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Properties of Composites Based on Polylactide Filled with Cork Filler

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Abstract: Introducing fillers into polymeric materials is one of the methods of modifying the properties or reducing the costs of polymeric materials. Thanks to their use, it is possible to obtain new materials with interesting mechanical and chemical properties. Some features are often improved among the new materials obtained, while others deteriorate. In this work, an attempt was made to obtain a polymer composite based on PLA filled with cork flour in amounts of 5%, 10%, 15%, 20% and 30% by weight. The processing and sample preparation process using injection molding technology was assessed and the basic mechanical properties were assessed. The research shows that it is possible to obtain PLA products with a cork filler without the mixing process on an extruder, but only by using an injection molding machine and appropriately selecting the parameters of the technological process. Tests of mechanical properties showed deterioration of parameters, but not to such an extent that the obtained composites were disqualified from use in products that are not subject to heavy mechanical loads. The undoubted advantage of the obtained materials is maintaining their so-called "green" character and thus the ability to biodegrade.

Keywords: polylactide; cork filler; composite; mechanical properties

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1. Introduction

Polylactide (PLA), also known as polylactic acid, is a thermoplastic polymer produced from renewable raw materials. It is fully biodegradable. The properties of PLA are mostly like polystyrene; after appropriate modifications, it is possible to approximate the properties of polyethylene or polypropylene. It also has good organoleptic properties, is suitable for contact with food and can be used to produce transparent films and blowing preforms, as in the case of PET bottles [1–10].

Current trends in PLA modification mainly focus on blends with starch and cellulose. In the former case, the aim is to reduce the price and degradation time; in the case of cellulose fibers, they increase stiffness and temperature resistance. Inorganic fillers are also used, such as chalk, mica, talc or glass. The addition of rubbers increases resistance to cracking. PLA is produced mainly from corn or sugar beets. It can also be produced from waste from milk processing. On average, 2.5 kg of corn grain with a moisture content of 15% is needed to produce 1 kg of polylactide. However, this efficiency depends on the efficiency of the processes, i.e., conversion of starch to dextrose, dextrose to lactic acid, polymerization reaction and, to the greatest extent, on the starch content in the grain [11–20].

PLA has found its way into 3D printing due to its properties and ease of printing. It has a relatively low melting point, which makes it easy to print on most standard 3D printers. It does not require high temperatures or special printing conditions. Unlike some other plastics used in this technology, PLA does not emit an unpleasant odor during the printing process. It can be easily dyed, which allows you to create colorful and aesthetic models. The undoubted advantage is low shrinkage during cooling, which makes it easier to obtain precise and accurate details in prints. It is worth remembering that PLA also has some limitations. It is a relatively brittle material compared to some other materials [21–26].

Current research trends indicate great interest in PLA and the possibilities of its modification using equal fillers, including organic fillers such as wood flour or cellulose fibers. Such composites are also used in 3D printing research [27–33].

The aim of this work is to evaluate the properties of PLA with different cork flour content. Cork filler is a substance added to some plastics to improve their mechanical and thermal properties. Cork fillers are of natural origin and come from cork, which is produced from the bark of the cork oak [34–38]. The literature states that it changes the mechanical strength and reduces density, which is beneficial in applications where weight reduction is important. Moreover, it improves thermal properties by influencing thermal stability. The ecological aspect is undoubtedly also important here [39–42]. Cork is a natural material and its use as a filler can reduce the so-called ecological (carbon) footprint of the product. In practice, the use of cork fillers may depend on the specific requirements of the application and on the properties to be improved [43–48].

Natural cork has many applications, starting from the construction, food, and aviation industries. This material is five times lighter than water, and is also compressible, flexible, biologically and chemically resistant, and consequently durable and flame retardant. It is a barrier and practically impermeable to liquids and gases; due to its low thermal conductivity coefficient of approximately 0.045 W/mK, it is often used as a thermal insulator, it dampens vibrations well and does not conduct electricity. Many of its unique properties result from its structure. It is referred to as a honeycomb structure. The cellular structure also effectively contributes to reducing density. The cork does not change its properties under the influence of heat and humidity [49–52].

2. Materials and Methods

2.1. Polylactide

Polylactide (PLA) from NatureWorks (Plymouth, MN, USA) called IngeoBiopolymer 3100HP was used for the research [53]. This material is designed for crystallization processing, which leads to higher heat distortion temperatures in opaque applications. It is processed by injection and extrusion. It is characterized by a good oxygen barrier and a low processing shrinkage coefficient. Before processing, the material should be dried so that its humidity is approximately 0.01%. The water content adversely affects the properties and final quality of the product (collapse of bubbles and moldings). Its melt flow rate MFR (210 °C/2.16 kg) is approximately 24 g/10 min. Due to the ability to crystallize, it is recommended to use an injection mold with an increased temperature in the range of 80–130 °C. Table 1 provides basic information about the PLA used in the research.

Table 1. Properties of Ingeo Biopolymer 3100HP [53].

Parameters	Unit	Value
Density	g/m^3	1.24
Mass flow rate index (MFR) 210 °C; 2.16 kg	g/10 min	24
Crystallization temperature	°C	165–180
Transparency		transparent
Tensile strength	MPa	65
Tensile elongation	%	3.4
Impact strength by Izod test	J/m	18.2
Flexural strength	MPa	112
Processing parameters		
Injection: temperature	°C	180–200
Injection: mold temperature	°C	25

2.2. Cork Filler

The cork filler used during the research was manufactured by CORKPOL (Ożarów Mazowiecki, Poland) with the designation 61789-98-8 [54]. It is a natural product with a grain size in the range of (0.2–0.8) mm and a density between (45–200) kg/m^3 and brown in color. There is a faint, not sticky odor. The ignition temperature of the cork is above 300 °C. Before processing, drying may be carried out to remove any moisture, even though the cork itself does not absorb moisture. Table 2 provides basic information about the cork filler.

Table 2. Properties of the cork filler [54].

Parameter	**Value**	
Grain size, mm	0.2–0.5 (0.8)	
Density, kg/m^3	45–200	
Color	natural, brown	
Thermal degradation, °C	>300	
Thermal conductivity, W/mK	~0.045	
Solubility	insoluble in water and dilute acids and organic solvents	
	In the radial direction	In a non-radial direction
Compression modulus, MPa (unboiled cork)	8–20	13–15
Compressive modulus, MPa (boiled cork)	6	8–9
Tensile modulus, MPa (boiled cork)	38	24–6
Tensile failure stress, MPa	1.0	1.0
Failure strain in tension, %	5.0	9.0
Poisson's ratio	0–0.97	0.26–0.50

2.3. Methodology of Research Preparation

To prepare samples for testing, a UT90 screw injection molding machine from Ponar Żywiec (Żywiec, Poland) of the UT series for thermoplastics was used, with a five-point, double lever mold closing system and a direct drive of the screw with a high-torque hydraulic motor. The station was additionally equipped with peripheral devices such as an injection mold with replaceable inserts for paddles and beams, a thermostat, a DARwag electronic scale, a KC 100/200 dryer and a grinder for grinding plastics.

Due to the significant water absorption of PLA, it was dried at 60 °C for 8 h before testing. Moisture and fog may adversely affect the quality of prepared test samples.

Then, PLA mixtures were prepared with cork content of 5, 10, 15, 20, 30% by weight, respectively. Properly weighted parts of PLA and cork filler were mixed in a drum mixer. Then, preliminary tests were carried out on the injection molding machine and, after correcting the technological parameters of the injection process, test samples were made in the form of standardized paddles for strength tests. It should be emphasized that during the tests, it was necessary to correct the temperature settings in individual zones in the cylinder. During the plasticization process of the plastic with the filler, a significant amount of heat was generated due to friction. Therefore, it was necessary to lower the temperatures in individual zones on the injection molding machine cylinder. The final process parameters are presented in Table 3.

Before starting the actual measurements, all samples were air-conditioned at a constant temperature of 23 °C and 50% humidity for 48 h. The static tensile test was carried out in accordance with the PN-EN ISO 527-1 and PN-EN ISO 527-2 standards on the Fu1000e testing machine. Heckert (Berlin, Germany) with a measuring head up to 10 kN. The measurement consisted of static stretching of standardized samples at a constant speed of 2 mm/min. During the test, the change in stress and elongation at break were recorded.

Table 3. Parameters of the injection process.

Injection Parameters	Unit	Value
	injection	
speed	mm/s	40
pressure	bar	80
	pressing	
time	s	10
pressing pressure	bar	60
	closing force	
mean	N	887
	closing mold	
pressure	bar	170
speed	%	40
mold protection time	s	5
cycle time	s	120
counter pressure	bar	5
	mold opening	
counter pressure	bar	10
cooling time	s	15
temperature	°C	25
	temperature	
Nozzle	°C	200
Zone 1		200
Zone 2		195
Zone 3		185

Impact strength was determined using the Charpy method according to the PN-EN ISO 179-1 standard, using a pendulum hammer from Wolfgang Ohst (Solingen, Germany) with an impact energy of 4 J. The measurement was performed on samples made without notches. Hardness was determined by the Shore method in accordance with the standard using an electronic Shore hardness tester with a scale of 0–100 D, manufactured by XINGWEIQIANG (Shenzhen, China).

Water absorption was performed using the weighing method in accordance with the PN-EN ISO 62 standard. The test was carried out on 10 paddle-shaped samples. This study was conducted over one month. Weighed samples were placed in water in a collecting vessel. After 24 h, the samples were removed and dried. Drying the samples from water remaining on their surface was carried out in two stages, i.e., initially, samples were placed vertically, and the duration of initial drying was on average about 10 min. The samples were then left on a dry cloth to evaporate any remaining water from the surface. This procedure usually took about 30 min. After the drying stage, the samples were visually inspected to eliminate darker spots, i.e., places where water remains. If found, additional drying time was used and was constant for all samples. The paddles were then weighed and placed back into the container of water. Samples are weighed on a scale with an accuracy of 0.001 g, in the range of 1–200 g.

3. Results

During the injection process, the mass of the moldings was controlled to monitor the stability of the technological process. The obtained results confirmed the correctness of the adopted technological parameters. Table 4 shows the results obtained.

Table 4. Average mass of injection of samples in the form of paddles.

Filler content, % wt.	0	5	10	15	20	30
average weight of samples, g	24.16	24.16	24.15	24.15	24.13	23.99
standard deviation	0.0684	0.0052	0.0082	0.0075	0.0098	0.0103

The test results for strength and elongation depending on the content of cork filler in PLA are presented in Table 5 and Figures 1 and 2. All samples fractured brittlely during the tensile test.

Table 5. Mechanical properties of PLA depending on the content of cork filler.

Filler content, % wt.	0	5	10	15	20	30
Tensile strength σ, MPa	69.56	48.28	45.82	39.84	34.08	25.96
Elongation at break ε, %	7.90	7.15	7.10	7.00	6.95	6.40
Young's modulus, MPa	3522.03	2700.98	2395.82	2276.57	1933.62	1622.50
Impact strength, J/m^2	18.87	11.92	10.92	10.21	8.87	7.42
Hardness, Sh'a, D	61.35	63.35	63.61	63.27	60.00	58.8

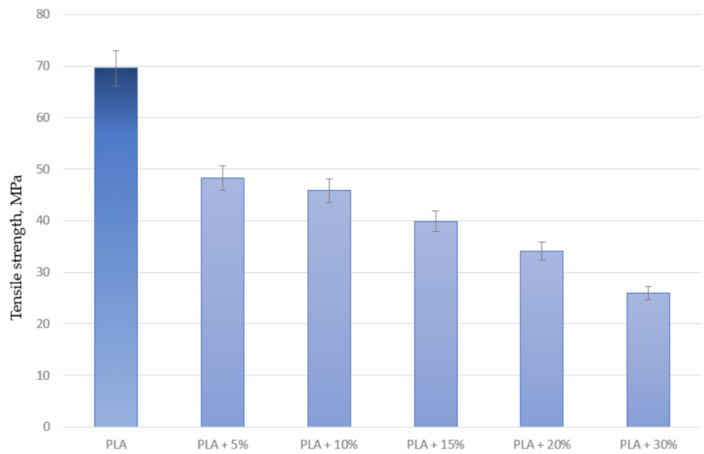

Figure 1. Tensile strength depending on the filler content.

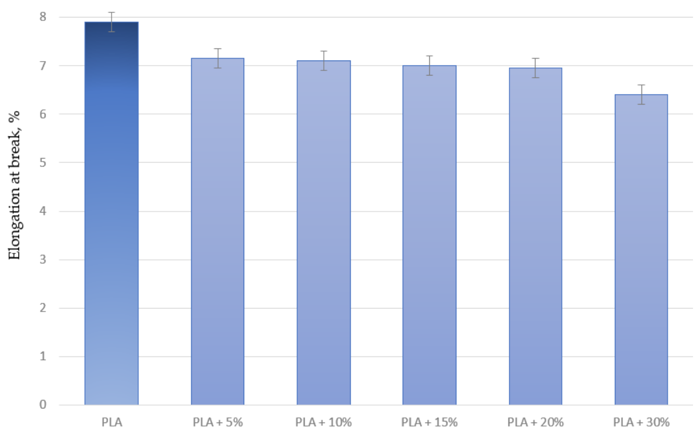

Figure 2. Elongation at break depending on the filler content.

With an increase in the content of cork filler, a systematic decrease in the strength value is observed, almost by half when filling with 30% wt. (Figure 1). However, the deformation rate at break is insignificant (Figure 2). These changes suggest specific behavior of the material depending on the filler content. Increasing the cork filler content may lead to changes in the structure of the composite, which may include the formation of more cork particles in one place. This can also lead to areas of greater porosity or imperfections, which ultimately reduces the strength of the material. At the same time, such an uneven distribution of the filler in the matrix may change the way the load is distributed in the material and thus reduce its strength.

Young's modulus is directly related to the measurement of material strength and deformability. Table 4 and Figure 3 present the results obtained. In this case, a slight decrease in this parameter is observed, which indicates the stiffness of the material. It can be concluded that the cork reduced the stiffness of the samples. Therefore, the addition of cork to a plastic matrix influences the interfacial relationship between the cork and the matrix. The weakening of these interactions can also lead to a decrease in the stiffness of the material, as evidenced by the results obtained.

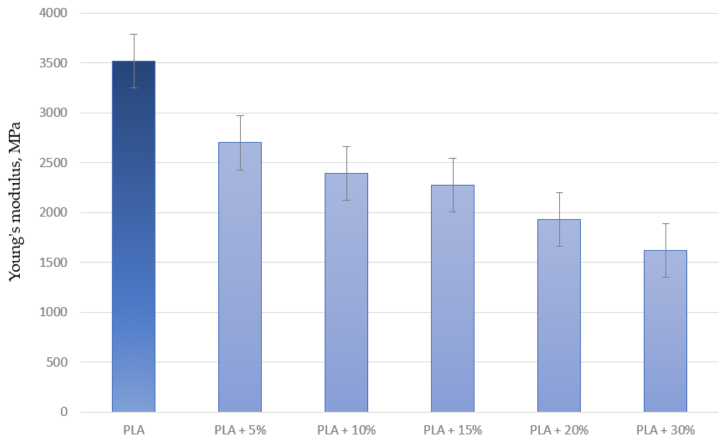

Figure 3. Young's modulus depending on the filler content.

The next stage in the assessment of the mechanical properties of the obtained composites was impact strength testing. The results are presented in Table 4 and Figure 4.

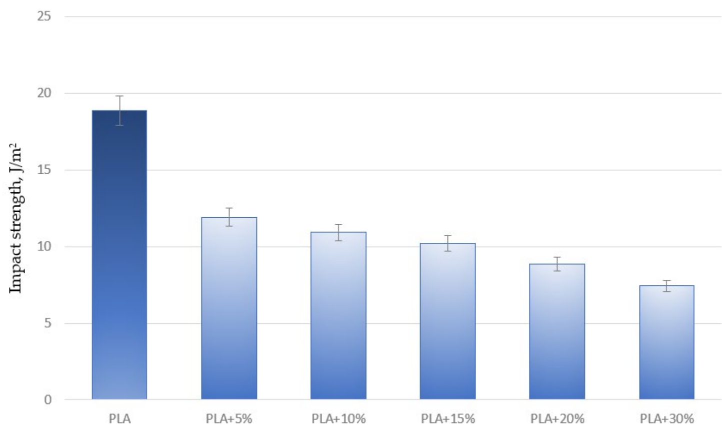

Figure 4. Impact strength depending on the filler content.

The addition of a cork filler in the composite significantly impairs the impact strength. The value of this parameter at a maximum filling of 30% wt. drops by almost half. Despite the deterioration of the impact strength of the composite, the results obtained do not disqualify it from practical applications. Such composites can still be used for products that are not dynamically loaded, such as structural members with low-impact resistance requirements. It is also important to consider other advantages of the composite, such as its lightness, biodegradability and the potential ecological benefits of using cork as a filler.

The last mechanical parameter to be assessed was hardness. The results obtained for this parameter are presented in Table 5 and Figure 5.

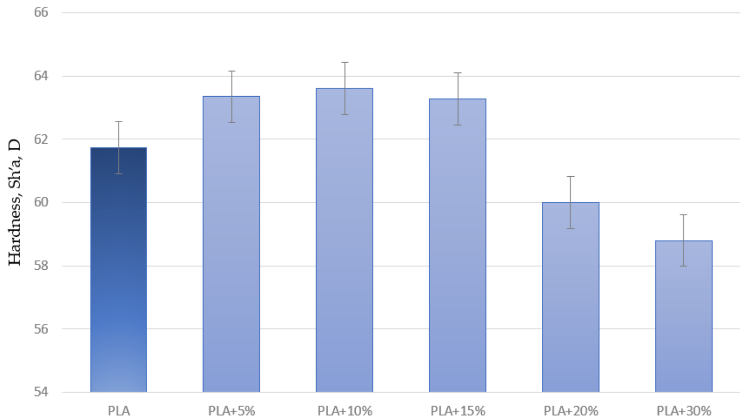

Figure 5. Hardness depending on the filler content.

As the amount of cork filler in the PLA matrix increases, the hardness increases to 15% wt. compared to pure PLA. A decrease in this parameter was observed only at the content of 20% wt. and 30% wt. This type of behavior suggests complex material behavior. It is difficult to talk about a deterioration of this parameter at contents above 20% wt. During such filling, part of the load is already transferred to the cork particles dispersed in the matrix. Because it is more susceptible to compression and deformation and is dispersed in the polymer matrix, the cork particles absorb part of the stress and thus the hardness is reduced.

From the point of view of the biodegradation process, water absorption is important. It is one of the main factors influencing and initiating this process. The determination of this parameter was carried out in accordance with the PN-EN ISO 62 standard. The measurement itself was extended to determine the change in mass of samples immersed in water over a period of 30 days. Figure 6 shows a photo of samples in the form of tensile test paddles that were immersed in water.

Figure 6. View of samples before the water-soaking process.

Each time after 24 h, the samples were dried, and their weight was measured. Figure 7 shows the measurement results of the mass change of the tested samples during the experiment. Table 6 shows the final results of the changes in the mass of the samples during exposure to water.

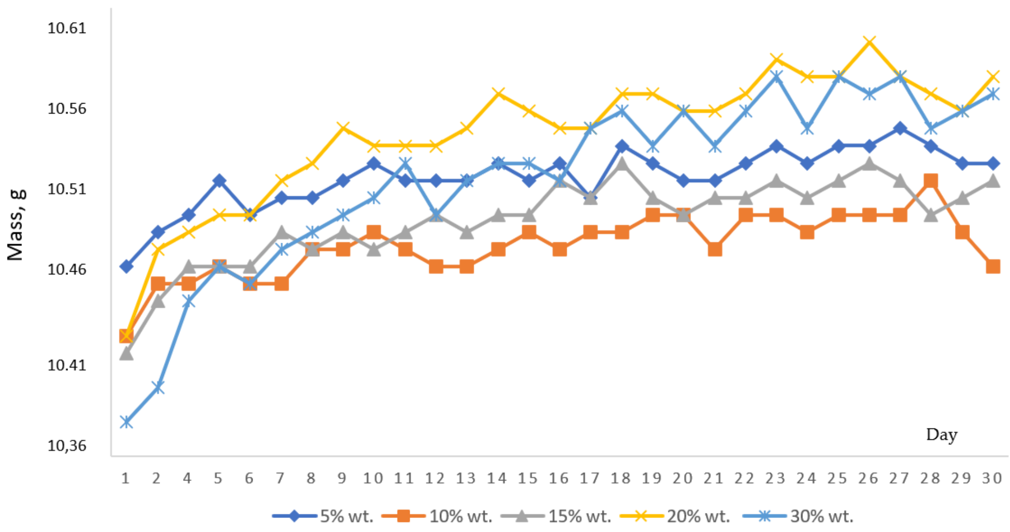

Figure 7. The course of water absorption of individual PLA samples with a cork filler over 30 days.

Table 6. Changes in the mass of PLA with a cork filler of appropriate content after 30 days of exposure to water.

Filler content	0%	5% wt.	10% wt.	15% wt.	20% wt.	30% wt.
mass before soaking in water, g	10.48	10.47	10.43	10.42	10.43	10.38
mass after 30 days, g	10.55	10.50	10.52	10.58	10.58	10.55
difference, g	0.08	0.07	0.10	0.15	0.20	0.08

The obtained results indicate that all samples absorbed water almost evenly over time, which suggests that the absorption process was stable and uniform. Despite this, the obtained changes in mass are not significantly large, which may indicate a moderate ability to absorb water from the tested materials. For pure PLA, the difference in mass is only 0.07 g, which may indicate a low ability of this material to absorb water. However, for a sample containing 30% wt. of cork, the difference in mass is 0.2 g, which suggests that the addition of cork increases the ability of the material to absorb water. It is worth noting that as the filler content increases, the amount of water absorbed increases. This proves the influence of the addition of cork on the composite's ability to absorb water. Cork, known for its porous structure, can facilitate the absorption of water by the material, which may be important in the context of its potential biodegradation.

The results suggest that the tested composite may be more susceptible to biodegradation due to its increased ability to absorb water. This is important for its further use and environmental impact.

4. Conclusions

Processing of PLA with a cork filler and direct production of products without the process of combining the filler with the polymer material by extrusion is possible. Selecting appropriate injection parameters allows you to obtain fully functional products, especially with small fillings.

The observation of a systematic decrease in strength and elongation with an increase in the content of cork filler suggests that it does not strengthen the material, but only allows it to reduce its share. By using this additive, we can reduce costs and maintain the biodegradable nature of the resulting composites. When designing products from such composites, it is necessary to assess how much filler should be added so that the decrease in mechanical parameters is not drastic. However, the product had the required minimum functional and durability characteristics.

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