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The Influence of Poly(Vinyl Alcohol) on Oil Release Behavior of Polylactide-Based Composites Filled with Linseed Cake

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Abstract: In order to limit the negative impact of industry on natural environment, ecological alternatives to conventional polymers are being proposed. One of the most popular “green” polymers is polylactide, which can also be successfully applied as a matrix of composites. The application of ground linseed cake as a filler for polylactide-based composites is in line with the idea of Circular Economy, and moreover it provides a modifying effect on the polymer by increasing its crystallinity and reducing its brittleness. This effect is caused by the presence of linseed oil which can be released to the polymeric matrix in a non-controlled way. In order to control the miscibility of the oil and the polymer, we modified the filler particles with poly(vinyl alcohol) before introducing it to the polylactide. We concluded that poly(vinyl alcohol), which does not mix with oil, encapsulated the active ingredients inside the filler particles. We evaluated the mechanical properties of the composites containing 5, 10, 20 and 30 wt% of the filler in a static tensile stress and by means of dynamic mechanical thermal analysis. Crystallinity and thermal properties were tested using differential scanning calorimetry as well as thermogravimetric analysis. Composites’ microstructure was evaluated by Scanning Electron Microscopy. It was found that modifying the oil-rich filler with poly(vinyl alcohol) helps to reduce its release to the matrix and thus limits the plasticizing effect of linseed cake. This result was in accordance with our hypothesis.

Keywords: Polylactide; poly(vinyl alcohol); waste filler; oil release

1 Introduction

In the era of environmental pollution, excessive waste production and climate crisis, product sustainability has become a crucial factor for consumers and producers alike. In order to fulfill the market’s demands and to limit the negative impact of today’s industry on our planet, researchers have been developing environmentally friendly alternatives for conventional products, especially in the field of polymeric materials. Commonly used plastics, which are mostly non-biodegradable and synthesized from non-renewable resources, can now be replaced with bio-based and biodegradable alternatives, such as polyhydroxyalkanoates (PHBs), thermoplastic starch, poly(butylene succinate) (PBS) or polylactide

(PLA) [1–7]. Out of these, PLA is the most common choice due to its relatively low price, good mechanical properties (comparable to those of poly(ethylene terephthalate)) and the ability to be processed in conventional ways [7]. What is more, the properties of PLA can be finely tuned using different modifiers: nucleating agents [8], chain extenders [9], plasticizers [10,11] or fillers [12–14]. Polylactide can also be successfully applied as a matrix of different composites. Even though conventional fillers (such as glass fiber) improve the mechanical properties of PLA [15], the organic, plant-based options are gaining more interest [16]. These “waste fillers”, i.e., byproducts from different branches of industry, are of special interest due to being in line with the idea of Circular Economy. For example, brewer’s spent grain has been successfully introduced to polycaprolactone biocomposites [17], the addition of coffee grounds has been shown to improve the stiffness of poly (butylene adipate-co-terephthalate) [18], and the application of almond shell flour as a filler for PLA results in increased hardness of composites [19]. The majority of post-agricultural waste fillers such as grain husks or nut shells mostly comprise of lignocellulose and improve the mechanical properties of composites [20,21], but some of them can also provide a more complex modifying effect. In our previous research we studied the application of linseed cake in the PLA-based composites [22–24]. As linseed cake (leftovers from mechanical oil extraction of linseed [25]) contains natural oil [26], it influences crystallization behavior and plasticizes the polymeric matrix [23,24]. Even though this modifying effect is mostly considered to be beneficial, it cannot be controlled and depends on the miscibility of the oil and PLA. What is more, the oil content in the linseed cake depends on the method of oil extraction, therefore it can vary to a great extent [26]. Therefore, a method of oil release control needs to be found in order to adjust the properties of the filler for the desired application. What is more, the analysis of the properties of PLA-based composites filled with modified linseed cake will help to fully understand the phenomena taking place during preparation and lifespan of similar materials.

There are numerous methods of chemical modification of plant-based fillers for polymeric composites, such as mercerization, silane treatment, benzoylation and acetylation [2,27,28]. The main purpose of chemical treatment of lignocellulosic fillers is to remove impurities, change the structure, and graft chosen functional groups on their surface, in order to improve their affinity to the polymeric matrix, as well as to increase thermal stability and limit moisture absorption [29,30]. However, in the case of oil-rich fillers a different approach needs to be applied.

Poly(vinyl alcohol) (PVA) is a polar, water-soluble polymer which can undergo biodegradation [31,32]. Due to the presence of -OH groups in its structure it can form hydrogen bonds with hydrophilic lignocellulosic particles. On the other hand, it does not mix well with nonpolar compounds such as vegetable oil, and it is known for its good barrier properties [33]. The blends of PLA and poly(vinyl acetate-co-vinyl alcohol) have been evaluated by Park and Im who found out that they are mutually immiscible [34]. However, as Yeh et al. point out, the -OH groups of PVA can interact with carbonyl groups of polylactide [35]. Considering all the aforementioned questions, we can hypothesize that PVA may be a good modifying agent for LC in order to control the oil release behavior: when the waste filler is covered with poly(vinyl alcohol), it can create a barrier surface to encapsulate the oil inside it and limit its release to the PLA matrix. This idea is schematically shown in Fig. 1. What is more, the polar nature of PVA will ensure its good adhesion to the lignocellulosic part of the waste filler and, to a certain degree, to PLA. The aim of this study is to evaluate the influence of PVA-modified linseed cake on the properties of PLA composites.

2 Materials and Methods

2.1 Materials

A commercially available grade of polylactide (PLA) Ingeo Biopolymer 4032D produced by Natureworks characterized by mass flow rate (MFR) of 7 g/10 min (210°C, 2.16 kg), density of 1.24 g/cm^3 and weight average molecular weight 100 000 g/mol was selected for the matrix of the composites.

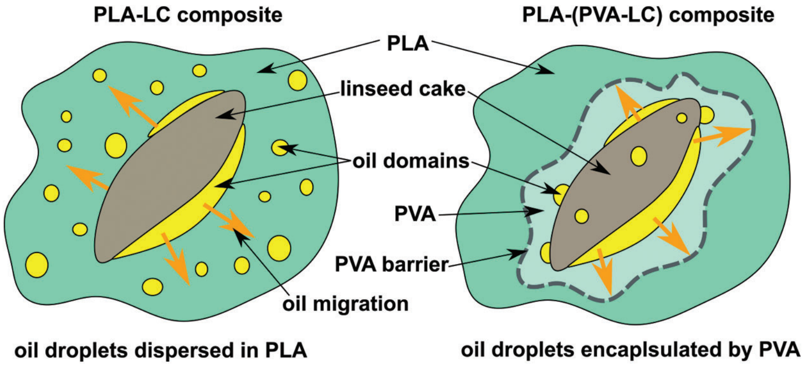

Figure 1: The idea of the study: application of PVA in order to control oil migration from linseed cake particles to PLA matrix

Linseed cake (LC) was obtained from a local Polish supplier. The waste filler contained about 30.4 wt% of natural oil, as established by Soxhlet extraction in petroleum ether. In order to modify the linseed cake, poly (vinyl alcohol) (PVA) grade Selvol Polyvinyl Alcohol 523 (hydrolysis degree of 87-89%, weight average molecular weight of 85000-124000 g/mol) produced by Sekisui Specialty Chemicals was applied.

2.2 Sample Preparation

The filler was modified in the following way: first, 100 g of PVA was dissolved in 1 L demineralized water. To ensure the complete dissolution of the polymer, the mixture was agitated for 15 minutes in 70°C. Then, 100 g of as-received linseed cake was added to the solution of PVA. After mixing with a magnetic mixer, the obtained suspension was poured to polypropylene containers. It was left to dry in a Pol Eko cabinet drier in 80°C for 48 h. The resulting PVA-LC sheets were crushed and then ground into a fine powder using a Bosch MKM 6003 grinder.

In order to prepare the PLA-based composites containing 5, 10, 20 and 30 wt% of the modified filler, the selected amounts of PVA-LC powder were hand-mixed with polymer pellets. In order to limit the risk of PLA hydrolysis during processing, the mixtures were dried for 24 h in 70°C in a Memmert ULE cabinet drier prior to each step of processing. The composites were manufactured by blending in a molten state using a Zamak EHD 16.2 co-rotating twin screw extruder with rotational speed of the screws set to 100 rpm and die temperature of 190°C. The extrudates were cooled in the air and pelletized. Normalized samples were injection molded using a Battenfeld PLUS-35 machine operating at the following parameters: $T_{injection}$ = 210°C, T_{mold} = 50°C, $p_{injection}$ = 72 MPa, $v_{injection}$ = 75 mm/min. Pure PLA was processed along with the composite samples, which were named according to their composition, e.g. the 5 PVA-LC sample contains 5 wt% of the PVA-LC filler. In order to evaluate the influence of PVA modification, the obtained results were compared with properties of PLA filled with 10% of unmodified linseed cake containing 30.4 wt% of oil. This reference material was named 10 LC, its wider characteristic can be found in our previous study [24].

2.3 Experimental Methods

The morphology of the composites was evaluated by Scanning Electron Microscopy (SEM). The samples' brittle fracture surfaces were sputtered with gold prior to the observations. The analysis was performed using a Zeiss Evo scanning electron microscope with electron accelerating voltage of 12 kV. Pictures were captured with a magnification of 300× and digitally processed.

The mechanical properties of the samples were evaluated according to the ISO 527-2 standard by means of a static tensile test using a Zwick Z010NT universal testing machine. The crosshead speed was 1 mm/min during the measurement of tensile modulus and 10 mm/min during the remaining part of the test. The values of tensile modulus E, tensile strength Rm, elongation at break ε and toughness were determined based on 7 separate measurements.

Thermomechanical properties of the composites and the neat polymer were tested using the dynamic mechanical thermal analysis (DMTA) technique in torsion mode using an Anton Paar MCR 301 apparatus. The 50 × 10 × 4 mm^3 samples were tested in the temperature range of 30-110°C, with 2°C/min heating rate, strain of 0.01%, and frequency of 10 Hz. The run of storage modulus (G″) and loss modulus (G′) curves was evaluated across the whole temperature range. The value of glass transition temperature (T_g) was determined as a peak of G″ *vs.* temperature curve. Based on the obtained data, filler effectiveness C and brittleness B [36] were calculated according to formulae 1 and 2, respectively:

$$C = \frac{G'_{30,C}/G'_{75,C}}{G'_{30,M}/G'_{75,M}} \tag{1}$$

where: $G'_{30,C}$ – value of storage modulus evaluated for a composite sample at 30°C, $G'_{75,C}$ – value of storage modulus evaluated for a composite sample at 75°C, $G'_{30,M}$ – value of storage modulus evaluated for the matrix polymer at 30°C, $G'_{75,M}$ – value of storage modulus evaluated for the matrix polymer at 75°C.

$$B = \frac{1}{G'_{30} \cdot \epsilon_b} \tag{2}$$

where: G'_{30}– value of storage modulus at 30°C [Pa], ε_b– value of elongation at break obtained in the tensile test [%].

Differential scanning calorimetry (DSC) was applied to assess the crystallization behavior and melting of the polymeric samples using a Netzsch DSC 204F1 Phoenix apparatus. The samples of 5.0 ± 0.2 mg were placed in aluminum crucibles with pierced lids, heated from 20°C to 210°C with the heating rate of 10°C/min, held in this temperature for 10 minutes and then cooled back to 20°C with the cooling rate of 10°C/min. An inert nitrogen atmosphere was applied. The heating and cooling cycle was performed twice in order to erase the thermal history of the samples. The crystallinity degree (X_{cr}) was calculated based on the second heating, using the following formula (3):

$$X_{cr} = \frac{\Delta H_m - \Delta H_{cc}}{(1-\varphi)\Delta H_{100\%PLA}} \cdot 100\% \tag{3}$$

where: ΔH_m – melting enthalpy of a sample [J/g], ΔH_{cc} – cold crystallization enthalpy of a sample [J/g], $\Delta H_{100\%PLA}$ – melting enthalpy of a 100% PLA, $\Delta H_{100\%}$ = 93 J/g [37], φ – filler content.

Thermal degradation of the PLA and PLA-based composites was evaluated using thermogravimetric analysis technique (TGA). Samples of 10 ± 0.2 mg were placed in open Al_2O_3 crucibles and heated from 30°C to 900°C with the heating rate of 10°C/min, in a Nitrogen atmosphere, using a Netzsch TG Libra apparatus. The obtained curve was differentiated using Netzsch Proteus software.

In order to analyze the ability of the composites and the pure PLA to absorb water, all samples were weighted using a laboratory balance and submerged in demineralized water. They were stored in 23°C in closed beakers for 480 hours. The samples were periodically removed from the water, wiped with a dry cloth and weighted again. The moisture absorption *MA* was calculated according to formula 2:

$$MA = \frac{m - m_0}{m_0} \cdot 100\% \tag{4}$$

where: m – mass of a sample [mg] , m_0 –initial mass of a sample [mg].

The absorption spectra of 10% solution of water used for immersion test of PLA and PLA-based composites in the range of 190-1100 nm with wavelength accuracy of 0.3 nm was determined with the use of Rayleigh UV 2601 UV-Vis spectrophotometer.

The chemical composition of the samples was analyzed using infrared spectroscopy method. FT-IR spectra were obtained in the attenuated total reflection (ATR) mode, using a Jasco FT/IR 4600 apparatus equipped with a diamond cell. A total of 64 scans were collected with scanning speed of 1 cm/min.

3 Results

3.1 Morphology

The SEM pictures of the samples brittle fracture surfaces are shown in Fig. 2. The unmodified PLA presents a structure typical for the amorphous form of this polymer. The fracture surface is smooth, which indicates that the material did not deform in a plastic way. No porosities or other structural defects can be seen. Addition of 5 wt% of the modified linseed cake changes the structure of the sample. Even though the surface is still typical for amorphous PLA fractured in a brittle way, it is more uneven. The filler particles are easy to distinguish in the fracture plane. No gap at the interface between the LC particles and PLA can be noticed, which indicates that modification with PVA provides good affinity of the phases. The linseed cake particles are well dispersed within the composite's volume and they do not form clusters. Interestingly, only two phases: the filler particles and the polymeric matrix can be distinguished in the picture. Therefore, the PVA remains on the surface on the filler during mixing with PLA and it does not create a separate phase. The increase of the PVA-LC percentage to 10 wt% does not result in notable changes of the composite's morphology. The filler particles are still well dispersed and embedded in the polymeric matrix. The fracture surface is more uneven due to presence of modified linseed cake, whose particles change propagation of cracks. The composite samples containing 20 and 30 wt% of

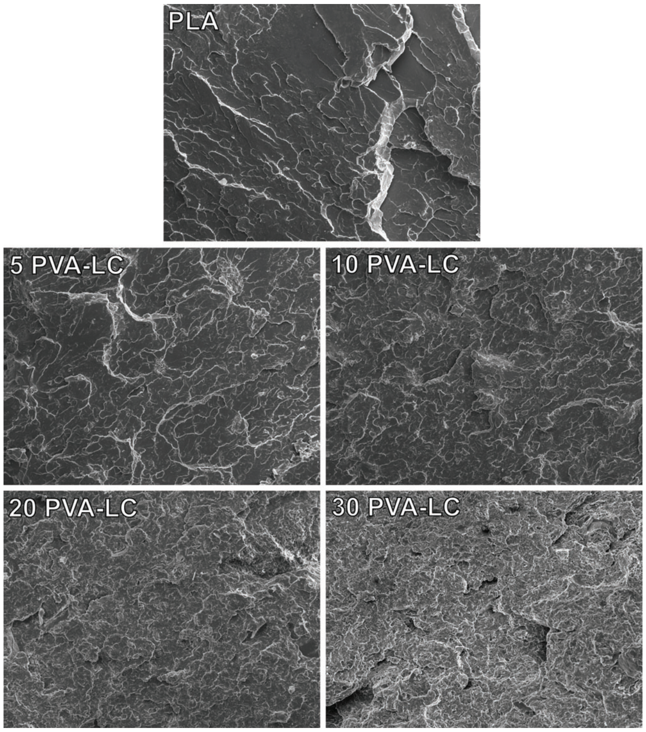

Figure 2: Brittle fractured surfaces of the pure PLA and its composites observed using SEM at a magnification of 300×

PVA-LC present the most distinct changes of morphology. The fracture surfaces are uneven and "granular" which is typical for plastic deformation of the semicrystalline polymer. This result can indicate addition of the modified waste filler causes and increase of PLA crystallinity. What is more, small pockets can be seen, whose presence indicates that pull out of the filler particles took place. Because of the high volumetric content of the filler its particles cannot be fully covered with the polymer and they can detach easily during fracture. What is more, in the case of the highly filled composites, a separate phase can be seen in the fracture surface. It can be recognized as PVA, which does not perfectly mix with PLA. It can be concluded that modification with poly(vinyl alcohol) is beneficial only in the case of addition up to 10 wt % of the filler.

3.2 Thermal Properties

The thermograms obtained during the second heating of the samples are shown in Fig. 3. The exothermic peak visible around 90-110°C can be attributed to cold crystallization of polylactide. It is then followed by endothermic melting peak around 160-180°C. This behavior is typical for polylactide, characterized by its dominant amorphous structure as an effect of the slow crystallization rate of polymers [10]. It can be observed that the addition of the hybrid filler did not change the course of the DSC curves. What is more, no additional peak coming from PVA melting is visible. This can be easily explained by the fact that the poly(vinyl alcohol) contained by the filler is amorphous, as it is shown by its thermogram in Fig. 3. Therefore, the peak visible for the composite samples comes from the melting of PLA and can be used for evaluating the crystallinity of the composites' matrices.

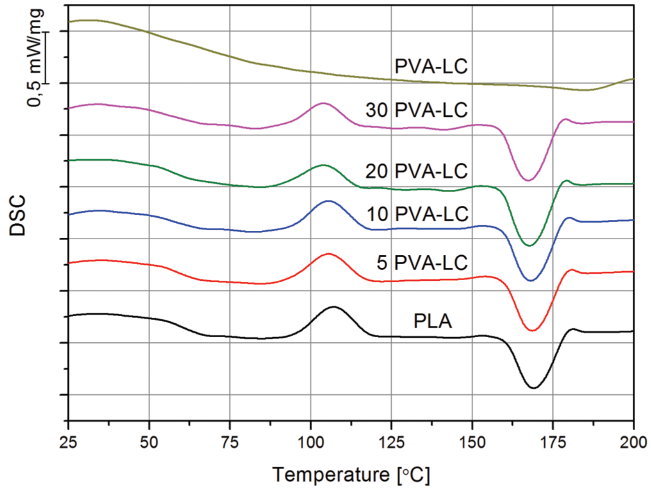

Figure 3: DSC thermograms obtained during the second heating of the samples

Based on the DSC measurements, the values of cold crystallization temperature (T_{cc}), melting temperature (T_m), cold crystallization enthalpy (ΔH_{cc}), melting enthalpy (ΔH_m), as well as crystallinity degree X_{cr}, were determined and are collectively presented in Tab. 1. It can be observed that both T_{cc} and T_m values decrease slightly as a function of filler content. Even though the decrease in the melting temperature can be an indicator of compatibility between the phases [34], the change is insignificant. A decrease in T_{cc} as well as an increase in crystallinity were observed in the case of PLA composites filled with unmodified linseed cake [23], which can be explained by the presence of the natural oil facilitating the arrangement of macromolecules. Even though a similar result is achieved due to the addition of PVA-modified LC, it cannot be solely ascribed to the modifying effect of the oil. As Yeh et al. have shown in their publication [35], blending PLA with poly(vinyl alcohol) also causes an enhancement of crystallinity

Table 1: Thermal properties of the composites and the PLA

Sample	T_{cc} [°C]	T_m [°C]	ΔH_{cc}	ΔH_m	X_{cr} [%]
PLA	108.0	170.3	22.64	33.25	9.26
5 PVA-LC	106.0	170.0	22.51	37.72	17.22
10 PVA-LC	106.2	169.6	24.13	36.36	14.93
20 PVA-LC	104.9	168.9	18.14	38.18	26.94
30 PVA-LC	104.4	168.5	23.10	34.61	17.68
10 LC [24]	94.5	176.0	9.09	57.64	57.57

due to good interactions between the phases. However, the results obtained for PVA-LC filled polylactide defy a simple explanation. Considering the non-linear relationship of the filler content and the X_{cr} value, it can be concluded that the crystallization behavior of the studied composites are a result of multiple factors.

The TGA and dTG curves obtained for the pure PLA, the composites, and the filler, are presented in Fig. 4. It can be observed that polylactide undergoes a typical one-stage decomposition [38] and its maximum rate (peak of dTG curve) is achieved at 361°C. The filler shows a different behavior: an initial mass loss in the temperature range of 40-120°C can be observed, which can be attributed to evaporating moisture [39]. The actual decomposition of the filler starts above 200°C, as indicated by multiple overlapping peaks 200-500°C. Their presence can be explained by thermal degradation of PVA side chains (around 300-350°C) and the polymeric backbone (the shoulder at 440°C) [39]. The peak around 360°C indicates the decomposition of cellulose [40]. What is more, the decomposition of the remaining linseed cake components such as protein and oil also occur in a similar temperature range, affecting the shape of the dTG curve [40–42]. The composite samples undergo a one-stage decomposition, similarly to pure PLA. Nevertheless, the dTG maximum is shifted to lower temperatures, towards the point of PVA side chains decomposition. A small shoulder indicating degradation of PVA backbone can also be seen around 450°C. It is understood that the addition of the filler characterized by low thermal stability also decreases the degradation temperature range of the composites. What is more, a similar effect was observed in the case of the addition of 1% of PVA to PLA and was explained by reduced molecular weight of the polymeric matrix due to the addition of the filler [43]. This explanation cannot be excluded either, but it is less probable, as the remaining tests did not show any decrease in the PLA's molecular weight.

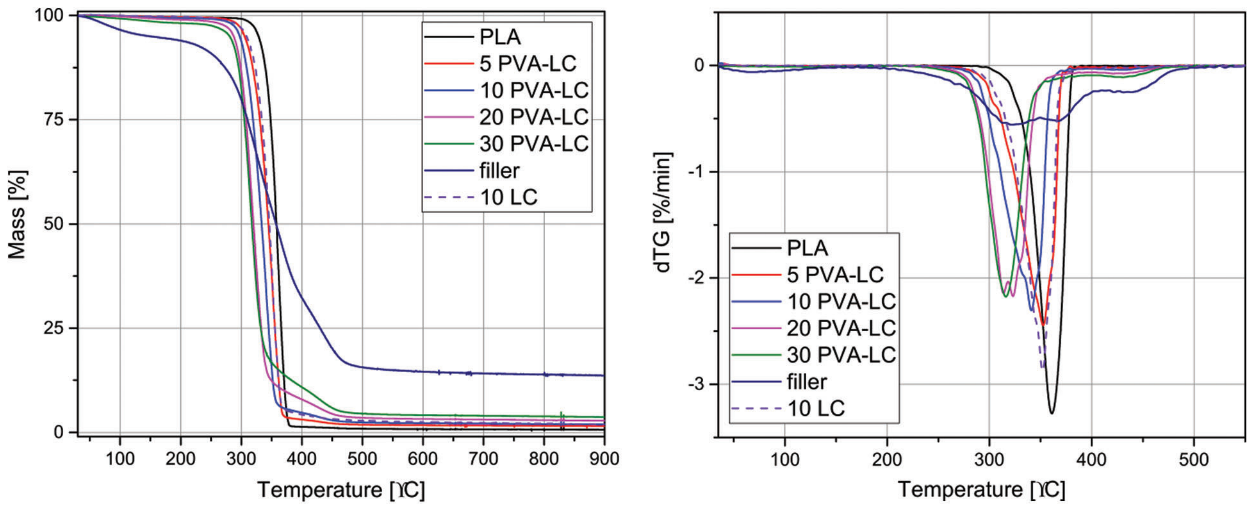

Figure 4: TG and dTG curves of the composite samples, the pure PLA and the filler

3.3 Mechanical Properties

Fig. 5 shows exemplary stress-strain curves obtained during tensile test. The relationship of the hybrid filler and the mechanical properties of the composites, that is tensile strength, toughness, tensile modulus and elongation at break, is presented in Fig. 6. It can be seen that tensile strength decreases along with the growing filler content. The Rm value of the composite containing 30 wt% of the PVA-LC filler is over 50% lower in comparison to the pure PLA. Similar effects were reported in the case of the PLA-PVA blends [44] as well as polylactide-based composites filled with linseed cake [24]. The decrease of Rm can be therefore explained by various factors, such as low mechanical strength of poly(vinyl alcohol) or insufficient adhesion between the polymer and the filler. Considering that the fracture of the filled samples occurs at higher strain than for the neat PLA, it can also be assumed that plasticization of the matrix by the linseed oil occurs.

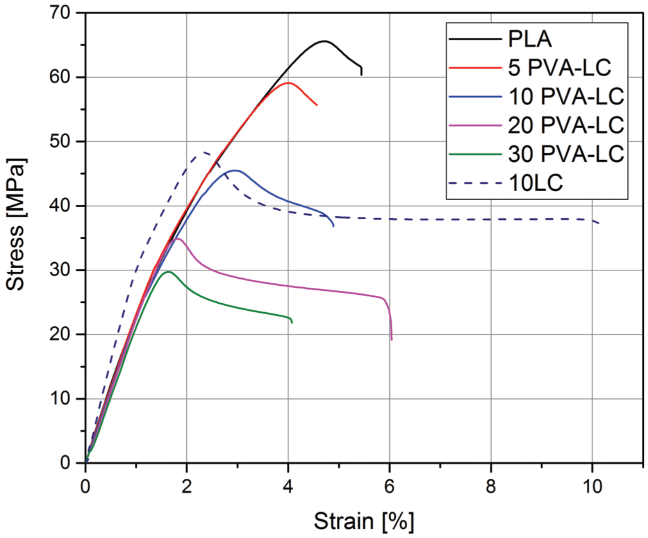

Figure 5: Stress-strain curves of the studied samples

Material toughness is the amount of energy required to break it. It can be evaluated in static conditions as the area under the stress-strain curve. As it can be seen in Fig. 6, the toughness of the composites changes due to the addition of PVA-LC filler. Incorporating as little as 5 wt% of the modified linseed cake into the polymer causes a drop from 256.8 kJ/m^2 to 171.4 kJ/m^2. However, further increase in the filler content up to 20 wt% does not cause a visible change in toughness, whose value remains stable around 170 kJ/m^2. Even though the samples break subjected to different stress the overall amount of energy needed to cause the fracture remains the same. Growing strain at break values compensate the decrease in stress. Only the composite containing the highest PVA-LC content needs notably lower amount of energy to break – its toughness is only 82.4 kJ/m^2.

Similarly to the values of tensile strength, tensile modulus also decreases as a function of filler content. As can be seen in Fig. 6, the relationship of E value and PVA-LC content is almost linear, but its slope is rather gentle–the difference between the highest and the lowest values is only 90 MPa. As demonstrated in our previous study, the addition of 30 wt% of the unmodified linseed cake to PLA caused a 300 MPa decrease in tensile modulus, which is a considerably more distinct change [23]. However, it should be stressed that the samples containing 30 wt% of PVA-LC in fact contain only 15 wt% of linseed cake. Nevertheless, it can be assumed that the plasticization of the polymeric matrix was partially limited due to the application of PVA.

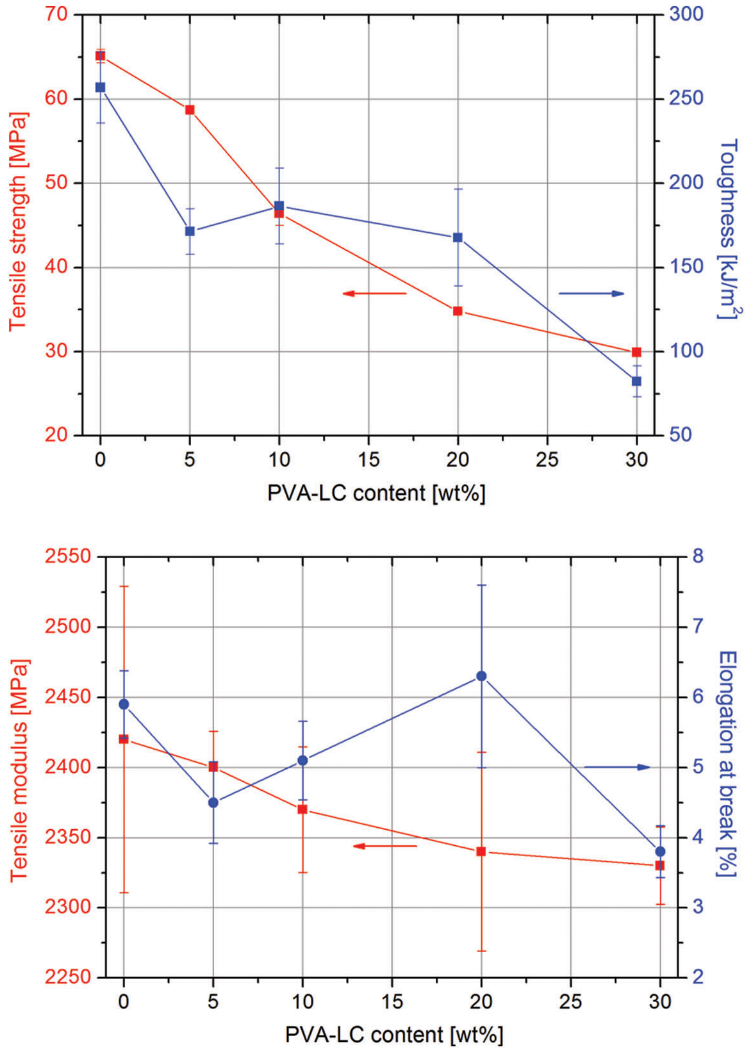

Figure 6: Mechanical properties of PVA-LC filled composites

The changes in elongation at break as a function of filler content are rather complex, but not random. As can be seen in Fig. 6, the addition of 5 wt% of PVA-LC causes a decrease in ε value, which can be caused by insufficient filler dispersion and low affinity between the phases in the composite. After that, elongation at break increases and achieves its maximum at 20 wt% of the modified linseed cake. This effect can be explained by the growing content of linseed oil, which facilitates the movement of macromolecules, enabling the sample to deform. In the case of the 30 PVA-LC specimen the content of plasticizing oil is too small to limit the influence of rigid lignocellulosic particle covered with PVA, which can act as internal notches, decreasing the elongation at break. Interestingly, in the case of PLA-based composites filled with unmodified linseed cake, the highest ε values were also achieved with the samples containing 10 wt% of the filler, which corresponds to the 20 PVA-LC sample [23].

3.4 Thermomechanical Properties

The run of storage and loss moduli (G′ and G″ respectively) as a function of temperature is shown in Fig. 7. The values of glass transition temperature (T_g) understood as peak of G″, G′ at 30°C and 75°C as well as filler effectiveness C and brittleness B are collected in Tab. 2.

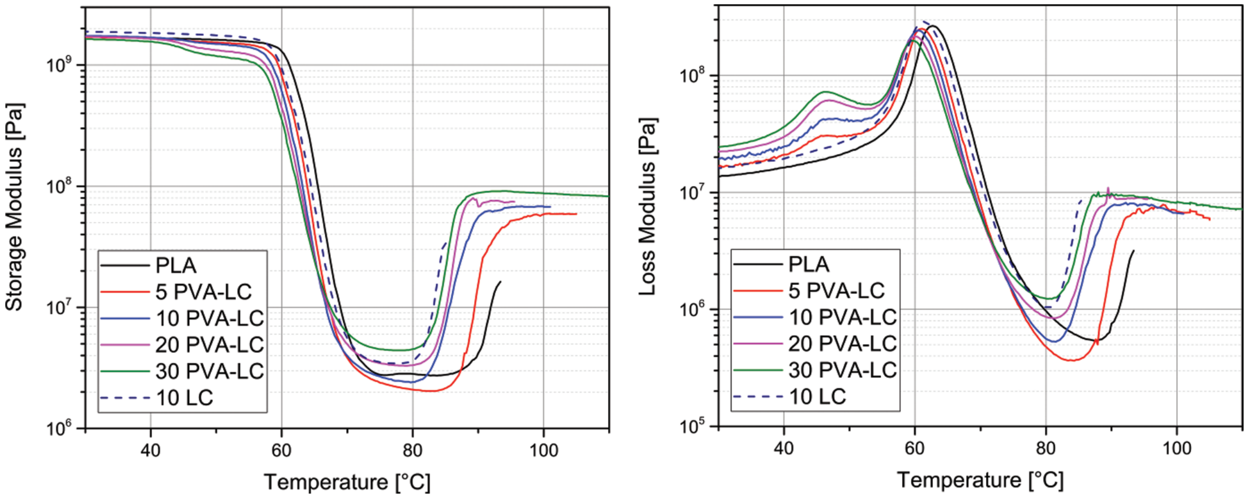

Figure 7: Storage and loss modulus values of PVA-LC filled composites as a function of temperature

Table 2: Thermal properties of the composites and the PLA

Sample	T_g [°C]	$G'_{30°C}$ [Pa]	$G'_{75°C}$ [Pa]	C [-]	B [Pa%/10^{10}]
PLA	62.7	$1.71\ 10^{9}$	$2.77\ 10^{6}$	–	0.99
5 PVA-LC	61.1	$1.70\ 10^{9}$	$2.38\ 10^{6}$	1.16	1.31
10 PVA-LC	60.6	$1.74\ 10^{9}$	$2.70\ 10^{6}$	1.04	1.13
20 PVA-LC	59.9	$1.72\ 10^{9}$	$3.45\ 10^{6}$	0.81	0.92
30 PVA-LC	59.6	$1.64\ 10^{9}$	$4.51\ 10^{6}$	0.59	1.60
10 LC [24]	61.3	$1.89\ 10^{9}$	$3.52\ 10^{6}$	1.10	0.33

The changes in thermomechanical properties of PLA consist of 4 stages. Initially the material is in a glassy state, as indicated by a plateau of G′. Around 60°C the value of storage modulus decreases several orders of magnitude and a distinct peak is visible on the G″, which can be attributed to relaxation of the PLA amorphous phase. After that, the polymer enters the rubbery state and another G′ plateau can be observed. Along with the increase in the temperature, the storage and loss moduli values increase once again, which is caused by cold crystallization of the PLA. This behavior of polylactide is consistent with the literature data [45,46] and with the results of the DSC measurement.

The composite samples showed a more complex run of G′ and G″ curves. The major difference can be seen in the lower temperature stage, below glass transition of PLA. A distinct decrease in storage modulus and peak of loss modulus around 46°C can be attributed to β-relaxation of the PVA phase [47]. The intensity of the low temperature G″ peak increases along with the filler content and corresponding PVA contribution. Similarly to the neat polymer, the composites enter the rubbery state and then undergo cold crystallization. However, the values of the G′ measured for the composites in elevated temperatures are higher than in the case of PLA. This difference is also indicated by the filler effectiveness. It can be seen that along with the PVA-LC content the C factor value decreases, which indicates higher effectiveness of the filler. This result is presumably caused by increased crystallinity of the PVA-LC filled samples in comparison to polylactide, as indicated by DSC results.

The values of PLA phase glass transition decrease as a function of filler content. A similar effect was observed for the polylactide samples filled with unmodified linseed cake and were explained by plasticizing effect of the filler [23]. Even though in this case the plasticization cannot be fully excluded, there are different factors which need to be taken into consideration. The decrease of T_g can indicate insufficient wetting of the filler particles by the polymer [48]. It can also be assumed that the presence of a higher amount of the relaxed PVA phase facilitates the relaxation of PLA macromolecules.

Brittleness is a complex parameter which combines both static and dynamic properties of a material. The higher its value, the worse the ductility of a substance. In the case of the studied materials, all of them can be classified as brittle ones. However, it can be seen that along with increasing filler content the B values initially decrease, achieve their minimum for the 20 PVA-LC sample, and then increase. The presence of 20 wt% of the modified linseed cake does not increase brittleness in comparison with the neat polymer, which can indicate a plasticizing effect of the linseed oil. In the case of the composite filled with 30 wt% of the filler the volumetric content is high enough to facilitate crack propagation.

3.5 Water Absorption

The amount of water absorbed by the samples over time is shown in Fig. 8. It can be seen that the neat PLA samples absorbed less than 0.6% of water and the equilibrium was achieved around 100 h. This result is typical for the hydrophobic polylactide [49] and also indicates lack of porosities in the injection molded samples. The addition of 5 and 10 wt% of the filler resulted in a 2- and 3-fold increase in water absorption, respectively. Nevertheless, the highest water absorption was denoted for the samples containing the highest amount of the filler–the 30 PVA-LC composite absorbed 12.7 wt% of water in 480 h. Taken into consideration that linseed cake containing mucilage [50] as well as poly(vinyl alcohol) are both hydrophilic [32], the result is reasonable.

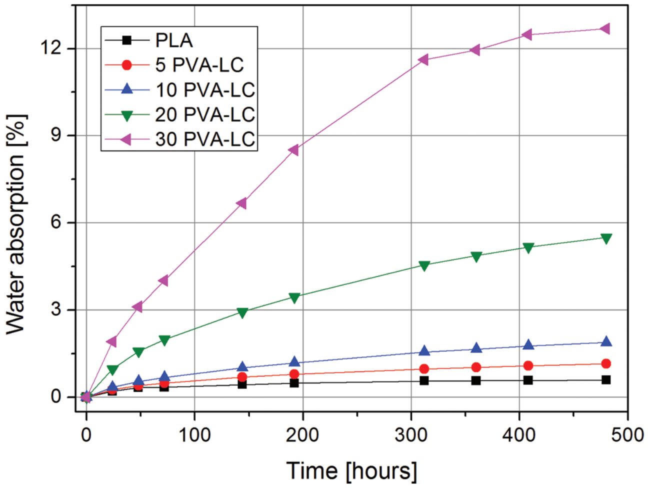

Figure 8: Water absorption of the samples as a function of time

The water used for immersing the samples for 480 h was tested using UV-Vis technique and the results are presented in Fig. 9. The increased absorbance band observed in the range of UV light for water after immersion of the composite samples may be an effect of partial migration of the oil from the linseed cake particles to water medium during immersion [51]. Interestingly, the composite samples show a peak around 200 nm, which is especially intensive for the materials containing 20 and 30 wt% of the filler. As similar spectra were recorded for the water solution of pure PVA [52], it can be assumed that this polymer is rinsed out of the PLA matrix. Considering that both the highest water absorption and the

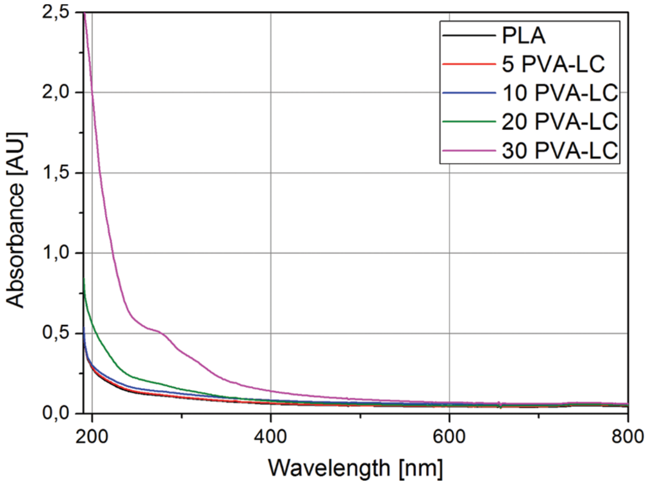

Figure 9: UV-Vis spectra of the water used to immerse the samples during water absorption test

amount of the dissolved PVA were obtained for the 20 PVA-LC and 30 PVA-LC, it can be concluded that in their case the modified filler particles created a continuous network inside the matrix, which enabled easier penetration of moisture inside the polymer and leaking of PVA. In the case of the composites containing lower percentage of PVA-LC the filler particles are covered with the hydrophobic PLA and separated from each other, so the water cannot easily diffuse into the sample. The additional overlapping inflexion at 280 nm observed for 20 PVA-LC and 30 PVA-LC samples may be ascribed to the absorption band of aliphatic carboxyl groups caused by the effect of scission of the PLA main chain at aliphatic ester bonds of PLA [53].

3.6 Infrared Spectroscopy

The FT-IR spectra of the pure PLA and its composites are presented in Fig. 10. Assignment of peaks is collected in Tab. 3. The result obtained for unmodified polylactide is typical for this polymer: the bands at 2996 cm^{-1} and 2946 cm^{-1} come from stretching of CH_2 groups of the polymeric backbone. The intensive

Table 3: FT-IR peak assignment

Peak [cm^{-1}]	Assignment	Reference
3504	OH stretching	[54]
2996	C-H stretching	[55]
2946	C-H stretching	[55]
1747	carbonyl stretching	[56]
1452	C-H stretching in methyl groups	[55–57]
1382	C-H stretching in methyl groups	[57]
1360	C-H stretching in methyl groups	[57]
1206	alkyl ketone chain vibration	[58]
1080	C-O-C stretching	[56]
1043	C-CH_3 stretching	[56]
920	flexural C-H	[58]

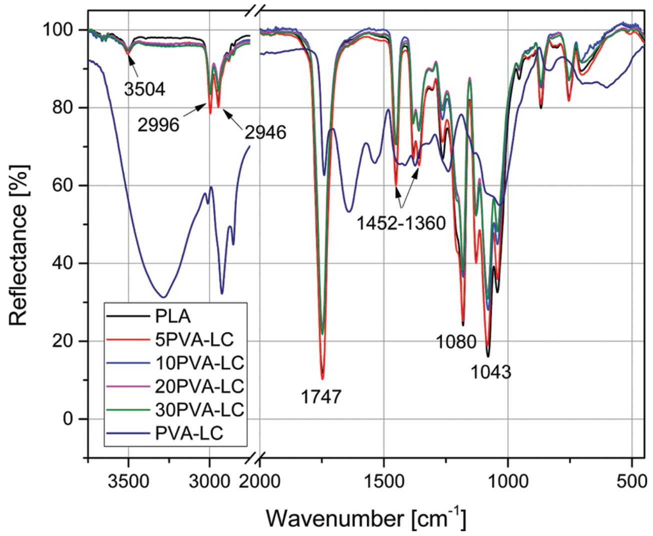

Figure 10: FT-IR spectra of the composite the samples and pure PLA

peak at 1747 cm^{-1} can be assigned to stretching vibrations of carbonyl groups. Presence of C-O-C and C-CH$_3$ groups are indicated by peaks at 1080 cm^{-1} and 1043 cm^{-1}, respectively. The infrared spectra of the composite samples are almost the same as the one obtained for the pure polymer. The spectrum obtained for PVA-LC filler does not overlap with the one of the composite sample. This result can be caused by several reasons. First of all, the FT-IR ATR method allows to obtain the information about the surface of the material only. It can be concluded that external layer of the composite samples is mainly composed of the matrix material. Any similarities of the filler and composite spectra come from the fact that the FT-IR peaks characteristic for poly(vinyl alcohol) such as C=O stretching around 1730 cm^{-1} and C-O stretching around 1100 cm^{-1} [39] are the same as the bands obtained for PLA. Therefore it can be concluded that the filler particles are well covered by the composite matrix.

4 Conclusion

Polylactide-based composites filled with PVA-modified linseed cake were successfully manufactured using the melt blending method. The results of the performed tests confirm the hypothesis that the application of the polar polymer helps to encapsulate the oil inside the filler particles and prevent its release to the composites' matrix. Because of this fact, the plasticizing effect of the linseed oil was limited, and no direct influence of the natural oil on the crystallization process of the PLA was observed. Obtained composite samples were stiffer in comparison with the PLA-based composites filled with unmodified LC, they also contained lower percentage of the crystalline phase. Separate oil domains could be observed only in the case of the samples with the highest content of oil-rich waste filler, which confirms the initial hypothesis about PVA influence. Nevertheless, the manufactured composites presented lower mechanical properties (both in terms of tensile modulus and toughness) in comparison with the pure polymer due to low interaction between the hydrophobic polylactide and hydrophilic poly(vinyl alcohol), especially in the case of highly-filled samples. The addition of the modified filler characterized by low thermal stability also caused a shift of thermal degradation to lower temperatures. It was shown that up to 10 wt.% of the PVA-LC the filler particles are well dispersed and covered with PLA. The addition of a higher percentage of the modified waste filler resulted in the clustering of its particles, which promoted water absorption and caused a deterioration of mechanical properties, which was especially notable in the case of the 30 PVA-LC sample.

In summary, it can be concluded that PVA as a biodegradable, non-toxic polymer may be a good modifying agent used for surface treatment of oil-rich natural fillers, which helps to limit the oil release to the polymeric matrix.

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