INTRODUCTION TO MODELLING THE CORRELATION
BETWEEN GRAIN SIZES OF FEED MATERIAL AND THE STRUCTURE AND EFFICIENCY
OF THE PROCESS OF CO-ROTATING TWIN-SCREW EXTRUSION
OF NON-FLAMMABLE COMPOSITES WITH A PLA MATRIX

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Abstract: Co-rotating twin-screw extrusion is an energy consuming process that is generally not fully optimised to a specific polymer. From the point of view of the efficiency of the extrusion process, the starting material should be characterised by small grain sizes in comparison to the screw channel area, small surface area to volume ratio and small internal friction between the pellets. To develop a model describing the effect of polylactide (PLA) grain size on the extrusion efficiency, a series of experiments with a twin-screw extruder were carried out during which the energy consumption; torque on shafts and temperature of the melt on the extruder die were monitored. As feed material, both the neat PLA with different grain sizes and the PLA with expandable graphite fillers and phosphorous-based flame retardants were used. Morphology and dispersion quality of the composites were examined using scanning electron microscopy (SEM); flammability, smoke production, mass loss and heat release rates were tested using cone calorimetry; and melt flow rate was determine using a plastometer. Moreover, the thermal properties of the obtained composites were determined using differential scanning calorimetry (DSC). The results show that the choice of the starting material affects both the efficiency of the extrusion process and the flame retardancy properties of the composite materials.

Key words: introduction to modelling; extrusion; parameters of the process; biodegradable polymers; polymers; flame retardancy

1. INTRODUCTION

The extrusion is the most common and the most widely used method in the production of thermoplastic composites and obtaining polymer mixtures with fillers, functional additives and modifiers [1,2]. The compounding process, as well as extrusion in general, can be described as 'constant dosing, transporting, plasticising, mixing and forming a polymer/composite stream' [1]. The greatest advantages of this process include the relatively low cost of energy inputs per kilogram of product, relative simplicity of processing equipment, possible scalability of the process and versatility of solutions. One extruder can be easily adapted to produce composites from different components. This is often done without interfering with mechanical parameters such as the geometry of the plasticising system and the shape of the head. Only the temperature settings, rotational speed of the screw and dosing amount are adjusted [3]. Several types of extruders are known, but for the purpose of producing composites, co-rotating twin-screw extruders are used, which provide a larger available surface of the extruder barrel, which already results in improved mixing properties of the components. The greatest advantage of the twin-screw extruders over the single-screw extruders is the possibility of using interlocking kneading segments, as well as mixing screws, thanks to which the mixing takes place both on the edge (screw-barrel) and on the above-mentioned elements inducing the shear forces [3,4]. The combination of these two features allows for better dispersion of the filler in the polymer matrix, but a limitation of the process is the fact that the shear forces cause an increase in temperature due to friction [5,6]. It is difficult to describe this process mathematically because there are many variables here that are specific both for the polymers themselves and even for polymer-filler systems [7–10]. Often, as modelling is conducted, a single section or even a single-screw element of an extruder is referred. Excessively high temperatures and friction alone can lead to the degradation of the polymer material, where the obtained product may lose its properties, which in turn may translate into problems in the processes of further forming the finished polymer composite.

The selection of the appropriate configuration of the plasticising system can therefore be presented as a search for a compromise between the best mixing of components and the lowest possible degradation of components, especially polymers [11,12]. One way to avoid the impact is to crush commercially available granules of polymers to reach smaller grain sizes [1,13]. The polymers are usually supplied in the form of pellets which are

easy to dose in single-screw extruders and injection moulding machines. The ratio of the bulk density to the actual density is also the parameter that affects the possibility of obtaining the right, high pressure during product formation. In the case of the production of composites, however, the aim is to obtain the best possible distribution of the filler in the polymer matrix, the lowest possible polymer degradation with simultaneous energy savings and the lowest possible wear of mechanical elements of the plasticising system: no high pressure is required, and it is even undesirable; what is more is that some of additives are fragile to temperature, shear forces and residue time in extruder [14–16].

All parameters of the co-rotating twin-screw extrusion process are selected each time because they depend not only on the polymer but also on the fillers and even their amount; so, it is practically impossible to create one, especially theoretical mathematical model, describing this process in its entirety and in every possible way. Combinations of materials, therefore, for the purpose of 'personalised' practical models are made, adequate for a given case, and its properties are also limited [17]. Modelling of this type consists of four parts: the selection of initial parameters and obtaining the assumed properties, components and their form based on the experiment, the next determination of the process input parameters [constants and variables] and the assumed output parameters, the boundaries of which will be used for the model according to the selected model, for example, the Hartley Plan or any other field of experimental research. Then, model calculations are performed, and finally, the model is validated [18–20].

Polylactide [PLA] was chosen as the polymer matrix because it is a biodegradable thermoplastic polymer and is the most produced among biodegradable solutions. It is also a material that, in order to be used in many products, requires modification of properties and additives, which makes it justified to conduct research on eco-friendly composites with the use of this material [21–23].

Carbon fillers are widely used in the processing of polymeric materials. The multitude of carbon structures allows to obtain many modification effects: from more complicated mechanical, cross-linking, thermal, electrical to basic ones, such as colorant and processing additives. Among graphitic fillers, the expandable graphite attracts attention due to its flame retardant properties. If it is heated, the flakes will expand and cut off the access of oxygen, which is called as 'intumescent effect' [1,24–27].

For flame retardant agents used in polymers, three main groups can be highlighted: mineral, chlorinated/brominated and phosphorus-based substances [28]. Mineral substances, such as aluminium and magnesium hydroxides, are less expensive but also provide poor flame-retarding effect, requiring higher concentrations, which, in turn, affect processing behaviour and physical and mechanical properties of final product negatively [29]. Chlorinated/brominated substances are proved to be very harmful for mankind and nature; so, usage of these substances in polymers, especially in biodegradable compositions, does not make sense [30,31]. Phosphorus-based formulations are a most promising choice due to their low toxicity and high efficiency [32,33]. Among them, ammonium phosphate [AP] is often used in research works by scientists for flame retarding of biodegradable polymers; so, it is a good choice for flame-retarding systems to decrease flammability of PLA [34,35].

This paper aims to indicate and develop initial constant parameters of extrusion (temperature, screw speed, throughput) for future modelling purposes and confirms their correctness, practical pre-proof for proposed composite and form of materials, as well influence of additives on base material. For temperature and shear forces, e.g., expandable graphite (fragile additive), it is crucial to provide sufficient mixing and filler particle distribution, combined with fast throughput and low shearing during process. As powdered polymers are sometimes used in the industry for polyolefins, especially masterbatches, there is no article, patent or industrial practice to use small-grain biodegradable polymers in processing, and for any polymer, influence and benefits of this solution is not widely described in scientific sources, such as articles, projects etc., especially lack numerical and mechanical descriptions and comparisons. This research will provide data that were never published before and that could be helpful to develop new class of composites with better properties, alongside with reduced wear of machines and significant energy savings during process, as well as decreasing usage of harmful and volatile stabilizers and lubrication agents in polymer processing.

2. MATERIALS, RESEARCH EQUIPMENT, SAMPLE PREPARATION AND METHODOLOGY

2.1. Materials

PLA LX175 in form of 3-mm-diameter pellets with melt flow ratio (MFR) 4–5 g/10 min (190°C, 2.16 kg) and density of 1.25 g/cm^3 was supplied from Total-Energies-Corbion bv, The Netherlands. Pellets were also pulverised to obtain powder with 200 μm medium and 300 μm maximum sized grains. Pre-expanded flake graphite (GR) GrafGuard® 250–50N with an average particle size of 350 μm and activation temperature of 250°C was delivered by Keyser & MacKay from NeoGraf Solutions, LLC, OH, USA. Ammonium polyphosphate Exolit AP 428 (AP) with mass percentage content of phosphorous 31–32 and nitrogen 14–15, average particle size 20 μm was brought by Clariant International Ltd, Switzerland.

2.2. Research equipment

A laboratory co-rotating twin-screw extruder (Buhler AG, Switzerland) with 20-mm diameter screws, 40 L/D (length-to-diameter ratio), 36 Nm max. torque on shafts, one free flow degassing unit, 3-hole forming head and interchangeable screw configuration was used. The temperatures of zones and screws speed were set even for every composition. Initial parameters are listed in Tab. 1, and configuration of screws is shown in Fig. 1.

Tab. 1. Initial parameters of extruder

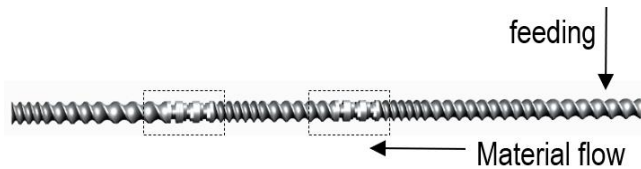| Parameter	Designation	Value
Screw speed	RPM (revolutions per minute)	200
Temperature – I zone	°C	155
Temperature – II zone	°C	165
Temperature – III zone	°C	175
Temperature – IV zone	°C	180
Temperature – extruder head	°C	185

Fig. 1. Screw configuration

Screws are composed of 30 segments each, where, despite normal transporting/compression elements, two sections of kneading elements with significant shear forces can be highlighted – where first section is responsible for intensive melting/plasticising effect (16.25–19 L/D), while the second one brings mixing performance (27–29.75 L/D). After every kneading section, free-flow degassing units are implemented to avoid gas or moisture residues in the final composite.

Both kneading sections are arranged from three right kneading elements each, where two have five discs with 45° offset of adjacent discs, and one has three discs with 90° offset of discs. After kneading sections, long two-flight (2D length) transportation segments are used to reduce the flow pressure on the free degassing unit. Kneading section is shown in Fig. 2.
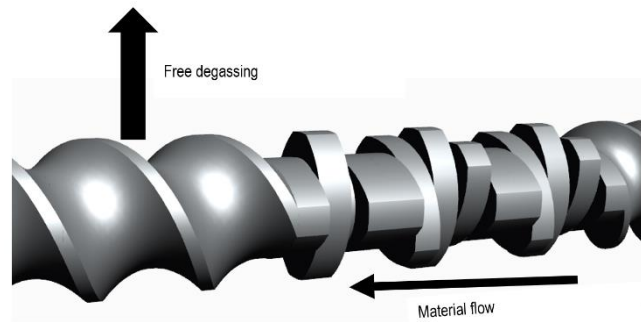

Fig. 2. Screw kneading section

PLA powder was obtained on modified disc-mill pulveriser, with self-designed milling discs with air-flow supply of material and compressed air cooling (20°C) of discs, with ≈300 kg/h efficiency of process.

For pre-drying of composite components, components were dried in drying ovens with forced air convection: SLW-53 and SLW-180 (Pol-Eko, Poland). Temperatures and time of drying were set at 65°C/7 h and 110°C/4 h for PLA and graphite filler, respectively. AP was not dried – it was added directly from sealed containers, delivered by the manufacturer of additives.

Components were fed by a volumetric dosing unit (Brabender Technologie GmbH, Germany), equipped with a coil screw and 3-finger agitator. The device was calibrated for every sample by three runs each, where the amount of inserts in the dose reservoir was strictly kept on same level, and after designating proper screw speed, four measurements of 5 min each were proceeded to ensure that material is fed with planned efficiency.

2.3. Sample preparation

Polylactide/Graphite/ammonium phosphate (PLA/GR/AP) composites were made on co-rotating twin-screw extruders mentioned in Section 2.2. Components were dried, weighted and pre-

mixed in a mixer to achieve a homogenous mixture. After mixing, materials were fed by a calibrated volumetric dosing unit to extruder the hopper. Composite left device in the form of straws, transported on belt conveyor with air cooling (fans), stainless steel dry gutter to stand-alone pelletizer. Obtained pellets were then dried and ready for examinations. Symbols and contents of composites are listed in Tab. 2.

Tab. 2. Labelling of neat PLA and PLA/GR/AP composites

Symbol	PLA (%wt)	Graphite (%wt)	AP (%wt)	Approx. throughput (kg/h)
S1	100	0	0	5
S2	100	0	0	2
S3	80	10	10	5
S4	80	10	10	2
G1	100	0	0	5
G2	100	0	0	2
G3	80	10	10	5
G4	80	10	10	2

AP, ammonium phosphate; PLA, polylactide

2.4. Research methodology

2.4.1. Extrusion process evaluation

During the process of preparing composites, described in Section 2.3, data were obtained for comparison and empirical proof of the effectiveness of the composite production process depending on the degree of fragmentation of the polymer matrix. Moreover, the prepared composites were subjected to the tests described below.

Parameters, which were measured by built-in extruder sensors, are the mean of three reads taken every 5 min after 10-min stabilisation of one extrusion run for every sample.
The parameters recorded during extrusion are listed in Tab. 3.

Tab. 3. Measured parameters of extrusion

Parameter	Designation
Torque on screws	Nm
Energy consumption (main drive power)	kW
Throughput	kg/h
Real temperatures of zones	°C
Temperature of melt on extruder head	°C

The experimental extrusions were carried out to maintain equal screw speed and temperature sets for every run, with two throughputs for every sample.

2.4.2. Phase morphology analysis

Scanning electron microscopy (SEM, SU8010, Hitachi, Japan) was used for examination of the morphology of both the pure PLA resin and PLA/GR/AP composites. For SEM imaging, composite straws were cracked, and breakthrough surface was then sputtered with gold.

2.4.3. MFR measurement

For research purposes, MFR measurements were conducted using LMI 4003 Plastometer (DYNISCO, USA), partially according to PN-EN ISO 1133:2011 standard. The measurements were carried out under the piston load of 2.16 kg at 190°C for each sample.

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 a gas flow rate of 50 cm^3/min. Samples of about 5–7 mg, sealed in aluminium crucible, were used. The samples were heated at a constant rate of 10°C/min from 0°C to 300°C.

The experiment was performed in accordance with the ISO 11357-1:2016 and ISO 11357-6:2018 standards.
The room temperature crystallinity, X_c, of PLA composites was evaluated using the following expression:

$$X_c = (\Delta H_m - \Delta H_{cc} w \Delta H^0_m) \times 100\%$$

where ΔH_m is the enthalpy of melting (J/g), ΔH_{cc} is the cold crystallization enthalpy (J/g), ΔH^0_m is the melting enthalpy of 100% crystalline PLA (93 J/g) and w is the fraction of the polymer in the composite materials (13).

2.4.5. Cone calorimeter flammability testing

The cone calorimeter testing was conducted using FIRE TESTING TECHNOLOGY iCONE CLASSIC where specimens with dimensions of 100 mm x 100 mm x 6 mm were placed on a testing plate layered with aluminium foils and placed under the burner device. Heat flux was set at 50 kW/m^2. The final result is the mean of burning of two specimens made from the same composite.

The experiment was performed according to the ISO 5660:2015 standard.

3. RESULTS AND DISCUSSION

3.1. Extrusion process evaluation

As mentioned in Section 2.4.1, parameters of extrusion of an extruder are obtained and listed in Tab. 4.

Tab. 4. Parameters from extrusion process

Sample	S1	S2	S3	S4	G1	G2	G3	G4
Throughput (kg/h)	5	2	5	2	5	2	5	2
Real throughput (g/h)	5017.06	2004.11	5026.23	1998.84	4931.5	1998.26	4712.24	2014.22
Torque on shafts (Nm)	20.16	15.12	18.36	11.16	27.36	19.44	27	20.88
Energy consumption (kW)	0.73	0.54	0.57	0.4	0.97	0.69	1.02	0.75
Energy consumption per kg (kW/kg)	0.146	0.269	0.113	0.200	0.197	0.345	0.216	0.372
Temperature of melt (°C)	197	198	198	199	199	200	201	201
Real temperature on heating sections (°C)								
I	156	156	156	155	156	157	155	155
II	168	167	166	167	166	166	162	162
III	178	176	174	177	177	178	177	179
IV	181	180	180	181	180	181	181	183
Extruder head	183	185	185	186	185	185	186	187
Losses on degassing unit					*		*	

Parameters of the extrusion process reveal that changing of polymer particle size significantly decreases torque on shafts and energy consumption: pure PLA brings 26% and 22% decrease on energy per kilogram for 5 kg/h and 2 kg/h, respectively. For samples with pulverised PLA, graphite lube effect is observed. What is more, for G series samples, energy is consumed mostly for shear melting of granules on first shear section, eliminating positive lube effect of graphite fillers. This phenomenon is also proved by energy consumption per kilogram of composite – for PLA/GR/AP composites, using smaller granules brings lowering of 48% for 5 kg/h throughput and 46% for 2 kg/h. What is more, while using smaller PLA particles, no sign of polymer was found on degassing units. For both 5 kg/h throughputs in G series, escaping of material through degassing channel is observed, especially in G3 sample case.

During extrusion of G3 and G4 specimens, the mixture of ingredients tends to separate in volumetric dose reservoirs: powders of graphite and ammonium phosphate flame retardant concentrated at the bottom of reservoir, while PLA pellets went up. The effect was partially neutralised by constant mixing using a 3-finger agitator in a volumetric dose reservoir, but separation was still visible.

3.2. Phase morphology analysis

Fig. 3 shows SEM images of neat PLA (samples G1 and G2) and PLA/GR/AP composites (G3 and S3). Differences in morphology between neat polymer and composite are apparent. Neat polymer after processing is homogeneous, whereas composite materials have porous structure. The pore distribution is homoge-

neous; the individual pores have a regular cylindrical shape. The cylinder diameters are ≈50 µm. The presence of pores is probably related to the expansion of the graphite flakes during the extrusion process.
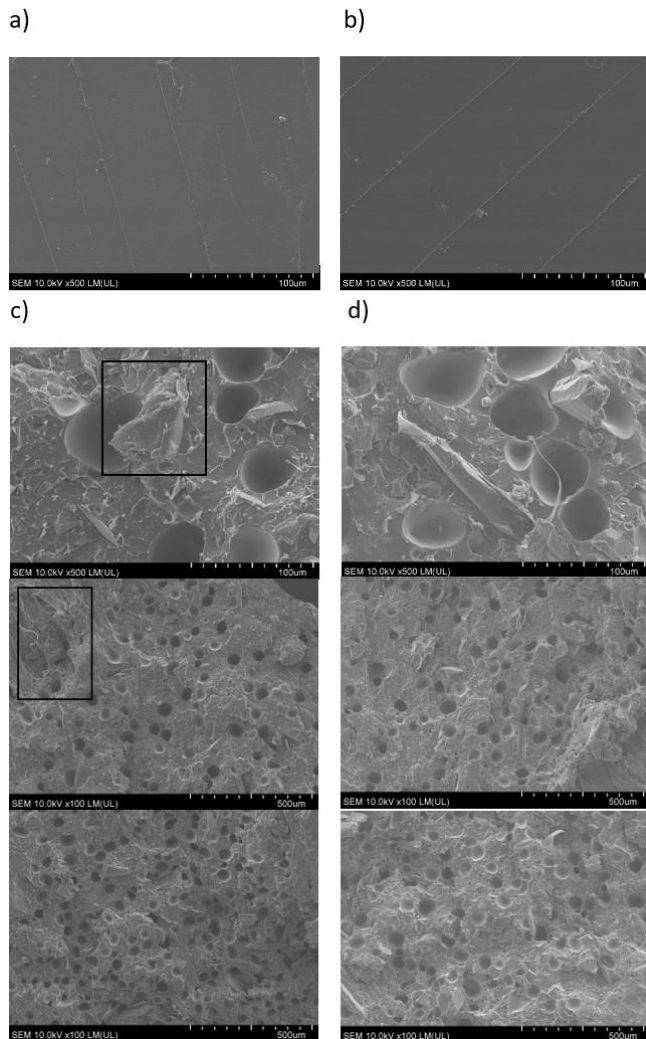

Fig. 3. SEM images of samples – (a) G1, (b) G2, (c) G3, (d) S3. Agglomeration in sample G3 is highlighted in black frame
SEM, scanning electron microscopy

The distribution of the filler in the PLA matrix in the spaces between the pores is homogeneous. However, comparing samples G3 and S3 leads to the conclusion that the filler dispersion in S3 is slightly better than that in G3. In sample G3, single agglomerates of graphite are visible

3.3. MFR measurement

MFR results for individual samples are listed in Tab. 5.

MFR is often a used method for examination of polymeric materials and composites and, among others, in comparable trials can reveal degradation processes. Results of measurement indicates that configuration of a screw used in co-rotational twin-screw extrusion process does not affect degradation of polymers through the process. For sample S1, MFR measurement proved that additional pulverisation of PLA did not result in extended degradation in comparison to sample G1. Lower values of MFR

parameter of samples S3 and G3 against non-graphite samples may be due to an increase in flow resistance associated with the use of solid filler point to conclusion, that additives did not affect in degradation of composite, in fact, lowering of MFR is right phenomenon for providing standard, inert fillers, as [36,37].

Tab. 5. MFR values

Sample	MFR (g/10 min)
Pure PLA (pellets)	5.51
S1	5.48
S3	4.41
G1	5.44
G3	4.00

MFR, melt flow ratio; PLA, polylactide.

3.4. Thermal property measurement

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 (ΔH_c), cold crystallization enthalpy (ΔH_{cc}) and melting enthalpy (ΔH_m), are summarised in Tab. 6 and Fig. 5P.
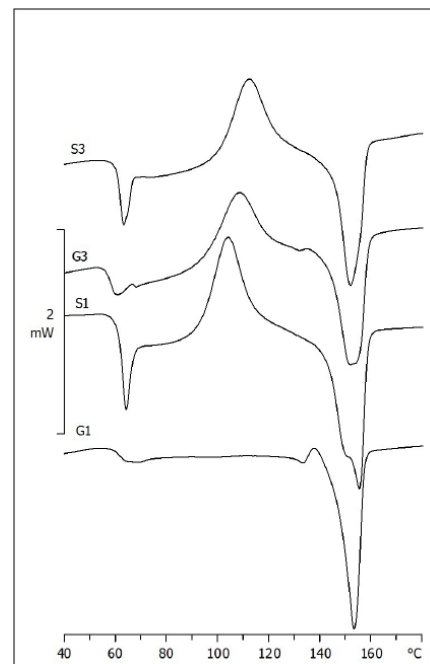

Fig. 4. First heating DSC thermograms of samples
DSC, differential scanning calorimetry

There were no changes in the thermograms during cooling stages. Glass transition temperatures in the second heating are similar and amount to about 60°C for all tested samples. A similar situation occurs in the case of melting temperatures, where the differences between the melting points of individual samples are also small. The conducted research shows that the addition of pre-expanded graphite reduces the melting enthalpy and the cold crystallization enthalpy in the second heating and increases the cold crystallization temperature. This effect may be due to the large size of graphite flakes (~400 µm), which makes it difficult to

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obtain sufficient dispersion of graphite in the polymer matrix [24]. For sample S1 during the first heating, the presence of two melting peaks was observed. The two melting peaks are related to the presence of two types of crystallites of different sizes and disorder [38]. The melting peak at lower temperature is attributed to the melting and recrystallization of the primary crystals into a more stable form. The second peak appearing at a higher temperature corresponds to the melting of the newly formed crystals [39]. All samples, except S1, showed an amorphous characteristic.

Tab. 6. DSC – Heating 1

Sample	Heating1					
	T_m (°C)	ΔH_m (J/g)	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	X_c (%)
G1	153.01	−25.99	61.18	-	-	-
S1	150.80/ 155.24	−27.37	62.47	103.85	23.23	4.5
G3	151.96	−22.99	58.07	108.36	21.68	0
S3	151.79	22.31	61.75	112.20	21.49	0

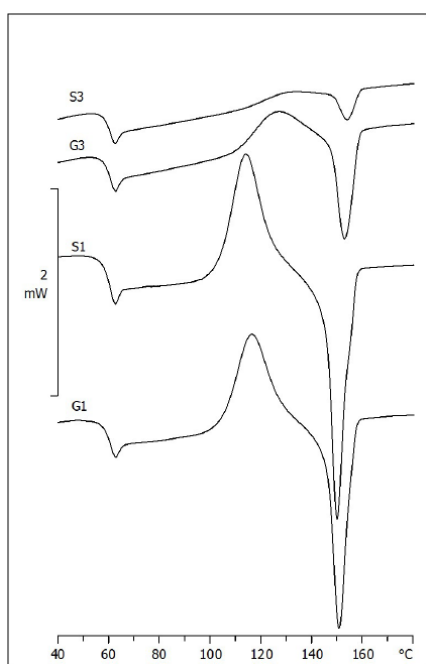DSC, differential scanning calorimetry

Fig. 5. Second heating DSC thermograms of samples
DSC, differential scanning calorimetry

Tab. 7. DSC – Heating 2

Sample	Heating 2					
	T_m (°C)	ΔH_m (J/g)	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	X_c (%)
G1	150.58	−26.23	60.43	116.53	27.81	0
S1	149.71	−27.62	60.04	114.02	27.90	0
G3	152.80	−11.74	60.08	125.86	11.72	0
S3	154.00	−2.77	60.70	133.51	3.17	0

DSC, differential scanning calorimetry

3.5. Cone calorimeter flammability testing

Flammability tests carried out using a cone calorimeter show that additives do not stop the combustion process completely. Nevertheless, additives lead to changes in the flammability parameters, which are compared in Tab. 8. Namely, the ignition time has been reduced significantly by 10–13 s in PLA/GR/AP composites in comparison to neat PLA. Flame retardancy effect is apparent as well. Despite the reduced time to ignition (TTI), peak heat release ratio (pHRR) in PLA/GR/AP is decreased by 30%–40%.

Tab. 8. Cone calorimeter data

Sample	TTI (s)	THR (MJ/m²)	pHRR (kW/m²)	MLR (g/[s·m²])	TTF (s)	TSP (m³)
G1	35	124.1	597.59	19.81	354	0.1
S1	34	110.6	576.86	18.13	331	0.1
G3	24	89.5	375.19	4.08	1442	3.23
S3	22	112.5	395.39	8.75	725	4.6

TTI, time to ignition, THR, total heat release, pHRR, peak heat release ratio, MLR, mass loss ratio, TTF, time to flameout, TSP, total smoke production

The improvement in flame retardant properties is also reflected in the two and a half times increased time needed to burn the whole specimen. It has also been observed that the presence of expandable graphite prevents the polymer from dripping during combustion. Mass loss ratio (MLR) decreased significantly, what is connected to time to flameout (TTF), because in all cases specimens were burnt fully without sudden stop of burning process. Additives affect smoke production: neat PLA was fully burned into CO_2, while combustion of the PLA composites results in releasing more volatile gases. This is a consequence of the fact that the oxygen supply is cut off by the expanded graphite, which prevents complete combustion.

4. CONCLUSIONS

Results confirmed that, as expected, grain size of polymer matrix changed processing properties of composites significantly, as well as material properties, uniformity and behaviour. Research brings sufficient proofs of advantages of using powdered PLA to conduct wider and detailed research trials to obtain data with variable initial parameters (screw speed, different temperatures, filler content, throughputs) for mathematical modelling of process in next stage of research.

Decreases in energy consumption and torque, as well as lesser temperature rise in extruder is undisputable and can affect in more energy efficient processing, as well as slower wear of mechanical elements of extruder machine, as well as proper work of degassing units and improved throughput.

SEM analysis proved that premixing along with a decreased particle size of a polymer leads to better particle distribution of powdered fillers. What is more, using of pellets cause agglomeration, which was not found in S series samples.

MFR measurements revealed that for both polymer grain sizes, flow rate values are similar. This fact is important because grinding of polymer can lead to degradation of material, which did

not occur in this case or as processing degraded pellets to a greater extent; after processing both composites, flow remains congenial.

The addition of solid fillers did not contribute to changes in the glass transition temperature and melting temperature. The effect of graphite addition on the enthalpy of melting, cold crystallization and the temperature of cold crystallization was noticed, which may result from not sufficient dispersion of graphite in the polymer matrix related to the large size of the flakes of the graphite used.

A cone calorimeter shows that modification with pre-expandable graphite and AP tend to flame retardancy of PLA by lowering MLR, pHRR and TTF. Samples made from granules were found out to be more flame resistant, which was is caused by agglomerates, which gathered near the surface, slowing combustion on first stages of burning. Despite promising results, more testing on additives is needed.

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