

# The influence of multiple processing on selected properties of a new polymer material based on thermoplastic starch

Krzysztof Moraczewski<sup>1</sup>, Cezary Gozdecki<sup>1</sup>, Marek Kociszewski<sup>1</sup>, Bartłomiej Jagodziński<sup>1</sup>, Krzysztof Szabliński<sup>1</sup>, Magdalena Stepczyńska<sup>1</sup>

<sup>1</sup> Faculty of Materials Engineering, Kazimierz Wielki University, Chodkiewicza 30, 85-064 Bydgoszcz, Poland

**Abstract.** The study discusses the results of research on the multiple processing of thermoplastic starch-based polymer compositions. The research subject was two compositions from the envifill® M product line (Grupa Azoty, Poland): M30 and MB173, intended for injection applications. The materials underwent four processing cycles, each consisting of extrusion and injection operations. The research included determining the mass flow rate, mechanical parameters (tensile strength, bending strength, Young's modulus, impact strength), thermomechanical parameters (storage modulus as a function of temperature), and thermal parameters (thermal resistance, phase transition temperature). The change in these parameters as a function of the processing rate was examined. It has been shown that if one wants to reuse waste from the tested compositions, MB173 turns out to be a better material. Even though in the case of the M30 material, the changes obtained do not disqualify this material for re-use, a greater control of the degree of prior processing and the amount of waste used is recommended.

**Key words:** thermoplastic starch; multiple processing; recycling

## 1. INTRODUCTION

In the context of growing ecological awareness and increasing pressure for sustainable resource management, the topic of conscious ecological processing of polymer materials is becoming increasingly important. Multiple processing of polymers, in particular thermoplastic starch (TPS), is a key element of the sustainable development strategy, as it allows the reuse of these materials, thus reducing their impact on the environment.

Thermoplastic starch, which is a biodegradable, renewable, and inexpensive polymer material obtained from renewable plant raw materials, has for a long time been increasingly considered as an alternative to traditional petroleum-based plastics. [1]. It is used, among others, in the production of packaging, in the construction, agricultural, and medical industries. Due to its biodegradable properties, TPS helps to reduce the amount of plastic waste, which is one of the main environmental problems [2].

Multiple polymer processing, including processes such as mechanical recycling, is an important element of the closed loop, enabling the minimization of CO<sub>2</sub> emissions and saving raw materials. However, regardless of the type of polymer, repeated processing can affect the mechanical and structural properties of the material, which is one of the main challenges associated with this process [3]–[7].

In recent years, thermoplastic starch has been the subject of many research works. Research in the field of thermoplastic starch processing has shown the relationship between process conditions and the final properties of the material. In the work of Teixeira et al. [8] the influence of various processing parameters, such as temperature, humidity, and mixing speed, on the mechanical properties of TPS was investigated. It turned out that appropriate adjustment of these parameters can significantly improve the durability and tensile strength of the material.

For example, thermoplastic starch after repeated processing may exhibit reduced tensile strength and increased brittleness [9]. Additionally, the research conducted by Olivato et al. [10] showed that the addition of natural fibers, such as jute or kenaf fibers, can compensate for unfavorable changes in polymer properties resulting from repeated processing. The research of Hejna et al. [11] focused on analyzing the degradation process of TPS after repeated processing. The results indicated a gradual decrease in the molecular weight of the polymer and a decrease in its strength, which confirms that repeated processing has a significant impact on the properties of thermoplastic starch.

Considering the presented articles, it is clear that multiple processing of thermoplastic starch is a complex process that is crucial to its final properties. Nevertheless, there are still many unknowns that require further research.

When considering the variety of available materials based on thermoplastic starch and research on this material, it is also worth paying attention to the innovative applications of this material as well as its processing processes.

For example, Xie et al. [12] investigated the effect of processing on TPS properties. They showed that by changing the extrusion conditions, it is possible to obtain materials with different properties, such as the degree of crystallinity and mechanical properties.

Another research, conducted by Liu et al. [13], focused on the possibility of thermal modification of thermoplastic starch. The authors focused on the reactions occurring during processing and showed that during this process: water diffusion, granule expansion, gelatinization, melting, decomposition and crystallization take place.

However, not only thermal modifications can affect the properties of TPS. Research by El-Wakil et al. [14] has shown that the addition of natural nanofillers, such as nanocrystalline cellulose, can improve the mechanical properties of TPS as well as increase its heat resistance.

An interesting approach is also observed in the formation of blends. The work of Sessini et al. [15] focuses on examining the impact of the addition of other biodegradable polymers on the properties of TPS. For example, TPS blends with polylactide (PLA) were tested, where it was noticed that the appropriate composition of these two materials can lead to a synergistic effect of improving mechanical properties and the barrier to gases.

Moreover, the use of nanotechnology is beneficial to improve the properties of TPS. As research by Yahia et al. [16] showed, the addition of silver nanoparticles to thermoplastic starch not only significantly increased its mechanical properties, but also gave it antimicrobial properties, which can be used in many areas, e.g. in the food packaging industry.

The work of Alexandre et al. [17] also focused on the addition of nanomaterials to TPS. In this case, the addition of clay nanoparticles to thermoplastic starch led to improved thermomechanical properties, which is important in the context of the possibility of repeated processing of this polymer.

Another intriguing approach to improving the properties of thermoplastic starch is the use of ionizing radiation. Such a method was investigated by Sanyang et al. [18]. In their study, gamma radiation was used to induce cross-linking of thermoplastic starch, which improved its mechanical and thermal properties.

In the context of thermoplastic starch, the issues related to multiple processing are not yet fully understood. Although there are many works in the literature devoted to the properties and applications of TPS, there are few studies on the impact of repeated processing on the properties of this polymer. For this reason, this work aims to understand better this process and its implications for TPS. This research will not only enable deepening knowledge about thermoplastic starch and its processing but may also contribute to the development of

new processing and recycling strategies that will allow for even more effective use of this resource.

A special aspect of this article is the type of polymer compositions used for research. The research used a polymer material new to the European market. The new line under the envifill® brand is based on the technology of obtaining thermoplastic starch, which is produced from renewable and compostable materials and does not contain plasticizers. Thermoplastic starch, based on which the envifill® line was created, is distinguished primarily by the fact that it can be used as an independent polymer in some applications and as a base or addition to polymer compositions, biodegradable or compostable.

Biodegradable polymers from the Azoty group are made from potato starch and other raw materials of plant origin and are not chemically processed. According to the company, it is an excellent alternative to traditional polymers (plastics), especially those used to produce various types of disposable products. These include foils, shopping bags, waste bags, cutlery, and catering sets, including packaging for takeaway meals, flowerpots, trays for food products, and coffee capsules.

Because the compositions from the envifill® line have a chance of being widely used on the European market in the production of various types of products characterized by biodegradability as an alternative to other biodegradable polymers, including polylactide, it seems advisable to test the resistance of selected polymer compositions to repeated processing. The stability of the parameters and properties of the tested materials is particularly important in terms of the use of waste generated in the production of plastic elements and the possibility of material recycling of products made from the tested compositions. The thematic scope of the article and the undertaken research activities fit into the promoted scope of the circular economy.

## 2. MATERIALS AND METHODOLOGY

### 2.1. Materials.

Two types of polymer compositions based on thermoplastic starch from the envifill® M line (Grupa Azoty, Poland) were used in the tests - M30 and MB173. Envifill® M is a line of biodegradable thermoplastic materials consisting of a mixture of thermoplastic starch (TPS) and polylactide (PLA), intended for injection applications. The materials included in the composition are made from renewable raw materials of natural origin, biodegradable and compostable (in natural conditions, in the presence of microorganisms). The TPS compositions used in the tests were chosen based on their varying processing parameters. Some properties of selected products of the envifill® M line obtained from product safety data sheets are presented in Table 1.

**TABLE 1.** Properties of selected products from the envifill® M line

Property	M30	MB173
Density [g/cm <sup>3</sup> ]	1.28	1.25
MFR (190°C/2.16kg) [g/10min]	9.0	30.0
Tensile strength [MPa]	35.0	50.0
Strain at break [%]	2.5	10.0
Young modulus [MPa]	1800	2300
Impact strength [kJ/m <sup>2</sup> ]	30.0	55.0

## 2.2. Methodology.

The granules of the tested polymer compositions were subjected to repeat processing. One processing cycle included two technological operations: extrusion and injection. Before each processing cycle, the materials were dried at 60°C for 24 hours. Extrusion was carried out on a single-screw extruder W25-30D (Metalchem, Poland). The temperatures of individual zones of the extruder cylinder and head were 140, 150, 155, and 160°C. The extruded material was air-cooled and granulated. Then, the obtained granulate was used to form test samples by injection molding. Injection was performed on a Tederic TRX80 Eco 60 industrial injection molding machine (Tederic, Taiwan). The temperatures of individual zones of the injection molding machine and the mouthpiece were 160, 170, 170, and 175°C. The mold temperature was 35°C. The injection and compression pressures were 48 and 45 MPa, respectively. The cooling time of the molded parts in the mold was 45 seconds. After each processing cycle, a certain part of the granulate was fed to subsequent cycles. In this way, 4 processing cycles were carried out in the research, which gives a maximum number of 8 technological operations to which the materials were subjected. The process used was intended to simulate the internal use of production waste or the material recycling process.

The mass melt flow rate (MFR) test was performed using a capillary plastometer type MP600 (Tinius Olsen, USA). The flow rate was determined at 190°C with a piston load of 2.16 kg. Before testing the materials were dried at 60°C for 24 hours. Ten measurements were made for each material, and the arithmetic mean was taken as the test result.

The determination of the mechanical properties of the tested materials under static tension was performed using an Instron 3367 laboratory testing machine (Instron, USA). The tests were carried out on standardized shapes with a measurement length of 80.0 mm and a thickness of 4.00 mm obtained by injection molding. The tests were carried out at a tensile speed of 50.0 mm/min. Ten samples of a given material were used for testing, and the arithmetic mean of these ten measurements was taken as the test result.

The mechanical properties during bending were performed using the OB-RPPD bending apparatus (OB-RPPD Czarna Woda, Poland) with a strain gauge force head with a range of 0-1000N. Paddle-shaped samples with a cross-section of 10 x 4 mm were placed on supports spaced 80 mm apart and loaded with a force perpendicular to the sample axis until its destruction. The bending speed was set at 5 mm/min.

\*e-mail: kmm@ukw.edu.pl

During the test, force values and the corresponding deflection arrow values were recorded. Based on these data, the values of flexural strength ( $\sigma_F$ ) and maximum deflection ( $\epsilon_F$ ) were recorded. Average values from six samples were calculated for each type of composition and the number of its processing.

Charpy impact testing of unnotched samples was performed using an XJ 5Z apparatus (Liangong, China). The tests were carried out on standardized shapes with dimensions of 4x10x80 mm, cut from samples for tensile strength testing. The hammer energy was 2 or 4 kJ (depending on the material). The speed of the impact hammer was 2.90 m/s. Ten samples of a given material were used for testing, and the arithmetic mean of these ten measurements was taken as the test result.

The thermomechanical properties were tested using a Q800 thermomechanical analyzer (DMA) (TA Instruments, USA). Measurements were performed in the range from 25 to 120 °C, with a heating rate of 3 °C/min, a strain of 15  $\mu$ m, and a strain frequency of 1 Hz. The tests were carried out on samples with dimensions of 4x10x80 mm, cut from samples for tensile strength testing.

The phase transition studies were performed using a Q200 differential scanning calorimeter (DSC) (TA Instruments, USA). The study was carried out using the heating-cooling-heating scanning. The first heating was intended to remove the thermal history. Controlled cooling was then carried out. The analysis was carried out on the second heating curve. All scanning runs were carried out in a nitrogen atmosphere, in the temperature range from 0 to 200°C, at a heating rate of 10°C/min. Samples weighing approximately 5 mg were cut from samples for tensile strength testing.

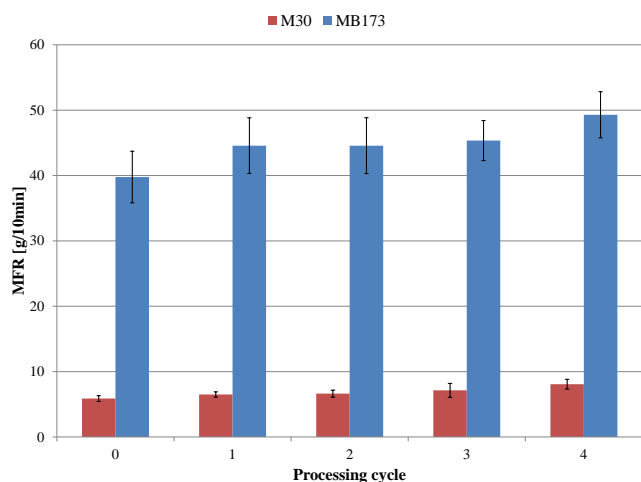
The thermal stability and thermal decomposition process were tested using a Q500 thermogravimetric analyzer (TGA) (TA Instruments, USA). The tests were performed in a nitrogen atmosphere, in the temperature range from 25 to 700°C, at a heating rate of 10 °C/min. Samples weighing approximately 15 mg were cut from samples for tensile strength testing.

## 3. RESULTS AND DISCUSSION

### 3.1. Melt flow rate.

The MFR values of primary M30 and MB173 determined in the study differed slightly from the values given in the data sheets of these materials. The differences may result from the test itself or slightly different characteristics of these polymers. It is known that the MFR values of the same type of polymer may vary slightly depending on the production batch. Therefore, some manufacturers provide a range of MFR values in their data sheets rather than a specific value. However, the results clearly show the significant difference between the MFR values of these two types of TPS (Fig.1). The determined average MFR values of primary M30 and M173 were 4.0 and 40.0 g/10 min, respectively. The MB173 is therefore characterized by 10 times greater flow rate than the M30.

As a result of research on the influence of processing cycles on MFR, it turned out that the MB173 was characterized by greater stability of this parameter.



**Fig.1.** Melt flow rate values of tested materials as a function of processing cycles

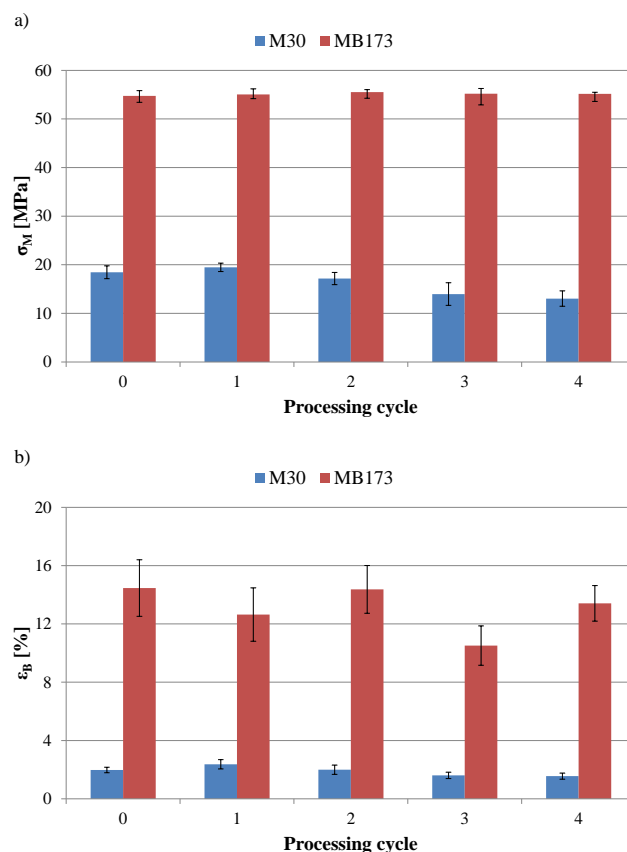
Although the numerical increase in the MFR value after 4 processing cycles was much higher than the increase observed for the M30 (9.52 g/10min MB173 vs. 2.2 g/10min M30), in percentage terms of the MB173 material had better results. The percentage change in MFR of M30 after 4 processing cycles was 138% of the value of the primary polymer, while MB173 was 124% of the value of the primary polymer. The characteristic of the MFR changes was also more favorable in the case of the MB173 material. For M30, each processing cycle increased the MFR value. In turn, for MB173, after the initial increase in MFR, the value of this parameter remained at a similar level after 2 and 3 processing cycles. Greater material flow stability may be more beneficial in the case of recycle processing, because possible changes in the MFR value between individual levels of the recycle "life" could adversely affect the process, causing problems with the production cycle and product quality.

### 3.2. Mechanical properties.

Also in the case of mechanical properties, the obtained values of tensile strength ( $\sigma_M$ ), elongation at break ( $\epsilon_B$ ), tensile modulus (Young's modulus) and impact strength ( $u_a$ ) differed from the values given in the safety data sheets of the tested materials. The possible cause of these differences is the same as that described in the case of MFR. However, the differences between these materials contained in the safety data sheets were again confirmed.

The MB173 material has a significantly higher tensile strength than the M30 material (54.7 MPa MB173 vs. 18.5 MPa M30) (Fig. 2a). Multiple processing has shown that both types of TPS differ significantly in the stability of this mechanical parameter. The  $\sigma_M$  value of the MB173 polymer remained at the original level regardless of the processing rate. Even after 4 processing cycles, no significant changes in this

parameter were observed. For the M30 polymer, the original  $\sigma_M$  value remained only until the first processing cycle.



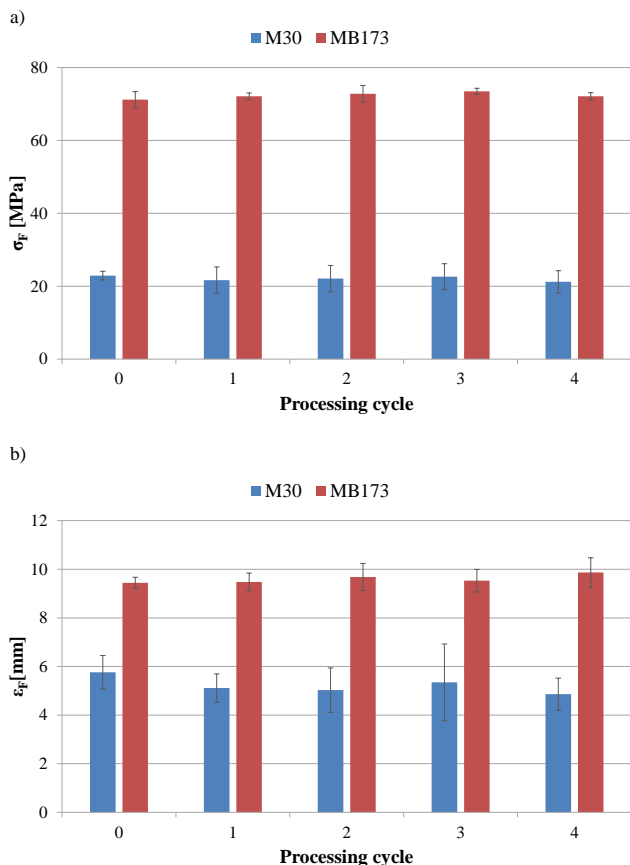
**Fig.2.** Dependence of a) tensile strength ( $\sigma_M$ ), b) strain at break ( $\epsilon_B$ ) on the number of process cycles of the tested materials

Each subsequent cycle resulted in a deterioration of tensile strength. After 4 processing cycles, the  $\sigma_M$  value was 13.0 MPa, which was approximately 70% of the value of the original polymer.

Changes in the  $\epsilon_B$  value as a result of repeated processing of materials depended on the type of polymer (Fig. 2b). In the case of the M30 polymer,  $\epsilon_B$  decreased from 2% for the original material to 1.6% for the material after 4 processing cycles. For the MB173 polymer, a decrease in  $\epsilon_B$  was obtained from 14.5% for the original material to 13.4% for the material after 4 processing cycles. Despite visible trends, the differences were too small to be of any significance in the case of reuse of recycle.

The characteristics of the tested polymer compositions during bending were also determined. Similarly, to the tensile strength, the MB173 material was characterized by a higher flexural strength ( $\sigma_F$ ) than the M30 material (71.2 MPa MB173 vs. 22.9 MPa M30) (Fig. 3a). Due to the homogeneity of the tested materials, the values of  $\sigma_F$  and  $\sigma_M$  should be close to each other. However, this is not the case in the examined materials. In the tests, the  $\sigma_F$  values were higher than the  $\sigma_M$  values (especially in the case of the MB173). The obtained differences may result from the presence of some

type of defects in the samples, which have a greater impact on the material when exposed to tensile forces than to bending forces.



**Fig.3.** Dependence of a) flexural strength ( $\sigma_F$ ), b) maximum deflection ( $\epsilon_F$ ) on the number of process cycles of the tested materials

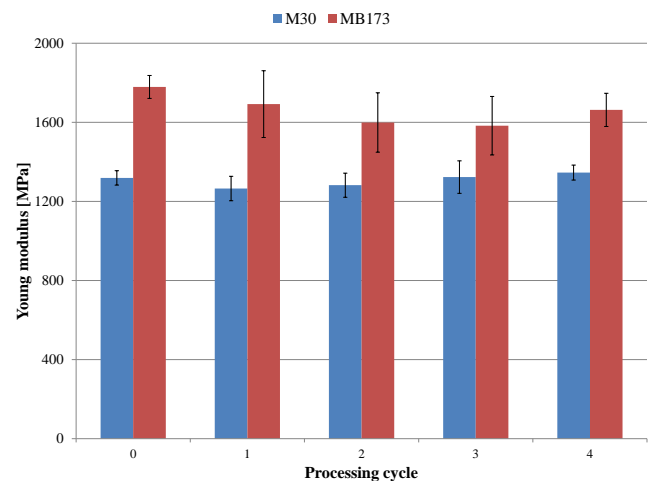
However, the flexural strength turned out to be an exceptionally stable parameter during repeated processing of the tested materials. In the case of both M30 and MB173, even after 4 processing cycles, the obtained  $\sigma_F$  values did not change significantly. The obtained values of primary materials and multiple processed materials were practically the same.

The MB173 material was characterized by a higher maximum deflection value during the bending test than the M30 material (9.4% MB173 vs. 5.8% M30) (Fig. 3b). Similarly, to the  $\sigma_F$  parameter, the  $\epsilon_F$  values were stable as a function of the processing rate, and the differences between the original materials and materials after 4 processing cycles were not significant.

According to the product data sheets, the MB173 type has a much higher Young's modulus than the M30 material, which was reflected in the results of the tests (1800 MPa MB173 vs. 1300 MPa M30) (Fig. 4).

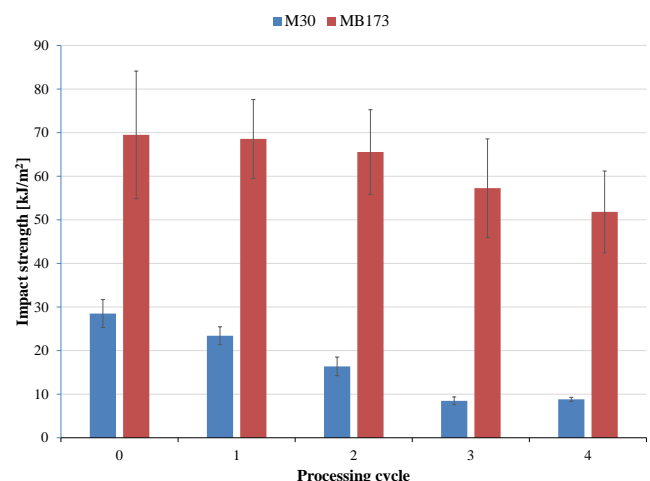
The nature of changes in material stiffness under the influence of multiple processing varied. The M30 material was characterized by the high stability of this parameter as a function of the number of processing times. The obtained

value of Young's modulus of this material was at a similar level regardless of the number of processing cycles, and the recorded changes were not greater than 3% of the original value. A decreasing stiffness was observed for the MB173 material. As the processing cycles increased, the value of Young's modulus decreased from 1800 MPa for the original material to 1650 MPa for the material after 4 processing cycles. The module after repeated processing was therefore 92% of the input value.



**Fig.4.** Dependence of Young's modulus on the number of process cycles of the tested materials

The tested materials also differed in their resistance to dynamic deformations. Impact strength values determined using the Charpy method were 28.5 kJ/m<sup>2</sup> for the M30 material and 69.5 kJ/m<sup>2</sup> for MB173, confirming the differences noted in the product data sheets (Fig. 5).



**Fig.5.** Dependence of impact strength on the number of process cycles

As a result of multiple processing of the tested materials, their impact resistance decreased. The M30 material reduced its impact strength from 28.5 kJ/m<sup>2</sup> for the original material to 8.8 kJ/m<sup>2</sup> for the polymer after 4 processing cycles. The impact resistance of the material therefore decreased to 38%

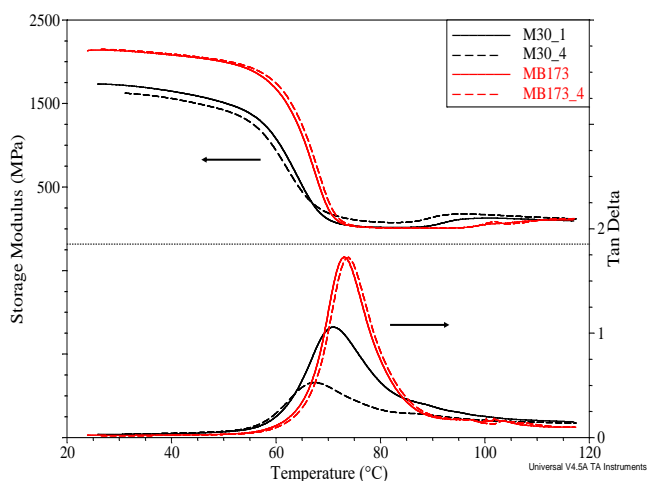
of the value of the original material. The MB173 material demonstrated much greater stability. Although the impact strength of this material decreased from 69.5 kJ/m<sup>2</sup> to 51.8 kJ/m<sup>2</sup> after going through 4 processing cycles, it still retained 75% of its original value.

To summarize the materials tested in terms of mechanical properties, the more favorable type of TPS composition, taking into account the reuse of recycle, is the MB173 type. The lack of large changes in tensile strength and Young's modulus, with much greater impact stability of this material, will not cause large changes in the mechanical properties of the final products made from recycle, even after introducing a high content of previously processed polymer into the final product.

### 3.3. Thermomechanical analysis.

The thermomechanical analysis of the tested types of TPS compositions was also carried out. The storage modulus of M30 and MB173 materials determined at 30°C (E'30) were 1720 and 2130 MPa, respectively. There is no comparative data in the literature or product data sheets, but the obtained values confirm the greater stiffness of the MB173 material obtained in Young's modulus test.

However, the characteristics of changes in the elastic modulus as a function of the temperature of both materials are similar (Fig. 6).



**Fig.6.** DMA curves of selected materials presenting the change in storage modulus as a function of temperature

Both types of TPS compositions are in a glassy state up to approximately 55.0°C. Then, in the range from 55.0 to 90.0°C, there is a sharp decrease in the elastic modulus associated with the transition of the polymers to the viscoelastic state. The storage modulus decreased from 1510 MPa for M30 and 2000 MPa for MB173 at 55.0°C to 20 MPa for M30 and 10 MPa for MB173 at 90.0°C. At higher temperatures, a slight stiffening of the material is also visible, related to the phenomenon of cold crystallization. As DSC tests have proven (presented later in the article), the cold crystallization process of the M30 material occurs at a lower temperature, hence the stiffening of this material occurs earlier than for the MB173 material. The glass transition temperature determined by DMA

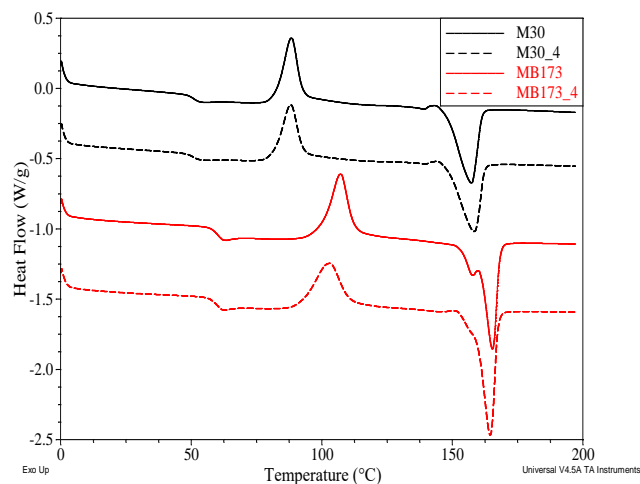
from the maximum of the tan $\Delta$  peak, was 71.0°C for M30 and 73.0°C for MB173.

Differences between materials were observed in their response to multiple processing. The MB173 material showed high stability of the storage modulus as a function of the processing. The module value remained at the same level regardless of the number of processing cycles. This concerned the storage modulus over the entire test temperature range. The glass transition temperature did not change either. After 4 processing cycles, it was still around 73°C.

In the case of the M30 material, changes in the storage modulus as a function of the processing depended on the temperature. Up to approximately 70.0°C, the storage modulus decreased with increasing processing times, and the decrease was a maximum of 6% compared to the value of the original material. Above 70°C, multiple processed samples were characterized by higher elastic modulus than the original material. The difference was up to 25% after 4 processing cycles.

### 3.4. Thermal analysis.

In the processing of polymeric materials and the subsequent use of finished products, parameters related to polymer phase transitions are important, i.e. the temperature of a given phase transition and the thermal effect of these transitions. Three phase transformations were recorded on the DSC curves of the tested materials: glass transition, cold crystallization, and melting of the crystalline phase (Fig. 7). The results of the second DSC heating curve analysis are presented in Table 2.



**Fig.7.** DSC curves of selected materials showing the observed phase transitions

**TABLE 2.** The results of DSC tests

Sample	T <sub>g</sub> [°C]	T <sub>cc</sub> [°C]	ΔH <sub>cc</sub> [J/g]	T <sub>m</sub> [°C]	ΔH <sub>m</sub> [J/g]
M30	50.9	88.3	22.0	157.2	24.7
M30_1	50.6	88.0	20.1	157.3	22.9
M30_2	50.2	87.9	21.9	157.6	25.7
M30_3	50.1	88.1	20.8	157.4	24.0
M30_4	50.8	88.0	20.4	158.2	24.4
MB173	60.6	107.1	29.3	165.2	31.8
MB173_1	59.9	103.5	27.9	164.2	32.0
MB173_2	59.7	103.7	28.3	164.4	32.2
MB173_3	59.9	103.2	27.3	164.4	32.5
MB173_4	59.6	103.0	27.8	164.4	33.9

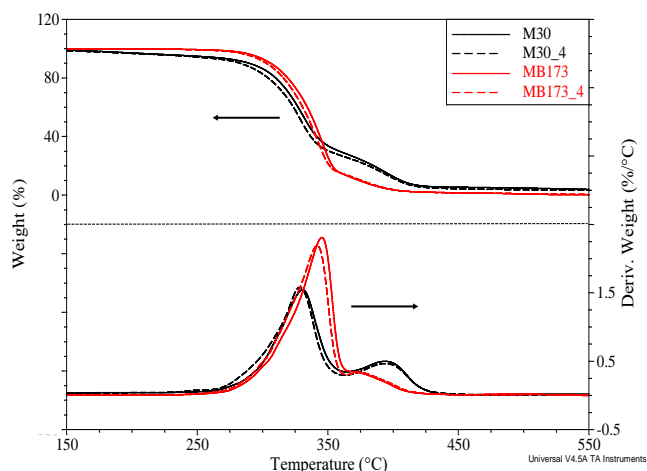
The M30 material was characterized by a much lower glass transition temperature than the MB173 material. The T<sub>g</sub> values determined from the second heating curves were 50.9°C for M30 and 60.6°C for MB173. The difference was therefore approximately 10°C. The cold crystallization process temperature (T<sub>cc</sub>) and melting temperature (T<sub>m</sub>) were also lower in the case of the M30 material. The determined T<sub>cc</sub> values for M30 and MB173 materials were 88.3 and 107.1°C, respectively. The cold crystallization process therefore took place at a temperature approximately 15°C lower for M30. The lower cold crystallization temperature of the M30 material results in a lower melting point of the crystalline phase. For M30, the recorded T<sub>m</sub> value was 157.2°C, while for the MB173 material it was 165.2°C. Therefore, it can be seen that the crystallites formed during the cold crystallization process are different for both types of TPS compositions. Crystallites that form at a higher temperature have a more perfect structure and/or larger size, which causes them to melt at a higher temperature. Due to the lack of information about the change in enthalpy of melting of 100% crystalline samples of M30 and MB173 materials, we are unable to calculate the initial degree of crystallinity of these materials. However, we are able to deduce some information regarding the degree of crystallinity by comparing the obtained ΔH<sub>cc</sub> and ΔH<sub>m</sub> values. The values of these parameters for all tested samples are very similar. The calculated differences between ΔH<sub>cc</sub> and ΔH<sub>m</sub> of individual materials are a maximum of 6 J/g. This means that most of the crystalline phase present in the material that melts is formed in the process of cold crystallization. The input materials are therefore almost completely amorphous, and the possible amount of the crystalline phase is small.

The obtained results of the DSC analysis therefore indicate that the tested types of TPS compositions differ in the structure of polymer chains and average molecular weight, which affects, among others, the recorded T<sub>g</sub> values and the course of the cold crystallization process described above. However, the exact nature of the differences is not possible to determine based on the research work carried out and requires more detailed studies.

Multiple processing of both types of TPS compositions did not cause significant changes in the phase transformations of the tested materials. After 4 processing cycles, the T<sub>g</sub> values

of both materials were at the same level as for the original materials. No significant changes were observed in the case of cold crystallization and melting processes of both materials. The T<sub>cc</sub> and ΔH<sub>cc</sub> values did not change practically after 4 processing cycles. T<sub>m</sub> and ΔH<sub>m</sub> values were also stable and did not change. After applying 4 processing cycles, the differences in the ΔH<sub>cc</sub> and ΔH<sub>m</sub> values remained low. This means that after repeated processing, the M30 and MB173 materials remained amorphous. Therefore, it can be concluded that repeated processing in any way did not affect the crystal structure and the degree of crystallinity of the tested materials.

An important material parameter that may change due to repeated processing is the thermal resistance of materials. Figure 8 shows the thermal curves of selected samples and Table 3 presents the results of TG tests. Thermal resistance was assumed as the temperature of loss of 5% of the sample mass (T<sub>5%</sub>).

**Fig. 8.** TG and DTG curves of selected materials showing the change in mass as a function of temperature**TABLE 3.** The results of TG tests

Sample	T <sub>d</sub> [°C]	T <sub>max1</sub> [°C]	T <sub>max2</sub> [°C]	R [%]
M30	247.4	330.4	394.8	1.3
M30_1	238.7	328.2	392.4	3.0
M30_2	234.1	325.4	394.1	2.5
M30_3	240.5	328.0	396.1	2.5
M30_4	239.2	328.4	394.6	1.9
MB173	294.6	345.2	378.3	0.5
MB173_1	294.7	350.1	375.0	0.3
MB173_2	294.7	350.1	378.1	0.3
MB173_3	291.6	344.3	377.9	0.4
MB173_4	291.1	341.6	377.8	0.2

The M30 material is characterized by much lower thermal resistance than the MB173 material (247.4°C M30 vs. 294.6°C MB173). The recorded difference in T<sub>5%</sub> was approximately 47.0°C. In both types of TPS compositions, the degradation was a two-stage process. However, in the case of the M30 material, the second degradation stage was more intense than in the case of the MB173 material. The recorded weight losses occur in the

temperature range: the first stage from 225.0 to 365.0°C, the second stage from 365.0 to 430.0°C. In the case of the M30 material, the maximum degradation rate ( $T_{\max 1}$ ) of the first degradation stage occurred at a lower temperature than in the case of the MB173 material (330.4°C M30 vs. 345.2°C MB173). However, the situation changes for the second stage of degradation. At this stage, M30 material is characterized by a higher temperature of maximum degradation rate ( $T_{\max 2}$ ) than the MB173 material (394.8°C M30 vs. 378.3°C MB173). The presence of two stages of degradation is probably caused by the fact of at least two components of the polymer composition in the material, which confirms the multi-component nature of the tested TPS types. By comparing the sizes of peaks resulting from the degradation of individual components of the polymer mixture and the temperatures of maximum degradation rate of individual degradation stages, it can be concluded that the content of the second component of the mixture is much higher in the case of the M30 material. The char residue (R) after testing of M30 and MB173 materials was little higher for the M30 samples. However, the differences are not large (max. 3% for M30 vs. max. 0.5% for MB173), it can therefore be seen that most of the volume of both materials is decomposed as a result of thermal degradation.

The tested materials demonstrated stability in terms of thermal resistance as a function of multiple processing. After 4 processing cycles, the recorded  $T_{5\%}$  values of both types of TPS compositions did not change significantly. The decrease in thermal resistance for M30 materials was 8.0°C and for MB173 material was 3.0°C. Also, the temperatures of maximum degradation rate of both degradation stages in the case of M30 and MB173 materials did not change significantly. For the M30 materials, the maximum observed change in  $T_{\max 1}$  and  $T_{\max 2}$  values was 5.0 and 2.2°C, respectively. For MB173 materials, the observed changes were very similar and amounted to a maximum of 4.9°C for  $T_{\max 1}$  and 3.3°C for  $T_{\max 2}$ . This means that both main components of the tested TPS types are characterized by high thermal stability in repeated processing operations and the registered changes will not negatively affect the industrial processing of recyclates and the quality of products obtained from them. There were also no changes in the level of residues after testing in the case of repeatedly processed materials. Still, the vast majority of the material decomposes during thermal degradation.

The changes were therefore irrelevant in terms of processing or use. Multiple processing did not affect the degradation process in the entire temperature range, because the obtained thermal curves are mostly the same and overlap.

It can therefore be concluded that the tested types of TPS compositions are characterized by high stability and thermal resistance, both in terms of the observed phase transformations and in terms of resistance to thermal degradation. Therefore, the reuse of recyclates of these materials, even those that have been subjected to a large number of processing cycles, should not negatively affect the processing process or the quality of the final products obtained.

#### 4. CONCLUSIONS

The following conclusions can be drawn from the conducted research:

- The MB173 thermoplastic starch composition was characterized by a ten times higher value of the mass flow rate than the M30 type material. The MB173 material also had slightly greater stability of this parameter as a function of the processing cycles.
- The MB173 material was characterized by better mechanical properties and better stability as a function of the processing times of the determined mechanical parameters. The determined values of tensile strength, strain at break, Young's modulus, and impact strength in the case of the MB173 material decreased less than in the case of the M30 material.
- The MB173 material showed high stability of the elastic modulus as a function of the processing rate. The module value remained at the same level regardless of the number of processing cycles. This concerned the elastic modulus over the entire test temperature range. The "mechanical" glass transition temperature also did not change. After 4 processing cycles, it was still around 73°C.
- The phase transitions of both types of thermoplastic starch compositions remained unchanged after multiple processing cycles. The glass transition temperature, cold crystallization, melting processes, the intensity for both materials as well as the degree of crystallinity remained at the same level as the original materials even after 4 processing cycles.
- The thermoplastic starch compositions that were tested demonstrated stable thermal resistance over multiple processing cycles. After four cycles, the changes in thermal resistance, maximum degradation rate and residue values were minimal, which indicates that they are not significant from both processing and usage perspectives. Multiple processing did not affect the degradation process over the entire temperature range, as the obtained thermal curves of the primary and processed materials were practically identical.

Upon review of the results, it can be concluded that MB173 is better suited for reusing waste or recyclate from other processes. The recorded changes in the tested parameters as a function of the processing rate were smaller than in the case of the M30 material. Therefore, the introduction of waste/recyclate that has already been processed several times should not have a negative impact on the manufacturing process and/or functional properties of the final products. Even though in the case of the M30 material, the changes obtained do not disqualify this material for re-use, greater control of the degree of prior processing and the amount of waste/recyclate used in the production process is recommended.

#### References

- [1] L. Avérous and P. J. Halley, "Biocomposites based on plasticized starch," *Biofuels, Bioprod. Biorefining*, vol. 3, no. 3, pp. 329–343, May 2009.
- [2] Y. Zhang, C. Rempel, and Q. Liu, "Thermoplastic Starch



- Processing and Characteristics—A Review,” *Crit. Rev. Food Sci. Nutr.*, vol. 54, no. 10, pp. 1353–1370, 2014.
- [3] M. Zenkiewicz *et al.*, “Effect of multiple injection moulding on some properties of polycarbonate,” *Arch. Mater. Sci. Eng.*, vol. 37, no. 2, 2009.
- [4] E. Fortunati *et al.*, “Investigation of thermo-mechanical, chemical and degradative properties of PLA-limonene films reinforced with cellulose nanocrystals extracted from Phormium tenax leaves,” *Eur. Polym. J.*, vol. 56, no. 1, pp. 77–91, Jul. 2014.
- [5] K. Moraczewski, R. Malinowski, D. Łączny, and M. Macko, “Surface modification of maize stem with polydopamine and tannic acid coatings,” *Surfaces and Interfaces*, vol. 26, p. 101319, Oct. 2021.
- [6] M. Zenkiewicz, J. Richert, P. Rytlewski, K. Moraczewski, M. Stepczyńska, and T. Karasiewicz, “Characterisation of multi-extruded poly(lactic acid),” *Polym. Test.*, vol. 28, no. 4, pp. 412–418, Jun. 2009.
- [7] K. Moraczewski, “Characterization of multi-injected poly( $\epsilon$ -caprolactone),” *Polym. Test.*, vol. 33, 2014.
- [8] E. de M. Teixeira, D. Pasquini, A. A. S. Curvelo, E. Corradini, M. N. Belgacem, and A. Dufresne, “Cassava bagasse cellulose nanofibrils reinforced thermoplastic cassava starch,” *Carbohydr. Polym.*, vol. 78, no. 3, pp. 422–431, Oct. 2009.
- [9] A. K. Bledzki, A. Jaskiewicz, and D. Scherzer, “Mechanical properties of PLA composites with man-made cellulose and abaca fibres,” *Compos. Part A Appl. Sci. Manuf.*, vol. 40, no. 4, pp. 404–412, Apr. 2009.
- [10] J. B. Olivato, M. V. E. Grossmann, F. Yamashita, D. Eiras, and L. A. Pessan, “Citric acid and maleic anhydride as compatibilizers in starch/poly(butylene adipate-co-terephthalate) blends by one-step reactive extrusion,” *Carbohydr. Polym.*, vol. 87, no. 4, pp. 2614–2618, Mar. 2012.
- [11] A. Hejna, J. Lenza, K. Formela, and J. Korol, “Studies on the Combined Impact of Starch Source and Multiple Processing on Selected Properties of Thermoplastic Starch/Ethylene-Vinyl Acetate Blends,” *J. Polym. Environ.*, vol. 27, no. 5, pp. 1112–1126, May 2019.
- [12] F. Xie *et al.*, “Characteristics of starch-based films plasticised by glycerol and by the ionic liquid 1-ethyl-3-methylimidazolium acetate: A comparative study,” *Carbohydr. Polym.*, vol. 111, pp. 841–848, Oct. 2014.
- [13] H. Liu, F. Xie, L. Yu, L. Chen, and L. Li, “Thermal processing of starch-based polymers,” *Prog. Polym. Sci.*, vol. 34, no. 12, pp. 1348–1368, Dec. 2009.
- [14] N. A. El-Wakil, E. A. Hassan, R. E. Abou-Zeid, and A. Dufresne, “Development of wheat gluten/nanocellulose/titanium dioxide nanocomposites for active food packaging,” *Carbohydr. Polym.*, vol. 124, pp. 337–346, Jun. 2015.
- [15] V. Sessini, M. P. Arrieta, J. M. Kenny, and L. Peponi, “Processing of edible films based on nanoreinforced gelatinized starch,” *Polym. Degrad. Stab.*, vol. 132, pp. 157–168, Oct. 2016.
- [16] R. Yahia *et al.*, “Synthesis and characterization of thermoplastic starch/PVA/cardanol oil composites loaded with in-situ silver nanoparticles,” *J. Appl. Polym. Sci.*, vol. 139, no. 3, p. 51511, Jan. 2022.
- [17] M. Alexandre and P. Dubois, “Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials,” *Mater. Sci. Eng. R Reports*, vol. 28, no. 1–2, pp. 1–63, Jun. 2000.
- [18] M. L. Sanyang, S. M. Sapuan, M. Jawaid, M. R. Ishak, and J. Sahari, “Effect of plasticizer type and concentration on physical properties of biodegradable films based on sugar palm (arenga pinnata) starch for food packaging,” *J. Food Sci. Technol.*, vol. 53, no. 1, pp. 326–336, Jan. 2016.