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NOVEL PLA COMPOSITES MODIFIED WITH STEEL FIBRES AND (3-THIOPROPYL) POLYSILSESQUIOXANE DERIVATIVES

Daria PAKUŁA*/, Bogna SZTORCH*, Eliza ROMAŃCZUK-RUSZUK*****
Bogdan MARCINIEC*/, Robert E.PRZEKOP***

*Adam Mickiewicz University in Poznań, Faculty of Chemistry, Uniwersytet Poznański 8, 61-614 Poznań, Poland
**Adam Mickiewicz University in Poznan, Centre for Advanced Technologies,
Uniwersytet Poznański 10, 61-614 Poznań, Poland
***Institute of Mechanical Engineering, Białystok University of Technology, Wiejska 45C, 15-351 Białystok, Poland

darpak@amu.edu.pl, bogna.sztorch@amu.edu.pl, e.romanczuk@pb.edu.pl
bogdan.marciniec@amu.edu.pl, rprzekop@amu.edu.pl

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Abstract: In recent years, a significant increase in the development of new composite materials with desirable mechanical, thermal or surface properties has been observed. One of the popular polymers on the market is polylactide. This article explores how to modify the polymer using steel fibres and organosilicon compounds (SSQ-SH, SSQ-SH-OCT, and SSQ-SH-OFP) to enhance its properties. Test samples were obtained by injection molding with varying concentrations of 0.5%, 1%, 1.5%, 2.5%, and 5% of steel fibres. Mechanical tests, including tensile strength, elongation at break, and impact strength, were conducted, along with an analysis of the contact angle. The modified samples showed higher impact strength values, with the PLA /steel fibres /SSQ-SH sample seeing an increase of 12%. The addition of modifiers with fluoroalkyl groups led to a contact angle increase of 8.5% compared to neat PLA. Thermal tests (TGA) were also carried out to determine the influence of fibres and organosilicon compounds on decomposition.

Key word: polylactide (PLA): steel fibres; composites; organosilicon compound; octa(3-thiopropyl)silsesquioxanes; injection molding

1. INTRODUCTION

For several years, researchers have been exploring new composite materials that exhibit desirable mechanical, thermal, or surface characteristics. A widely studied polymer in this regard is PLA, which belongs to the family of polyester polymers. PLA is considered a highly promising option to replace petroleum-based materials as it is derived from sustainable sources such as corn starch or sugarcane [1]. Not only does PLA possess excellent mechanical and thermal properties, but it is also both degradable and biocompatible, making it a highly appealing alternative [2].

Polylactide can be produced through polycondensation of lactic acid or ring-opening polymerization of cyclic lactic diester (lactide) [3]. Notably, this process is more cost-effective than petroleum-based polymers, requiring significantly less energy (25–55% less). With advancements in technology, it is projected that this energy reduction could decrease to less than 10% in the future [4]. Furthermore, the production of PLA has a significantly lower carbon footprint, generating far fewer greenhouse gas emissions when compared to traditional plastics.

Polylactide is a remarkably versatile material that can be utilized in a wide range of manufacturing processes. These include injection molding, extrusion, and 3D printing, making it a highly sought-after choice for various industries such as construction, automotive [5], packaging [6], clothing [7], and electronics [8]. Its extensive applications encompass from bottles [9], tea bags, dishes [10], to packaging for cosmetics [11]. One of the most significant advantages of PLA is its high biocompatibility, which makes it an ideal material for biomedical purposes. In the medical field, it is commonly used to create bioresorbable sutures, implants, orthopedic devices, vascular scaffolds, and drug delivery systems [12].

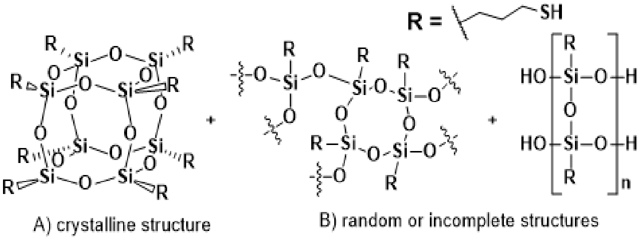
Polylactide is a versatile material whose properties can be influenced by a variety of factors such as the isomer ratio, processing temperature, crystallinity, and molecular weight [13-15]. One of the key advantages of PLA is its favorable processing qualities, high transparency, and good strength. However, it also has certain drawbacks that may limit its suitability for some specialized applications. These drawbacks include in particular high brittleness and a relatively slow degradation rate [16]. Given these limitations, researchers are actively exploring new modifiers that an enhance the desired properties of PLA. These modifiers can take the form of natural or chemical fillers, each with their unique set of benefits and drawbacks e.g. calcium carbonate [17], diatoms [18], wood fiber [19], straws [20], husks [21], TiO2 [22-23], glass fibres [24], graphene [25], graphite [26]. Currently, many works describe the combination of PLA with metallic particles [27-29]. The addition of steel fibers can improve the mechanical properties [30-31]. Steel fibers are often used as reinforcement in composite materials to provide added strength and toughness. In 3D printing, when incorporated into PLA, they can enhance the overall structural integrity of the printed objects [30,32]. Steel is a material commonly used in medicine, it is used to produce, among others: surgical tools, elements of prostheses and orthoses. Special grades of stainless steel are used in medicine, which are characterized by high corrosion resistance and low biological reactivity [27]. However, it is worth noting that the metallic particles do not integrate with the matrix material (PLA). Therefore, modifiers are being sought to improve the bonding of the metallic particles to the composite matrix. Ultimately, the choice of modifier will depend on the specific needs of the application at hand. One of the effective approaches to modifying polymers is through the incorporation of organosilicon compounds, including silsesquioxanes, silanes, and polysiloxanes, into the polymer matrix [33-34]. These compounds can have a significant impact on various physical and chemical properties, such as rheological or thermal properties, as well as mechanical properties [34]. Silsesquioxanes are a type of hybrid organosilicon compound with a general formula of RSiO3/2, consisting of a core (Si-O-Si) and attached reactive or inert groups like isobutyl or phenyl groups [35]. Silsesquioxanes typically exhibit high biocompatibility and lack of cytotoxicity. Scientific literature provides data demonstrating the high biocompatibility and absence of cytotoxic effects of silsesquioxanes with various functional groups, including those substituted with amino or thiopropyl groups [36]. A detailed description of fillers for polymer applications can be found in our previous review [37].

This paper discusses the enhancement of polylactide by using steel fibers and organosilicon compounds which were used to modify fibers. To gauge the effectiveness of these modifications, different mechanical tests such as tensile strength and impact strength were conducted. Additionally, tests were carried out to determine the impact of these additives on surface properties, specifically through an analysis of the contact angle. Thermogravimetric analysis was also performed to determine the effect of fibers and compounds on thermal stability. The results showed that by adding a small amount of modifiers, the polymer becomes more flexible and has higher contact angle values. This paper presents an effective and economical method of modifying polymers.

2. MATERIALS AND METHODS

Materials: Polylactide (PLA) Ingeo 2003D type was purchased from NatureWorks (Minnetonka, MN, USA). Low-alloy steel fibers with the following composition were used in the work: Fe, 0.295 % Si, 0.525 % Mn, 2.08 % Ni, 0.535 % Cr, 1.29 % Mo, 0.52 % V, 0.11 % Cu. The chemicals were purchased from the following sources: 3-Mercaptopropyltrimethoxysilane (99%) from UNISIL; methanol p.a. from P.P.H Stanlab; hydrochloric acid (35-38%), toluene, tetrahydrofuran from Chempur. Azoisobutyronitrile (AIBN) (98%) was purchased from FLUKA, octene (OCT) (97%) from ABCR and chloroform-d from Merck Group. Allyl 2,2,3,3,4,4,5,5-octafluoropentyl ether (Allyl-OFP) was synthesized according to the method described by Maciejewski et al. in the literature [38]. Toluene was degassed and dried by distilling it from P2O5 under an argon atmosphere. (3-thiopropyl)polysilsesquioxane was prepared according to the literature [39-40] and our previous article [41] (Fig.1).

Synthesis of chemical modifiers: A crystalline and amorphous product was obtained by the hydrolytic condensation reaction of 3-thiopropyltrimethoxysilane. The amorphous product (hereinafter referred to as SSQ-SH), which is a viscous, thick oil, consists of closed cages (T8) and incompletely condensed silanols. Two derivatives, partially substituted with hydrophobic groups, were obtained by a radical reaction initiated by AIBN. The functionalization was carried out according to literature data [41] with octene (hereinafter SSQ-SH-OCT) and allyl 2,2,3,3,4,4,5,5-octafluoropentyl ether (hereinafter SSQ-SH-OFP). Modifiers containing both reactive thiol and hydrophobic groups (octyl, fluoroalkyl) were obtained.



A) crystalline structure
B) random or incomplete structures

Fig.1. Products of the hydrolytic condensation reaction of 3-thiopropyltrimethoxysilane

Preparation of samples: Stage 1: The first stage covered the modification of steel fibers with organosilicon compounds. For this purpose, 2 g of a modifier (SSQ-SH or SSQ-SH-OCT or SSQ-SH-OFP) and 100 ml of THF were added to 100 g of fibers, and then mixed on a laboratory evaporator for 2 h at room temperature. The solvent was allowed to evaporate slowly and then the modified fibres were dried at 50°C for 1 hour. Stage 2: The second step involved obtaining a concentrate. The polymer and modified steel fibres were homogenized using a laboratory two-roll mill ZAMAK MERCATOR WG 150/280. A portion of 900 g of PLA Ingeo™ 2003 D was mixed with 100 g steel fibres until the final concentration of the additive of 10% w/w. The mixing was performed at the rolls temperature of 215°C for 15 min., getting to full homogeneity of the concentrates. Masterbatch was granulated by a grinding mill WANNER C17.26 sv.

The prepared masterbatches were diluted 1:1 with PLA directly in the Engel e-victory 170/80 injection molding machine. Standardized specimens for mechanical tests were obtained according to PN-EN ISO 20753:2019-01. Final system concentrations of steel fibres were 0.5% w/w, 1% w/w, 1.5% w/w, 2.5% w/w, 5% w/w.

Methods: Water contact angle (WCA) measurements were performed using the sessile drop technique (5 μL) at room temperature and atmospheric pressure with a Krüss DSA100goniometer (Krüss Optronic GmbH, Hamburg, Germany).

Tensile tests of the obtained specimens were performed on a universal testing machine INSTRON 5969 with a maximum load force of 50 kN. The traverse speed for the tensile strength measurements was set at 2 mm/min.

The Charpy impact strength test (unnotched samples) was performed according to ISO 179-1 on an Instron Ceast 9050 impact pendulum tester.

Thermogravimetry (TG) was performed using a NETZSCH 209 F1 Libra gravimetric analyser (Selb, Germany). Samples of 4 ± 0.2 mg were placed in Al2O3 crucibles. Measurements were conducted under nitrogen (flow of 20 ml/min) in the range of 30–1000°C and a 10°C/min heating rate.

Images of steel fibres and composites were taken with the digital light microscope Keyence VHX-7000 (Keyence International NV/SA, Osaka, Japan) with a VH-Z100R wide angle zoom lens (Keyence International NV/SA, Osaka, Japan) at 100× magnification. The images were taken using the function of depth composition and 3D image creation.

3. RESULTS AND DISCUSSION

From the microscopic analysis, it can be seen that the steel fibers are characterized by different sizes. The length range determined by the optical microscope was from about 40 µm to 2000 µm (Fig.2). Based on the literature review, it has been determined that no research has been conducted to date on the incorporation of modified steel fibers with organosilicon compounds into a polylactide matrix.

The article describes the process of producing polylactide composites reinforced with steel fibers and steel fibers modified with organosilicon compounds having reactive thiol groups and/or hydrophobic groups, respectively. An analysis of tensile strength and impact strength was carried out, as well as surface tests were performed, which allowed to characterize the degree of hydrophobicity of the materials.

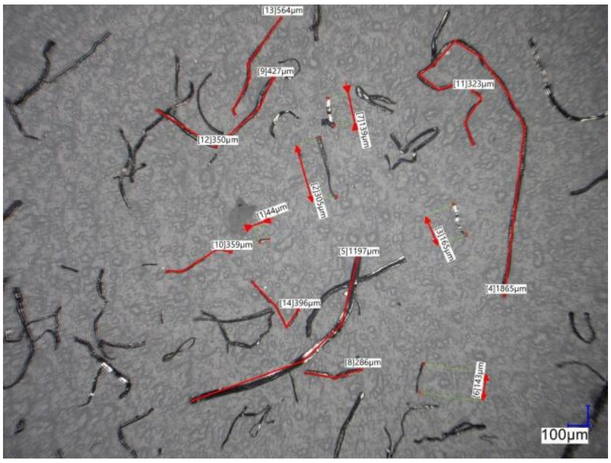


Fig. 2. Optical microscopic images of steel fibres

Fig. 3 presents optical microscope images of the surfaces (left) and fracture surfaces (right) of composites at the highest fiber concentrations (5% wt). Based on these images, the effect of different silsesquioxane (SSQ) additives (SSQ-SH, SSQ-SH-OCT, SSQ-SH-OFP) on the material structure can be observed. The surface of neat PLA is relatively homogeneous, and the fracture surface is smooth. Figure 3B-B' clearly shows steel fibers on the PLA surface, with sharp and distinct boundaries between the fibers and the matrix in the fractures. The fracture surface is rough, indicating poor adhesion between the fibers and PLA. The addition of SSQ-SH improves the adhesion of steel fibers to the PLA matrix, resulting in a more integrated structure and reduced visibility of fibers in the fractures (Fig. 3C-C'). Similarly, SSQ-SH-OCT leads to better dispersion and homogeneity of the material (Fig. 3D-D'). In contrast, the addition of SSQ-SH-OFP shows the presence of fiber agglomerates mainly on the surface (Fig. 3E-E'), which may indicate uneven dispersion and potentially inferior mechanical properties of the material. This is related to the high hydrophobicity of fluoroalkyl groups, leading to poorer miscibility between the system components. The surface of the fractures with additives is less rough, indicating better embedding of the fibers in the matrix.

Fig. 4 shows the impact strength results for neat PLA, steel fiber reinforced PLA, and modified filler/PLA. The measurement method used is characterized by large standard deviations, which is visible on the graph in the form of errors bars. Neat PLA's impact strength is 17.1 kJ/m2 (black straight line in the graph - reference). The addition of steel fibers did not significantly affect the impact resistance, and the changes in values are within ± 1.0 kJ/m2.

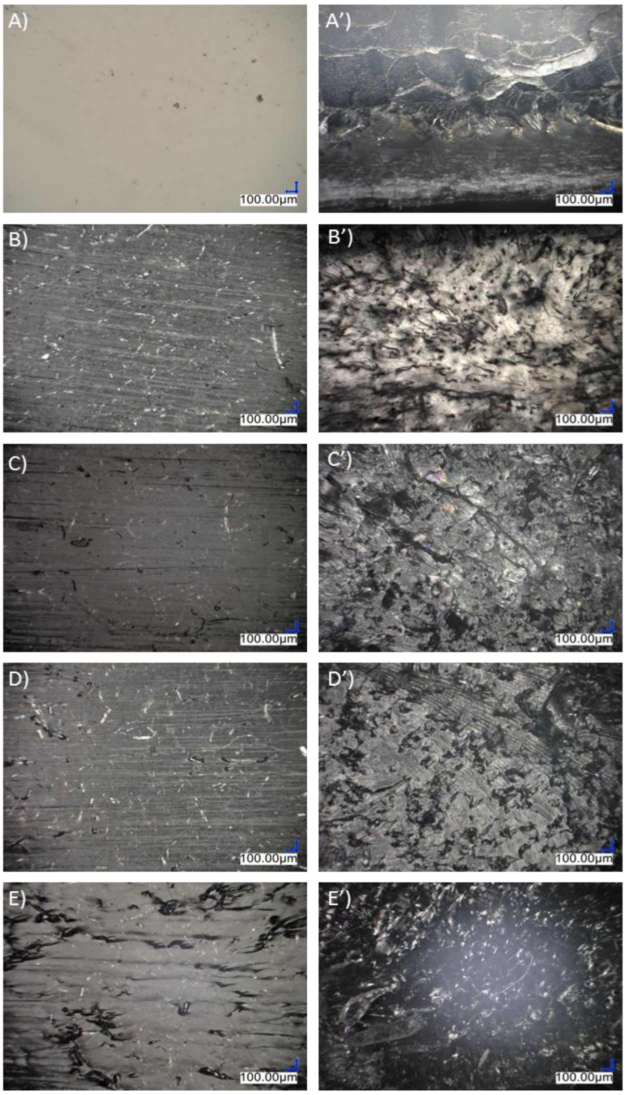


Fig. 3. Microscopic images of composites: A) neat PLA, B) PLA + 5% steel fibres, C) PLA + (5% steel fibres/SSQ-SH), D) PLA + (5% steel fibres/SSQ-SH-OCT), E) PLA + (5% steel fibres/SSQ-SH-OFP)

Composites with the addition of organosilicon modifiers are characterized by higher impact strength values. This may be due to three factors: 1) improved dispersion of the modified fibers in the polymer matrix; 2) plasticizing effect of organosilicon compounds; 3) the influence of thiol groups which may interact with the polylactide matrix. Thiol groups present in modifiers act as proton donors, facilitating the formation of hydrogen bonds between the -SH groups and the carbonyl groups in polylactic acid (PLA) chains. These hydrogen bonds can influence the degree of crystallinity in PLA, which in turn affects its mechanical properties. In our previous work, we presented the impact of (3-thiopropyl) polysilsesquioxane on the mechanical properties of polylactide, including potential interactions between the modifier and the matrix [42]. Modifiers can act as a plasticizer, reducing the brittleness of the polymer, thanks to which the resulting composite is able to absorb more energy during impact. The highest values were obtained for the PLA/steel fibres/SSQ-SH composite, which may indicate a significant impact of thiol groups on the improvement of the mechanical properties of the polymer. The tests carried out show that the addition of a small amount of organosilicon compounds by weight in relation to the entire composite affects the change in the properties of the materials, which gives an effective method of modification and is also important in the economic aspect.

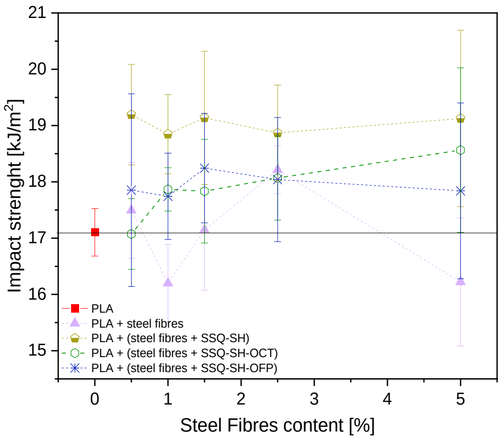


Fig. 4. Impact strength of composites

Tensile strength tests were also carried out (Fig.5A), examples of force-elongation curves for selected materials are shown (Fig. 5B), and elongation at break was determined (Fig.6). Neat PLA has similar characteristics to PLA+(steel fibres+SSQ-SH), but the displacement of the sample with the modifier was higher. Displacement is slightly higher for the samples with modifiers, compared to neat PLA, but the maximum force values are comparable for all tested materials. However, the differences shown for the example samples are not statistically significant (Fig. 5B). The slight differences may be due to the different lengths and uneven arrangement of the steel fibres. The addition of steel fibers did not affect the reinforcement of the composite matrix, and changes in strength values are ± 1 MPa. The addition of organosilicon compounds (SSQ-SH-OCT, SSQ-SH-OFP) reduced the tensile strength value. Composites with the addition of the SSQ-SH-OFP modifier have the lowest strength. This decrease can be attributed to the highly hydrophobic characteristics of the fluoroalkyl groups within the SSQ-SH-OFP modifier. These hydrophobic groups probably result in diminished interactions between the modifier and the polymer matrix, which is also observed in microscopic photos (Fig. 3). For the sample with 5% concentration (steel fibres/SSQ-SH-OFP) the value decreased by 5.1 MPa. The obtained results show that the new materials, which also consist of organosilicon compounds, are characterized by higher flexibility and lower strength. This may be due to the plasticizing effect of modifiers, as well as the presence of discontinuities in the polymer phase introduced with the addition of filler [33].

Literature data confirm that metal powder act as a weak interface thereby lowering strength and toughness [43]. It is possible that the use of fibers may similarly deteriorate mechanical strength. The addition of organosilicon compounds slightly improves the plasticity of composites. Higher elongation at break values (Fig.6) indicate increased mobility of the polymer phase, attributable to the addition of a plasticizing modifier. This is due in part to the modifier's penetration between the macromolecular chains of the polymer, which reduces the intermolecular forces acting along these chains [44]. Similar results can be seen in impact tests.

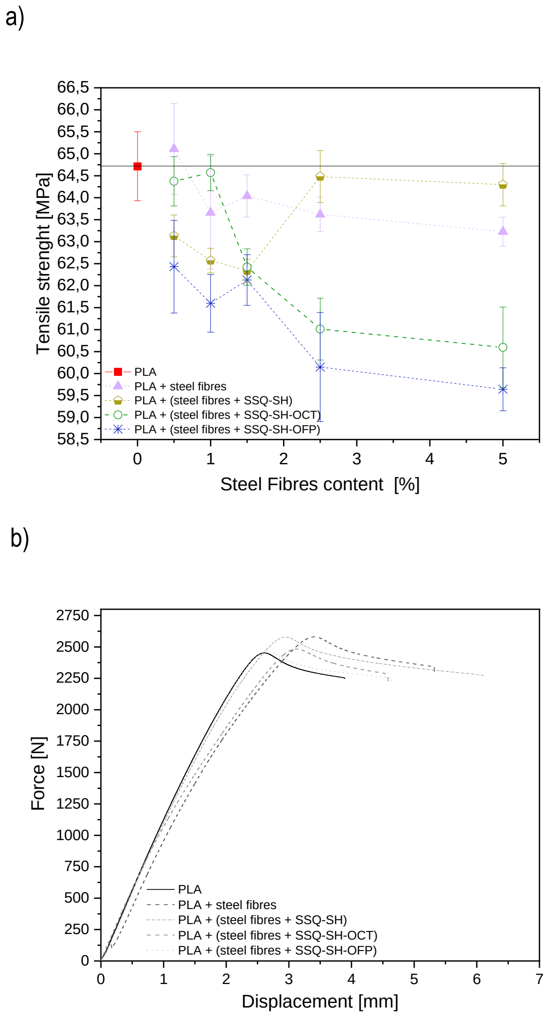


Fig. 5. a) Tensile strength of composites, b) force-elongation curves

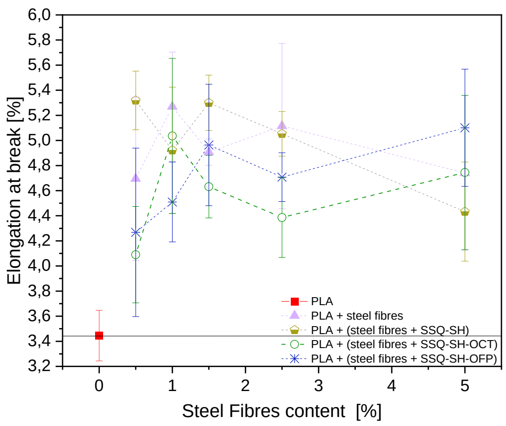


Fig. 6. Elongation at break of composites

In the study, samples with the highest concentration of steel fibers were subjected to thermogravimetric analysis in an inert gas (N2) flow (Fig.7). The onset temperature and temperature at the maximum rate of mass loss were determined from the TGA/DTG curves. The results showed a significant decrease in the decomposition start temperatures of the modified composites (Table 1). The introduction of steel fibers was found to lower both the onset temperature and temperature at the maximum rate of mass loss. The analysis of the composites revealed that the thermal stability was not affected by the organosilicon compounds. When 5 wt.% steel fibers or modified steel fibers were added, the onset temperature was lowered from 16.0°C to 18.4°C. Sample fiber/SSQ-SH was characterized by 32.6°C lower temperature at the maximum rate of mass loss compared to neat PLA. One possible explanation for this behavior of the samples is that the steel conducts heat, which results in faster heating of the composite systems and ultimately leads to lower initial temperatures and temperatures at maximum weight loss rates. In the study by Sztorch et al., it was also observed that the addition of metallic powders can lower the onset degradation temperatures of composites. This phenomenon is also evident in the case of adding steel fibers to PLA [45].Table 2 summarizes the obtained results.

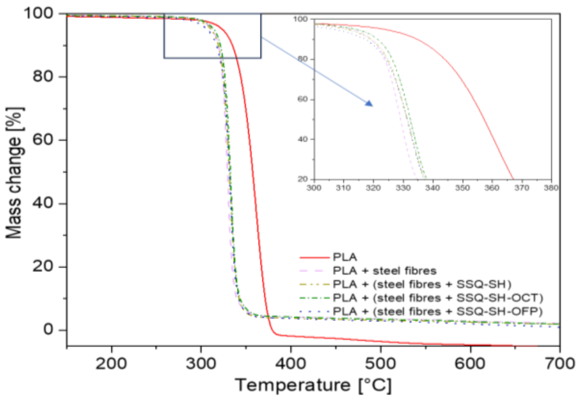


Fig. 7. TGA curves of composites

Tab. 1. Results of TGA analysis

Sample	Onset temperature [°C]	*ΔT* [°C]	Temperature at the Maximum Rate of Mass Loss [°C]	*ΔT* [°C]
Neat PLA	342.2	-	362.1	-
PLA + steel fibres	323.8	18.4	329.5	32.6
PLA + (steel fibres + SSQ-SH)	324.2	18.0	332.1	30.0
PLA+ (steel fibres + SSQ-SH-OCT)	326.2	16.0	333.1	29.0
PLA+ (steel fibres + SSQ-SH-OFP)	324.5	17.7	332.9	29.2

The neat PLA sample has a hydrophilic surface with a contact angle of 76.5°. The addition of fibres and organosilicon compounds influenced surface changes of the composites (Fig. 8). PLA/steel fibres materials are characterized by a higher water contact angle (for a 1.5% sample, the value is 81.7°). Changes towards higher values may be caused by a change in the microstructure to a rougher one, and thus characterized by higher values of the contact angle. Samples in which SSQ-SH is used are characterized by lower values compared to neat PLA. The thiol groups present in the modifier's structure are moderately polar and hydrophilic because of the difference in the electronegativity of sulfur and hydrogen, which leads to interaction with water, decreasing the contact angle[46]. SSQ-SH-OCT and SSQ-SH-OFP are characterized by the presence of both reactive thiol groups and groups determining the hydrophobic character (octyl, fluoroalkyl). The highest increase in the contact angle value was observed for PLA + composites (steel fibres+SSQ-SH-OFP). With the increase of the organosilicon modifier, the value of the contact angle increases. For the 5% sample, there is a noticeable change of 8.5% compared to neat PLA. Fluorinated materials are characterized by low surface energy and exhibit both oleophobicity and hydrophobicity [47-48]. The addition of the SSQ-SH-OFP derivative led to an increased contact angle. This rise can be explained by the hydrophobic fluoroalkyl groups in SSQ-SH-OFP, which repel water and lower surface energy, thereby enhancing hydrophobicity of materials.

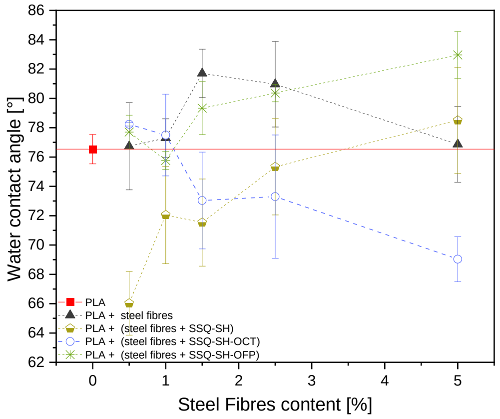


Fig. 8. Water contact angle of composites

4. CONCLUSION

This study presents the first investigation into the modification of steel fibers with organosilicon compounds (SSQ-SH, SSQ-4SH-4OCT, and SSQ-4SH-4OFP), for their incorporation into polylactice matrix. Through a series of mechanical, thermal and surface property tests, it has been demonstrated that these modifications lead to significant changes in the properties of the resulting composites. The incorporation of steel fibres and organosilicon compounds into PLA resulted in changes in their strength properties, including an increase in impact strength and elongation at break values, as well as a change in the contact angle value. The compounds used acted as plasticizers in the polymer matrix, which made the material more flexible. Additionally, the hydrophobic groups in the compounds (primarily fluoroalkyl groups) affected the surface properties (increase of 8.5% compared to neat PLA).

By adding small amounts of organosilicon additives, certain properties were improved, making this an effective, efficient, and economically advantageous method. These findings suggest a promising potential for the use of organosilicon-modified steel fibers in PLA composites. Preliminary tests indicate that this modification strategy can lead to enhanced composite materials with improved performance properties. Future research will focus on further exploring the optimization of these modifications, assessing long-term durability, and evaluating additional applications to fully realize the potential benefits of this innovative approach.

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Daria Pakuła: https://orcid.org/0000-0001-6741-3019

Bogna Sztorch: https://orcid.org/0000-0001-5166-8391

Eliza Romańczuk-Ruszuk: https://orcid.org/0000-0001-5228-4920

Bogdan Marciniec: https://orcid.org/0000-0001-5203-1376

Robert E. Przekop: https://orcid.org/0000-0002-7355-5803