg at 190°C and 1 mm die.

2.4.4. Thermal properties measurement
Differential scanning calorimetry (DSC) was performed with a METTLER TOLEDO DSC1 calibrated with pure indium and zinc standards, under nitrogen atmosphere, at gas flow rate 50 cm3/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 experiment was performed in accordance with the ISO 11357-(1-3): 2009 standards.

2.4.5. Cone Calorimeter flammability testing
The cone calorimeter testing was conducted on FIRE TESTING TECHNOLOGY iCONE CLASSIC where specimens with dimensions of 100 mm x 100 mm x 5 mm were placed on testing plate layered with aluminum foil and placed under the burner of device. Heat flux was set on 50 kW/m². Final result is the mean of burning two specimens made from the same composite.

The experiment was performed according to the ISO 5660: 2002 standard.

3. Results

3.1. Extrusion process parameter comparison
Extrusion process real parameters were obtained as average value on graph from extruder sensors shown on control panel of device, while throughput was measured as mean of three 2-minute gatherings of pellets from pelletizer. Results are listed on table 4.
Table 4. process actual measured parameters

| Code            | Temp – zone I (°C) | Temp – zone II (°C) | Temp – head (°C) | Throughput (kg/h) | Torque (Nm) | Current (A) |
|-----------------|--------------------|---------------------|------------------|-------------------|-------------|-------------|
| PLA – Ø12       | 174                | 180                 | 185              | 0.581             | 1.70        | 1.39        |
| PLA/E90/1 – Ø12 | 174                | 180                 | 185              | 0.561             | 1.68        | 1.38        |
| PLA/E90/5 – Ø12 | 176                | 181                 | 185              | 0.600             | 1.67        | 1.37        |
| PLA/M88/1 – Ø12 | 175                | 180                 | 185              | 0.622             | 1.65        | 1.36        |
| PLA/M88/5 – Ø12 | 175                | 180                 | 185              | 0.568             | 1.68        | 1.68        |
| PLA – Ø14       | 171                | 180                 | 184              | 1.048             | 1.70        | 1.39        |
| PLA/E90/1 – Ø14 | 173                | 180                 | 185              | 0.960             | 1.71        | 1.40        |
| PLA/E90/5 – Ø14 | 172                | 181                 | 185              | 1.080             | 1.68        | 1.38        |
| PLA/M88/1 – Ø14 | 174                | 180                 | 185              | 1.220             | 1.70        | 1.38        |
| PLA/M88/5 – Ø14 | 174                | 181                 | 185              | 0.990             | 1.68        | 1.38        |

Parameters obtained from extrusion process reveals no significant differences on motor current and torque on screw for both of plasticizing units, while throughput on 14 mm diameter plasticizing unit increased from 71 to 91 % in comparison to 12 mm unit.

What is more, 1 % of M88 graphite increased throughput in comparison to neat resin on both 12 and 14 mm diameter units – 7 and 16 % respectively, while 5 % addition decreases throughput value – 2 and 5 % respectively. Opposite influence was observed in E90 graphite case. 1 % of this filler lower throughput to 3,5 and 8 %, whilst 5 % concentration increased this parameter 3 % on both units.

3.2. Phase morphology analysis
SEM images of PLA/Graphite composites after extrusion are shown on figure 1. In samples with E90, size of filler flakes is found to be 400 µm approximately, while for flakes of MG192 size is 107 µm approx.

Figure 1. SEM images of PLA/Graphite composites after extrusion

SEM images reveal good dispersion of fillers in both plasticizing units used in work. Samples with 5% content of graphites are more accurate for dispersion observations due to higher concentration of additive particles.
3.3. Melt Flow Ratio (MFR) measurement

MFR results for individual samples are listed on table 5.

| Sample          | MFR (g/10 min) |
|-----------------|----------------|
| PLA – Ø12       | 66.23          |
| PLA/E90/1 – Ø12 | 137.13         |
| PLA/E90/5 – Ø12 | 155.1          |
| PLA/M88/1 – Ø12 | 50.00          |
| PLA/M88/5 – Ø12 | 39.22          |
| PLA – Ø14       | 53.33          |
| PLA/E90/1 – Ø14 | 70.82          |
| PLA/E90/5 – Ø14 | 126.35         |
| PLA/M88/1 – Ø14 | 50.33          |
| PLA/M88/5 – Ø14 | 36.87          |

Melt Flow Ratio is one of common method used in examination of polymer and their composites, and, among others, in comparable trials can reveal degradation processes. Results of measurement indicates, that addition of E90 pre-expanded graphite increases MFR value, while using M88 graphite cause decrease in parameter value on both plasticizing systems. However, 12 mm diameter unit tends to degrade material to greater extent than 14 mm unit.

3.4. Thermal properties measurement

Data obtained by DSC method are listed on table 6.

| Sample          | Heating 1 | Cooling | Heating 2 |
|-----------------|-----------|---------|-----------|
|                 | $T_m$ [°C] | $\Delta H_m$ [J/g] | $T_g$ [°C] | $\Delta H_g$ [J/g] | $T_c$ [°C] | $\Delta H_c$ [J/g] | $T_m$ [°C] | $\Delta H_m$ [J/g] | $T_g$ [°C] | $\Delta H_g$ [J/g] | $T_c$ [°C] | $\Delta H_c$ [J/g] |
| PLA – Ø12       | 172.20     | -51.83  | 65.45     | - | - | 176.01 | -40.04 | 59.14 | 108.03 | 35.30 |
| PLA/E90/1 – Ø12 | 175.16     | -48.16  | 57.28     | 102.87 | 33.24 | 96.08  | 6.50  | 167.13 | -46.66 | 59.00 | 105.02 | 28.94 |
| PLA/E90/5 – Ø12 | 173.38     | -54.42  | 57.16     | 98.38  | 30.05 | 98.70  | 23.29 | 167.40 | -48.61 | 59.02 | 103.86 | 25.36 |
| PLA/M88/1 – Ø12 | 173.86     | -55.23  | 58.06     | 99.53  | 30.51 | 100.22 | 35.27 | 163.24 | -45.35 | 57.14 | 95.67 | 7.68  |
| PLA/M88/5 – Ø12 | 174.71     | -52.57  | 57.50     | 97.52  | 29.83 | 98.55  | 23.41 | 167.03 | -50.35 | 60.10 | - | - |
| PLA – Ø14       | 173.08     | -49.52  | 60.01     | 98.35  | 28.30 | 101.38 | 33.37 | 167.58 | -40.82 | 61.30 | 100.18 | 14.67 |
| PLA/E90/1 – Ø14 | 175.43     | -50.71  | 58.07     | 99.04  | 31.30 | 96.73  | 8.56  | 166.75 | -46.90 | 58.84 | 92.35 | 3.55  |
| PLA/E90/5 – Ø14 | 173.90     | -51.76  | 59.07     | 99.87  | 32.21 | 100.05 | 33.35 | 166.90 | -46.40 | 59.73 | 99.68 | 13.54 |
| PLA/M88/1 – Ø14 | 174.09     | -51.88  | 58.08     | 99.05  | 28.86 | 100.71 | 36.80 | 165.44 | -40.14 | 59.54 | 89.67 | 3.07  |
| PLA/M88/5 – Ø14 | 174.59     | -55.38  | 59.19     | 99.36  | 31.56 | 97.37  | 31.84 | 167.28 | -49.53 | 59.80 | 96.18 | 5.86  |
| PLA/M88/7 – Ø14 | 174.21     | -51.45  | 57.81     | 99.38  | 29.86 | 99.89  | 31.64 | 167.23 | -46.10 | 60.75 | 93.02 | 3.46  |
Table 6 shows the values of the glass transition temperature (Tg), cold crystallization (Tcc), melting temperature (Tm), crystallization temperature (Tc), crystallization enthalpy (∆Hc), cold crystallization enthalpy (∆Hcc) and melting enthalpy (∆Hm). Fig. … presents a comparison of the DSC curves of individual composites for heating 1 and heating 2.

Based on the DSC research, it appears that the addition of carbon fillers does not affect the glass transition temperature values in relation to pure PLA processed in the extruder.

The glass transition temperature is in the range of 58-60 °C. This is probably due to the weak interaction between graphite particles and polylactide particles [14].

The values of the melting points and the enthalpy of melting in heating 1 are similar for all samples, filled and unfilled.

During the tests, for all the tested samples, except for pure, unprocessed PLA, the crystallization peak was observed. In the case of composites with the addition of carbon fillers, an increase in the enthalpy of crystallization was observed in relation to unfilled samples.

The melting points of all samples in heating step 2 are similar and are in the range (approx. 166 - 168 °C). The addition of graphite, similarly to the heating stage 1, did not cause significant changes in the value of this temperature. The glass transition temperature values did not change significantly after adding carbon fillers.

The addition of carbon fillers reduced the value of the cold crystallization temperature in relation to the values obtained for PLA 0, PLA AX 12, PLA AX 14. It was observed that the addition of graphite reduces the cold crystallization enthalpy.

3.5. Cone Calorimeter flammability testing

Cone calorimeter examination was conducted on 100x100x5 mm specimens made on heated press. Results are listed on table 7.

| Code          | Time to ignition (TTI) [s] | Peak heat release ratio (THRR) [kW/m²] | Total heat release (THR) [kW/m²] | Mass loss rate [g/(s·m²)] | Time to Flameout (TTF) [s] |
|---------------|---------------------------|----------------------------------------|----------------------------------|----------------------------|---------------------------|
| PLA – Ø12     | 38.5                      | 570                                    | 94.8                             | 25.3                       | 337.5                     |
| PLA/E90/1 – Ø12 | 23.5                      | 559                                    | 97.1                             | 20.06                      | 320.5                     |
| PLA/E90/5 – Ø12 | 19                        | 294                                    | 79.7                             | 6.26                       | 752.5                     |
| PLA/M88/1 – Ø12 | 28.5                      | 551                                    | 97.9                             | 23.91                      | 289                       |
| PLA/M88/5 – Ø12 | 30                        | 541                                    | 104.5                            | 23.98                      | 289                       |
| PLA – Ø14     | 36                        | 670                                    | 94.4                             | 28.3                       | 240                       |
| PLA/E90/1 – Ø14 | 22                        | 545                                    | 95.75                            | 20.25                      | 304                       |
| PLA/E90/5 – Ø14 | 22                        | 273                                    | 78.8                             | 6                         | 832                       |
| PLA/M88/1 – Ø14 | 26                        | 517                                    | 98.4                             | 21.49                      | 319                       |
| PLA/M88/5 – Ø14 | 31.5                      | 558.5                                  | 102.5                            | 22.35                      | 292.5                     |

Any addition of pre-expanded graphite (E90) shortens time needed to ignition significantly – in comparison to pure PLA ignition time drops to 15 - 19 seconds less for PLA/E90 composites. Samples with 5 % concentration of E90 exhibit promising flame retardancy effect – despite lowering TTI, mean heat release, particularly peak of this parameter, one of most significant to estimate fire-prevent abilities is decreased nearly by half, as well as total heat release on test is lower than for pure PLA in nearly 15 %. What is more, time needed to burn whole specimen take 2.5 times longer than pure PLA. Observations of specimens during burning show, that addition of pre-expanded graphite prevents composite from dripping during fire exposition.
4. Conclusions

Results show that the screw diameter plays the key role in efficiency of extrusion. Increasing of the plasticizing unit diameter from 12 mm to 14 mm without changing drive and heating systems results in almost twice increase in throughput and does not affect screw torque and motor current.

Phase morphology of obtained composites remains similar internal structure on 12 and 14 mm diameter units.

MFR measurements reveal that composites prepared on 14 mm diameter plasticizing unit are less degraded than composites made on 12 mm unit. Both screws have the same compression ratio, number of coils and coil pitches lengths exact to screw diameter, volume of every coil pitch is bigger on 14 mm unit than on 12 mm. While pitch is filled up with material on feeding zone, deeper and longer pitch contains more material. If there is more material, more heat needs to be delivered to reach temperature – this dependence can be observed on temperatures of first heat zone in table 4. On 12 mm unit temperatures of first zone is near or exact to initial parameter (± 1 degree), while 14 mm system actual temperatures decreased significantly. Process of extrusion was carried out after reaching 175°C and stabilization of temperature on first zone. Temperature drop during processing means that heat transfer was bigger and took more time on 14 mm unit and the material on smaller unit reach temperature faster, so more thermal degradation processes were occurred on 12 mm unit.

Temperature of cold crystallization during second heating decreased by 10 degree Celsius after processing with 14 mm diameter screw. Drop of cold crystallization temperature is also observed.

Incorporation of pre-expandable graphite provides significant improvement in flame-retardancy properties of composite, however application of 12 mm processing unit results in shortening of time to ignition, as well as increase of peak heat release rate and decrease in time to flameout, of proving more degradation rate of the polymer matrix than in 14 mm unit case. Pre-expandable graphite shows promising results to be used as component in flame retardancy additives mix - further investigation is required.
References

[1] Rosato D. V., et al., *Handbook of composites*, Van Nostrand Reinhold Company/Springer US, New York 1982

[2] Jurkowski B., Jurkowska B., *Sporządzanie kompozycji polimerowych*, Wydawnictwa Naukowo-Techniczne, Warsaw 1995, p 14-15

[3] Ibid., p 15-18

[4] Sikora R., *Przetwórstwo tworzyw polimerowych – podstawy logiczne, formalne i technologiczne*, Wydawnictwo Politechniki Lubelskiej, Lublin 2005, p 181, 36, 422

[5] Stasiek J., *Wytłaczanie tworzyw polimerowych – zagadnienia wybrane*, Wydawnictwa Uczelniane Uniwersytetu Technologiczno-Przyrodniczego w Bydgoszczy, Bydgoszcz 2007, p 5-100

[6] Patil H., Tiwari R. V., Repka M. A., *Hot-Melt Extrusion: from Theory to Application in Pharmaceutical Formulation*, AAPS PharmSciTech, 2016 17(1) p 20–42.

[7] Obłój-Muzaj M., Świerz-Motysia B., Szablowska B., *Polichlorek winylu*, Wydawnictwa Naukowo-Techniczne, Warszawa 1997, p 16-59

[8] Obłój-Muzaj M., Świerz-Motysia B., Szablowska B., *Polichlorek winylu*, Wydawnictwa Naukowo-Techniczne, Warszawa 1997, p 60-144

[9] Vasanthi K., *Biodegradable Polymers - A Review*, Polymer Sciences 2017, 3, p 1-7

[10] Smith R. et al., *Biodegradable polymers for industrial applications*, Woodhead Publishing Limited, Abingdon 2005

[11] Yusuf M., et al., *Natural Colorants: Historical, Processing and Sustainable Prospects*, Natural Products and Bioprospecting 2017, 7, p 123–145

[12] Stribeck A., et al., *Scattering of X-rays during melting and solidification of thermoplastic polyurethane. Graphite as nucleating agent and stabilizer of the colloidal melt*, Polymer 2018, 153, p 565-573

[13] Sengupta R., *A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites*, Progress in Polymer Science 2011, 36(5), p 638-670

[14] Thirumal M., et al., *Effect of expandable graphite on the properties of intumescent flame-retardant polyurethane foam*, Journal of Applied Polymer Science 2008, 110(5), p 2586-2594

[15] Wang Z., Han E., Ke W., *Influence of expandable graphite on fire resistance and water resistance of flame-retardant coatings*, Corrosion Science 2007, 49(5), p 2237-2253

[16] Batakliev T. et al, *Physico-chemical characterization of PLA- based composites holding carbon nanofillers*, Applied Composite Materials, 2021, p 1-18