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Mechanical Properties of Polylactide Filled with Micronized Chalcedonite

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Abstract: One of the methods of changing the mechanical properties of polymeric materials is by the creation of composites with various substances whose task is to strengthen and fill them. Thanks to the use of fillers, we can obtain new materials with interesting mechanical and chemical properties. Among the materials obtained, some of the features are often improved, while the others deteriorate. In this study, an attempt was made to obtain a polymer composite based on a PLA filled with macaroni chalcedonite in the amount of 5%, 10%, 15%, 20% and 30% by weight. The properties of the mechanically obtained mixtures were assessed. The tests show that the number of substances in the composite had a significant effect on changing the properties of the obtained material.

Keywords: polylactide; composite; mechanical properties; modified chalcedonite

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1. Introduction

Polymer materials make a huge contribution to the development and technological progress in many areas of the economy. They have become synonymous with modernity and progress. On the other hand, they have also become a problem at the global scale. End-of-life products are deposited in landfills, and they are found in the natural environment, and their degradation may take hundreds of years [1]. Due to this fact, considerable effort is being put into reusing these materials. It should be added here that the processes of purification and separation into various materials are time-consuming, and they are still expensive. The main problem in controlling these processes is to find a solution to them [2–5].

The alternatives are biodegradable plastics made of raw materials of a natural origin as well as oil ones. Among the various polymers, poly (lactic acid) (PLA) is the most promising material. It is based on renewable resources, and it can be used in various industries as a replacement for traditional polymer materials, especially in the field of packaging. In the circular economy, it can be considered as a promising biopolymer due to its properties and estimated commercial costs [5,6]. Polylactide (PLA) is a linear thermoplastic polyester that is completely biodegradable under industrial composting conditions. It can be processed using typical technologies: injection, extrusion, thermoforming, and extrusion blow molding [7,8]. It is obtained by the condensation polymerization of lactic acid or cyclic lactides. Lactic acid, as a preliminary product, is obtained by the bacterial fermentation of starch that is usually derived from maize or from milk processing [9,10]. It is used in the packaging industry, medicine, and agriculture. It can also be successfully processed many times [11–13]. Since, it is obtained from renewable resources and it is biodegradable, it is called "double green". It constitutes about 40% of all of the currently known and used biodegradable polymers [14–16]. Its properties are like those of polystyrene. It is stiff, brittle; the brittle temperature is about 57 °C, and the flow temperature is 170–180 °C. It has good transparency and gloss. It shows good strength properties and a low value of elongation at break (approx. 3–4%). Its disadvantages are undoubtedly, its easy water sorption property, which means that it must be dried before processing [17–20] and it has a relatively high density (1.25 g/cm^3) compared to those of

PP and PS. Having a high polarity means that it does not allow for good adhesion to non-polar polymers (PE and PP) in multilayer structures. It also has a lower heat resistance level compared to that of PET, and it has unfavorable barrier properties against moisture and gases. The bottles made of polylactide decompose under industrial composting conditions after 75–80 days [21–25]. Its disadvantages also include a low impact strength, which disqualifies it from many applications. To improve it, pure PLA introduces various fillers, all of which are of natural origin, such as plant fibers, wood flour, shells of various nuts and mineral fillers such as magnesium and aluminum hydroxides, calcium carbonate, or phosphogypsum. It is important here to maintain its biodegradability while producing a PLA-based composite, and the substances used should not have a negative impact on the environment. In this study, micronized chalcedonite (Crusil M20) was used to fill the PLA. Chalcedonite is a natural siliceous sedimentary rock that is mainly composed of silicon oxide (SiO_2) [26–28]. After grinding, it is used in the following industries: chemical, building materials, and plastics processing [27]. The extensive research on chalcedonite and its varieties testifies to its wide use in, among others, water treatment, construction and building materials, the chemical industry, and plastics processing. Its significant advantage is the lack of heavy metals content, which is why it is widely used [29,30]. The aim of this study is to determine the effect of a filler admixture (micronized chalcedonite) on the mechanical properties of polylactide.

2. Materials and Methods

2.1. Polylactide (PLA)

In this study, polylactide (PLA) from NatureWorks (Plymouth, MN, USA), under the name IngeoBiopolymer 3100HP [31], was used for the research. It is designed to crystallize during processing, thereby leading to higher heat distortion temperatures in opaque applications. It is processed by injection and extrusion technology. It is characterized by a good oxygen barrier and a low processing shrinkage rate. Before processing, the material should be dried so that its humidity is approx. 0.01% because the water content affects the properties and final quality of the product (bubbles and moldings collapse). Its melt flow index MFR (210 °C/2.16 kg) is approximately 24 g/10 min [31]. Due to its ability to crystallize, it is recommended to use an injection mold with an elevated temperature in the range of 80–130 °C.

2.2. Micronized Chalcedonite

Crusil M20 micronized chalcedony from CRUSIL Sp. z o.o. (Inowłódz, Poland) was used [32]. This substance is a chemical type of SiO_2 silica. The mineral's origin means that it contains up to 97% silica with a very extensive pore system. This silica is extremely reactive, and it has a high specific surface area. This enables the extensive use of it. The chemical composition test shows a high content of silica and minimal amounts of oxides of calcium, magnesium, aluminum, iron, and manganese. Due to the very limited area of occurrence, it is considered to be one of the unique rocks. In Poland, it occurs in the deposits of Deborzynka, Gapinin, Lubocz, and Teofilów in Wysoczyzna Rawska near Tomaszow. Table 1 shows the chemical content of individual components, while Table 2 shows the properties of Crusil M20 [32].

Crusil M 20 is made of natural chalcedonite rock. The extracted material is subject to mechanical processing, washing, drying, and grinding in drum dryers at a temperature that is above 300 °C. During the screening process, the material obtained has an appropriate particle size curve (grain size) [26–29,32].

Table 1. Chemical parameters of micronized chalcedonite Crusil M20.

Composition, % wt.	
SiO_2	>98.5
Al_2O_3	<0.02
Fe_2O_3	<0.09
CaO	<0.05
MgO	<0.05
K_2O	<0.08
Na_2O	<0.05
TiO_2	<0.02

Table 2. Parameters of micronized chalcedonite Crusil M20.

Parameters	Value
Specific density	2.60 g/cm^3
Bulk density	0.59 g/cm^3
Bulk density	1.17 g/cm^3
Loss on ignition LOI 1 h 950 °C	0.90%
Standard refractoriness PN-EN 993-12sP	173 (1730 °C)
Granulation D97	20 µm
Granulation D50	6.45 µm
Optical properties L/a/b	95.8/0.32/1.2

2.3. Research Methodology

For the preparation of the test samples, a UT90 horizontal screw injection molding machine by Ponar Żywiec, the UT series for thermoplastics, was used, and it was equipped with a five-point, double-lever, mold-closing system and a direct drive of the screw with a high-torque hydraulic motor. The peripheral devices consisted of an injection mold with replaceable inserts for the paddles and bars, a thermostat, a DARwag electronic scale, KC 100/200 dryer, and a grinder for grinding the plastics.

The PLA together with the filler was dried in a drawer dryer at 90 °C for 48 h. Then, the material for injection was prepared in a rotary mixer, with the percentages of the individual materials given in Table 3.

Table 3. Composition of individual PLA + Crusil M20 mixtures.

Lp.	PLA, % wt.	Crusil M20, % wt.
0	100	0
1	95	5
2	90	10
3	85	15
4	80	20
5	70	30

The regranulate was prepared for the prepared portions of the material and the filler. The pre-processing process had a good spread of the filler in the plastic matrix. After selecting and setting the parameters of the injection molding machine, the samples for testing in the form of paddles and bars were made based on plastic cards. The process parameters are presented in Table 4.

Table 4. The parameters of the sample injection process.

Injection Parameters		Values
injection:		
speed		30%
pressure		120 bar
processing temperature	zone 1	200 °C
	zone 2	190 °C
	zone 3	180 °C
	zone 4	160 °C
	zone 5	80 °C
pressure:		
time		8 s
holding pressure		50 bar
closing force:		
average		844 N
closing the mold:		
pressure		170 bar
speed		40%
time to secure the form		5 s
cycle time		120 s
against pressure		5 bar
mold opening:		
against pressure		10 bar
cooling time		30 s
temperature		80 °C

The strength properties test during the static tensile test was conducted in accordance with the standard in [33] using the Fu1000e testing machine by Heckert (Chemnitz, Germany) with a measuring head up to 10 kN. The measurement was based on static stretching at a constant speed of 2 mm/min of the normalized samples in accordance with the relevant standards in this regard. During the test, the change in force and the elongation at break were recorded. The impact strength was determined by the Charpy method using a pendulum hammer by Wolfgang Ohst (Rathenow, Germany) in accordance with the standard [34]. Hardness testing was conducted according to the Shorea method, scale "D", in accordance with the standard [35] of the electronic hardness testers from XINGWEIQIANG (China). We also tested the water absorption after 7 h and after 24 days in accordance with the standard [36].

3. Results and Discussion

The injection process was controlled by checking the weight of the individual samples. Table 5 shows the average masses of the individual samples depending on the filler content. Along with its increasing share, the mass of the samples prepared for the individual studies increased.

The results of the tests of strength and elongation at break depending on the filler content are presented in Table 6 and Figures 1 and 2, respectively.

Table 5. Changes in the mass of samples depending on the content of the Crusil M20 filler.

Filler Content, %wt.	0	5	10	15	20	25	30
The average weight of the paddles, g	24.48	25.07	25.61	26.20	26.83	27.87	27.80
Average weight of the bars, g	14.78	15.04	15.59	15.65	15.90	16.24	16.58

Table 6. Strength and elongation at break depending on the content of the Crusil M20 filler.

Contents, % wt.	0	5	10	15	20	25	30
Tensile strength, σ, MPa	68.10	61.60	59.00	57.30	54.60	52.30	49.80
Standard deviation	2.91	1.50	0.82	1.76	1.76	0.79	1.07
Elongation, ε, %	4.8	5.4	5.7	3.9	3.5	3.3	2.9
Standard deviation	0.09	0.15	0.09	0.12	0.13	0.12	0.11

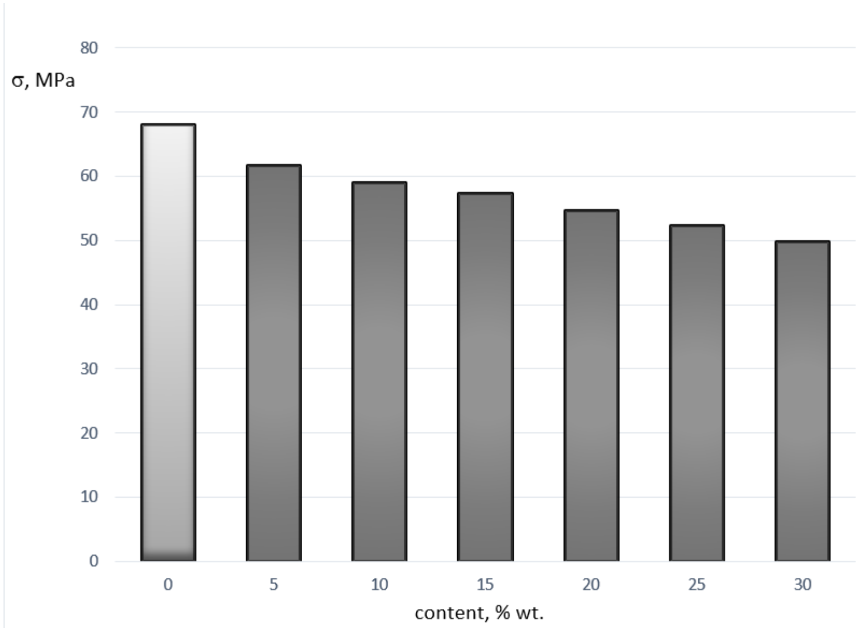

Figure 1. Change in tensile strength depending on the content of the Crusil M20 filler.

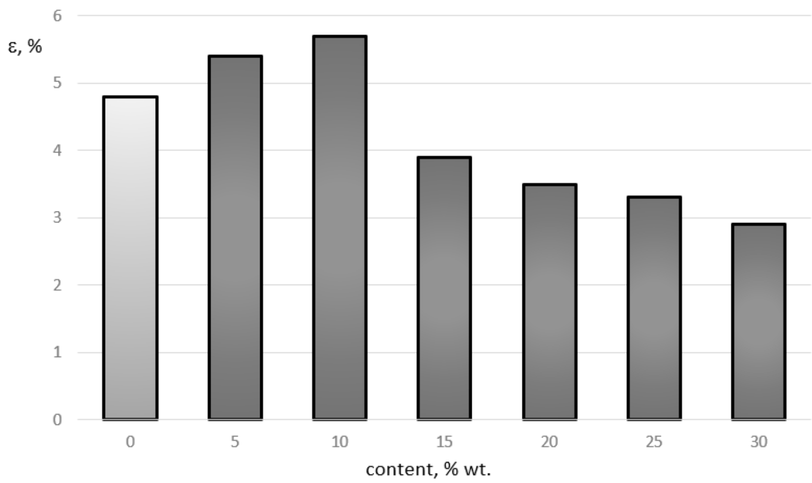

Figure 2. Change of elongation at break depending on the content of the Crusil M20 filler.

It was observed that with the increase in the filler content, a systematic decrease in the strength value in relation to the pure material can be seen. In the case of deformation, from the content of 5% wt. to a mass of up to 10% wt. chalcedonite, the elongation value increases little with respect to the pure material. On the other hand, at the higher filler contents, a slight decrease in this value is observed. It can be concluded here that the addition of a filler in the form of chalcedonite in the range from 5% wt. to 30% wt. reduces the stress value, while the deformation oscillates within the limits of the starting material.

In the case of the impact toughness measurement, interesting results were observed, which are similar in principle to the elongation. They are presented in Table 7 and Figure 3.

Table 7. Impact strength depending on the content of the content of the Crusil M20 filler.

Contents, % wt.	0	5	10	15	20	25	30
Impact strength, kJ/m^2	15.25	29.12	31.87	31.87	23.25	21.12	18.50
Standard deviation	0.54	1.14	1.28	1.54	1.24	1.56	1.52

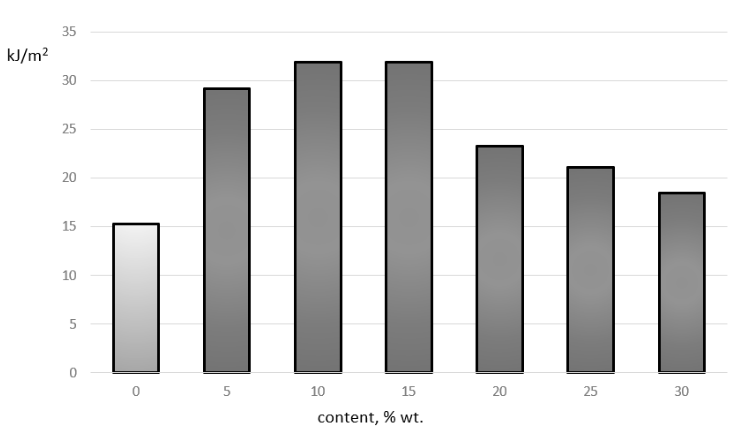

Figure 3. Change in impact strength depending on the content of the Crusil M20 filler.

Pure PLA has an impact strength of 15 kJ/m^2. The addition of the filler causes a significant improvement in this parameter, and for the contents from 5% wt. up to 15% wt., the almost twofold improvement persists. Only with the content of 20% wt., a decline in the value is observed. Generally, the addition of micronized chalcedonite to PLA improves this parameter. Pure PLA has an average level of impact strength, and it is a very brittle material, while the small abundance of this filler improved this material property.

The results of the material hardness measurements are presented in Table 8 and in Figure 4. The addition of micronized chalcedonite does not cause a significant change in the impact strength value in the individual compositions compared to the pure PLA. The results oscillate around the same value, and the difference is minimal, and it can be neglected due to the measurement uncertainty, as evidenced by the value of the standard deviation obtained during the individual measurement series.

Table 8. Hardness depending on the content of the Crusil M20 filler.

Contents, % wt.	0	5	10	15	20	25	30
Shore hardness, scale D	61.0	61.6	61.4	61.5	61.5	60.9	61.0
Standard deviation	1.38	0.67	1.71	0.75	0.83	0.84	0.85

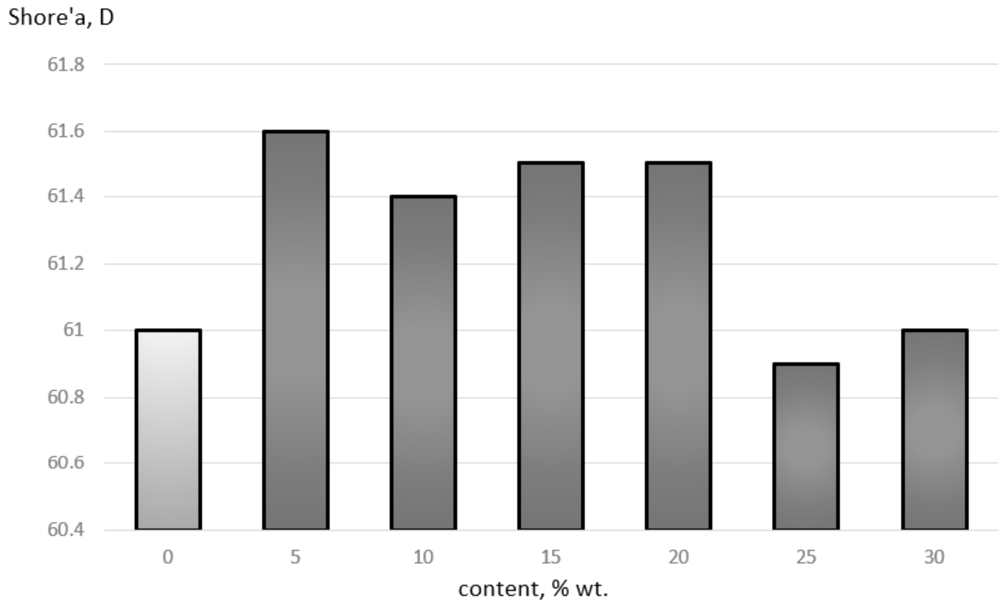

Figure 4. Change of hardness depending on the content of the Crusil M20 filler.

The final stage of the laboratory tests was to analyze the absorbability of the samples. For this purpose, the test samples were placed in a vessel that was filled with water at room temperature. The water absorption test was divided into two parts. In the first one, the samples were immersed for 24 h, and then, their mass was measured, and the differences in the masses of the individual samples were calculated before and after the immersion. The same operations were performed after the samples had been immersed for 7 days.

The results obtained are presented in Table 9. It was observed that the weight increase in the samples after 7 days was almost twofold higher than it was after 24 h. Water absorption has a direct impact on the biodegradation process in industrial composting conditions, for which PLA is intended, and the moisture content and the speed of absorbing water from the environment are of great importance for this process.

Table 9. Absorbability of PLA filled with micronized chalcedonite Crusil M20.

Contents, % wt.	0	5	10	15	20	25	30
Average weight of samples before soaking, g	10.534	10.850	11.102	11.380	11.594	12.041	12.060
Average weight of samples after soaking for 24 h, g	10.523	10.866	11.083	11.364	11.596	12.054	12.053
Average weight of samples after soaking for 168 h, g	10.577	10.892	11.143	11.420	11.632	12.075	12.097
Weight difference after 7 h	0.021	0.017	0.018	0.015	0.016	0.015	0.016
The difference in weight after 168 h	0.042	0.042	0.041	0.040	0.037	0.034	0.037

4. Conclusions

The conducted research confirms that the addition of micronized Crusil M20 chalcedonite changes the mechanical properties of PLA. Along with the increase in the amount of filler in the material, the strength deteriorates, while the elongation at break becomes higher compared to that of the pure PLA, the impact strengths are similar here, and this increase is marked, however, the hardness, depending on the amount of filler, remains at a comparable level.

Summing up, it can be said that the PLA can be freely filled with this substance, which will, among other things, reduce the price of 1 kg of plastic, and its content should be dependent on the requirements for the final product.

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