

High Impact Polylactide Based on Organosilicon Nucleation Agent

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Abstract Various sectors of the industry are searching for new materials with specific requirements, providing improved properties. The study presents novel composite materials based on polylactide that have been modified with the organosilicon compound, (3-thiopropyl) polysilsesquioxane (SSQ-SH). The SSQ-SH compound is a mixture of cage structures and not fully condensed random structures. The composite materials were obtained through injection moulding. The study includes a comprehensive characterization of the new materials that analyze their functional properties, such as rheology (MFR), mechanical strength (tensile strength, Charpy impact strength), and thermal properties. SEM microscopic photos were also taken to analyze the microstructure of the samples. The addition of a 5% by-weight organosilicon compound to polylactide resulted in a significant increase in MFR by 73.8% compared to the neat polymer. The greatest improvement in impact strength was achieved for the 5% SSQ-SH/PLA composite, increasing it by 32.0 kJ/m² compared to PLA, which represents an increase of up to 187%. The conducted research confirms the possibility of modifying the properties of the polymer by employing organosilicon compounds.

Keywords Octa(3-thiopropyl)silsesquioxane; 8SH-POSS; Polylactide (PLA); Injection moulding; Composites

Citation: Pakuła, D.; Sztorch, B.; Romańczuk-Ruszk, E.; Marciniak, B.; Przekop, R. E. High impact polylactide based on organosilicon nucleation agent. *Chinese J. Polym. Sci.* 2024, 42, 787–797.

INTRODUCTION

Poly(lactide), often referred to as poly(lactic acid) or PLA, is a polyester polymer that has gained significant attention as a promising alternative to traditional petroleum-based materials.^[1] What sets PLA apart is its sustainable origin, as it is derived from renewable resources like corn, wheat, or rice, making it an eco-friendly and biodegradable choice.^[2] PLA exhibits remarkable mechano-thermal properties, making it a valuable material for various applications.^[3] There are two primary methods for synthesizing PLA: polycondensation of lactic acid and ring-opening polymerization of a cyclic lactic diester known as lactide.^[4,5] These methods result in the formation of PLA with different characteristics, providing flexibility for various applications. In addition to its eco-friendly sourcing and versatile synthesis methods, PLA production is notably more energy-efficient compared to the production of petroleum-based polymers.^[6] It requires 25%–55% less energy, making it an attractive option for sustainable manufacturing. Furthermore, ongoing research and technological advancements hold the potential to further reduce the energy requirements for PLA production, possibly to less than 10% in the future.^[7] This makes PLA a key player in the pursuit of environmentally friendly and energy-efficient materials in the modern world.

Poly(lactide)'s properties can vary depending on its isomer ratio, processing temperature, crystallinity, or molecular weight.^[8] PLA is known for its good processing properties,^[9] high transparency, and strength. However, it also has several significant drawbacks, including high brittleness.^[4] These limitations make it unsuitable for some specialized applications. Due to these challenges, scientists are interested in exploring ways to overcome these limitations.^[4]

Poly(lactide) (PLA) is a versatile material that finds applications in various industrial fields such as construction,^[10] decoration,^[10] automotive,^[11] packaging,^[12] clothing,^[13] and electrical and electronics sectors.^[14] It is commonly used in the production of bottles, tea bags, dishes, and cosmetic packaging.^[15] Additionally, it is widely used in the production of bioresorbable sutures, implants, orthopedic products, vascular scaffolds, and other biomedical applications due to its high biocompatibility.^[16]

The introduction of organosilicon compounds such as silsesquioxanes, silanes, and polysiloxanes into a polymer matrix has the potential to modify its rheological, thermal, mechanical, and structural properties.^[17,18,19,20] Silsesquioxanes containing amino, hydroxyl, and epoxy groups, when introduced into a poly(lactide) matrix, function as effective lubricating agents that enhance the material's elasticity, resulting in higher elongation at break and Izod impact strength.^[21] Poly(ethylene glycol) POSS (PEG-POSS), with organic poly(ethylene glycol) groups attached at the corners of the cage, added to PLA/PCC blends improves compatibility and affects the crystallization of composites because PEG-POSS

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Received December 11, 2023; Accepted January 15, 2024; Published online March 7, 2024

acts as a crystallization nucleus.^[22] Trifluoropropyl-POSS, due to its unreactive groups in relation to PLA and strong interactions with each other, creates agglomerates in the material in higher concentrations. However, composites with content up to 2.5 wt% were characterized by good dispersion (close to the molecular level), which resulted in a lower cold crystallization temperature and an increase in the elasticity of the material.^[23] Oligomeric ladder silsesquioxanes (LPSQ-R), where R = OH, (OH)₂, COOH, COOMe, were used as property modifiers of poly(L-lactide)/poly(D-lactide) (PLLA/PDLA). As a result of the presence of groups capable of donation/acceptance interactions, increased thermal stability was observed at temperatures >533 K. The decomposition temperature (T_d) of the material increased by 20–30 °C compared to neat PLLA/PDLA, even with relatively small amounts of LPSQ-R additives.^[24]

The research conducted by Sztorch *et al.* focused on assessing the impact of cubic structures of spherosilicates (OSS) with functional octadecyl (OD) and (trimethoxysilyl) (TMOS) groups with different molar ratios on the rheological and mechanical parameters of polylactide (PLA)-based composites. Among the tested configurations, the composite marked as OSS-2OD-6TMOS showed the most favorable set of properties. In the case of OSS-2OD-6TMOS, an improvement in the ability to crystallize and an increase in the hydrophobicity of the material were observed. The addition of OSS-2OD-6TMOS also contributed to the plasticization of the material, which resulted in increased mechanical strength of the entire composite.^[25] The limonene derivative of spherosilicate significantly improved the processing properties of polylactide in terms of rheology, interlayer adhesion and mechanical properties. Modifications with the compound included both samples obtained by injection and 3D printing.^[26] The incorporation of SSQ-8SH, consisting of a stable core containing Si—O—Si units and attached thiopropyl groups into the polymer matrix can result in uniform dispersion of the modifier, which can significantly affect the physicochemical properties.

The aim of this work was to develop and obtain a new composite material based on polylactide by adding (3-thiopropyl)polysilsesquioxane (SSQ-SH). SSQ-SH consists of a mixture of cage-like structures and partially condensed random structures. The production of these composite materials was achieved through an injection molding process. In various industries, there is potential for the utilization of novel materials designed to meet specific needs, offering enhanced parameters and properties. Therefore, the study provides a comprehensive examination of these innovative materials, encompassing an analysis of their functional characteristics, including rheological properties as indicated by the melt flow rate (MFR), mechanical strength, which includes tensile strength, and Charpy impact strength, as well as their

thermal properties. The research outcomes firmly establish the effectiveness of enhancing and modifying the properties of the polymer by incorporating organosilicon compounds.

EXPERIMENTAL

Materials

Polylactide (PLA) type Ingeo 2003D was purchased from NatureWorks (Minnetonka, MN, USA). The chemicals were purchased from the following sources 3-mercaptopropyltrimethoxysilane (99%), methanol from P.P.H Stanlab; hydrochloric acid (35%–38%), toluene, tetrahydrofuran, dichloromethane from Chempur, chloroform-d from Merck KGaA.

Procedure for Synthesis of (3-Thiopropyl)polysilsesquioxane

(3-Thiopropyl)polysilsesquioxane was prepared according to the literature data.^[27] The ¹H-NMR spectrum of the oil product shows no distinct, separated multiplets. The shifts (²⁹Si-NMR) at –56.37~(–60.38) (Si—OH), –64.42~(–67.15) (Si—O—Si) indicate a mixture of different structures in the product.^[27]

Preparation of Granulate

PLA 2003D and SSQ-SH were homogenized using a laboratory two-roll mill ZAMAK MERCATOR WG 150/280. A portion of 950 g PLA and 50 g of SSQ-SH was mixed until the final concentration of the SSQ-SH was 5%. The mixing was performed at the rolls temperature of 215 °C for 20 min., to achieve full homogeneity. The masterbatch was granulated with a grinding mill WANNER C17.26 sv and then dried for 24 h at 50 °C.

Injection Moulding Process

The prepared masterbatches were diluted 1:1 with PLA directly in the Engel E-victory 170/80 injection moulding machine. In Table 1 the injection moulding parameters were collected. A holding pressure of linear increment over time was applied. The mould temperature was maintained at 30 °C. Standardized specimens for mechanical tests were obtained according to PN-EN ISO 20753:2019-01. Final system concentrations were 2.5%, 1.5%, 1%, 0.5%, 0.25%, 0.1%, 0.05% and 0.025%.

Analyses

Thermogravimetry (TGA) was performed using a NETZSCH 209 F1 Libra gravimetric analyzer (Selb, Germany). Samples of 5±0.2 mg were cut from each granulate and placed in Al₂O₃ crucibles. Measurements were conducted under nitrogen (flow of 20 mL/min) in the range of 30–800 °C and 10 °C/min heating rate. Sensitivity: 0.1 µg.

Differential scanning calorimetry (DSC) was performed using a NETZSCH204 F1 Phoenix calorimeter. Samples of 6±0.2 mg were cut from each granulate and placed in an aluminum crucible with a punctured lid. The measurements were per-

Table 1 Injection moulding parameters.

	Die	Zone 3	Zone 2	Zone 1	Feed	Moulding form
Temperature (°C)	200	195	195	190	40	30
Holding pressure	<i>t</i> (s)			0.0	11.0	
	<i>P</i> (bar)			900	1100	
Clamping force (kN)	Holding time (s)		Cooling time (s)		Screw diameter (mm)	
	800		11		50	
					25	

formed under nitrogen in the temperature range of 20–220 °C and at a 10 °C/min heating rate.

For impact strength tests, the obtained materials were injection moulded into dumbbell specimens of type 1B under PN-EN ISO 527-1:2020-0133 and PN-EN ISO 178:2019-06. A Charpy impact test (with no notch) was performed on an Instron Ceast 9050 impact machine according to ISO 179-135.

X-ray diffraction studies (XRD) were performed using a Bruker D8 Eco Advance diffractometer with Cu-K_{α2} radiation at the following parameters: 40 kV and 25 mA. The angular range (2θ) of 5°–60° with a step width of 0.01 and a step time of 3 s was used. The Al₂O₃ sample was used as the XRD standard to correct an instrumental line broadening. A background correction of the K_{α2} stripping has been performed.

The effect of the modifier addition on the mass flow rate (MFR) was also determined. The measurements were made using an Instron plastometer, model Ceast MF20 according to the applicable standard ISO 1133. The measurement temperature was 210±0.5 °C, while the piston loading was 2.16 kg.

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.

A scanning electron microscope (SEM 3000, Hitachi, Japan) was used to analyze the microstructure and quality of the produced composite samples after injection moulding. Fractured composite materials were investigated. Before the measurement, the samples' cross-sections were coated with a thin layer of Au-Pd. The applied voltage for SEM observations was 15 kV.

Surface structure and breakthroughs were analyzed under Digital Light Microscope Keyence VHX 7000. All of the pictures were recorded with a VHX 7020 camera.

RESULTS AND DISCUSSION

Melt Flow Rate (MFR)

The melt flow index (MFI) is a crucial rheological property used to assess the flowability of polymer melts under static load. The melt mass-flow rate (MFR) was determined for ground moulded samples following the injection moulding process, as depicted in Fig. 1. Neat poly(lactide 2003D) exhibits an MFR of 6.5 g/10min at 210 °C (illustrated by the red point on the graph). The addition of organosilicon (SSQ-SH) leads to a significant increase in the MFR parameter for each concentration tested, which contributes to improving the processing of the composite by reducing the temperatures or increasing the speed of the process. Even a small amount of SSQ-SH (0.025% and 0.05%) results in MFR parameter improvements of 1.29 and 2.13, respectively. Concentrations ranging from 0.1% to 2.5% exhibit similar values, with an MFR increase of 2–3 g/10min compared to the reference. For the composite containing 5% silsesquioxane (5% SSQ-SH MFR=11.29 g/10min), a significant increase in MFR by up to 73.8% was observed compared to the neat polymer. The modifier in the form of SSQ-SH oil introduced into the PLA matrix plays the role of a plasticizer in the system, which has already been proven in our previous study,^[25] improving its lubricating properties. This results in higher MFR values and increased flexibility, ultimately improving impact resistance (as discussed in Section *Impact strength*).

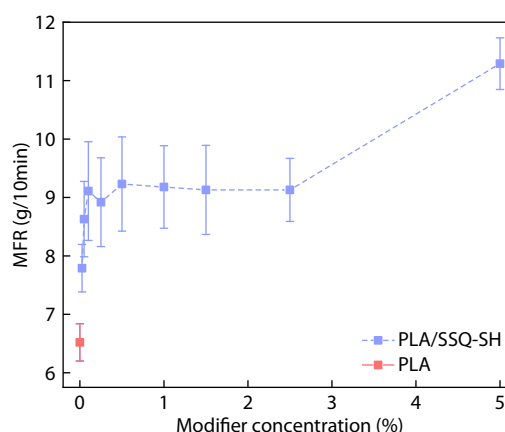


Fig. 1 Melt flow rate (MFR) results.

Morphology of the Composites

X-ray diffraction

Fig. 2 shows the XRD results of the reference sample (neat PLA) and selected SSQ-SH concentrations. In the presented work, all analyzed concentrations of SSQ-SH were examined, however, Fig. 2 shows selected (0.025%, 1.0%, 1.5%, 2.5%), as the analysis did not reveal changes in the crystallinity of the material with the addition of different concentrations of SSQ-SH. In the neat PLA, there is a broad peak at $2\theta=10^\circ-27^\circ$ and $30^\circ-36^\circ$, this is related to the semicrystalline structure of PLA. The same peaks appear in other tested samples. The absence of visible peaks from SSQ-SH with different concentrations is related to too low an additive concentration, which means that the reflections are of low intensity and cannot be distinguished from noise. Additionally, the peaks from the main compound (PLA) are characterized by high intensity, therefore peaks with lower intensity are not visible.^[28,29]

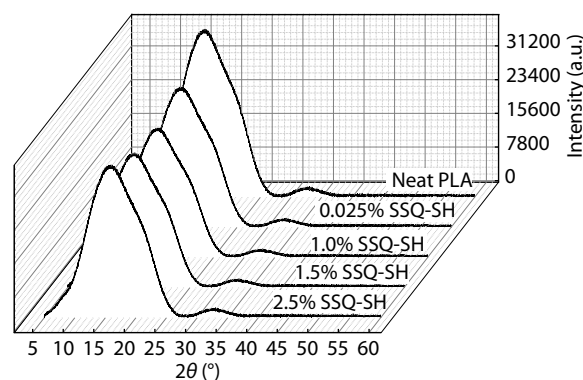


Fig. 2 X-ray diffraction (XRD) data for neat PLA and selected SSQ-SH concentrations.

SEM/EDS

Fig. 3 shows the surface structure after mechanical testing (image from a scanning electron microscope, SEM). Fig. 4 shows the EDS mapping of the sample surface with 5% SSQ-SH. The presented images show that with increasing the addition of the modifier, the microstructure of the material changes. The fractured surface of the sample with low modifier concentration is smoother compared to the other tested samples, which indicated a brittle fracture. This is consistent with the lower impact

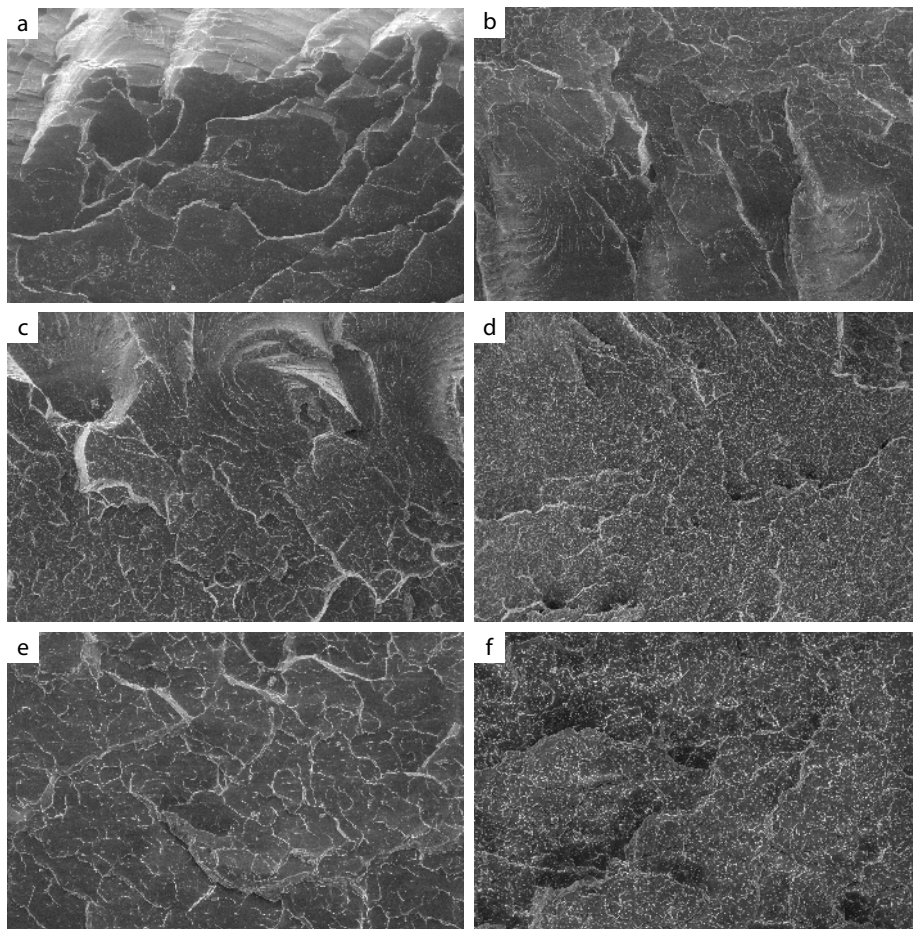


Fig. 3 SEM images of fractured samples (a) 0.025% SSQ-SH (MAG 150 \times), (b) 0.5% SSQ-SH (MAG 150 \times), (c) 1% SSQ-SH (MAG 150 \times), (d) 5% SSQ-SH (MAG 150 \times), (e) 0.5% SSQ-SH (MAG 500 \times) and (f) 5% SSQ-SH (MAG 500 \times).

strength compared to composites with higher modifier concentrations (see Section *Impact strength*). The material with the lowest concentration shows steady, wide cracks, while the presence of a higher content of SSQ-SH (Fig. 3) causes the formation of many narrower cracks. As the concentration of SSQ-SH increases, the fracture surface becomes coarse (Figs. 3a–3d), indicating that plastic deformation may have occurred during fracture. The modifier has a plasticizing effect and improves the mixing of composite phases, which is why it is more coherent and has fewer defects in the form of microcracks. Moreover, the rougher surface structure at the highest concentration of SSQ-SH may be caused by a change in the degree of crystallization in

the tested samples, which was also shown in the DSC analysis. SEM-EDS analysis (Fig. 4) shows that individual elements are regularly distributed, which indicates that the obtained material is homogeneous.

Optical microscopy

Spherulitic crystallization occurred in all tested mixtures, which was confirmed by the analysis of optical microscope images (Fig. 5). The rate of growth dynamics of spherulites is related to the enhancement of the mobility of PLA chains in mixtures at high temperature.^[30,31] Additionally, the dynamics could be influenced by strong nucleation by hydrogen bonds between the PLA carbonyl groups and the –OH and –SH groups in the

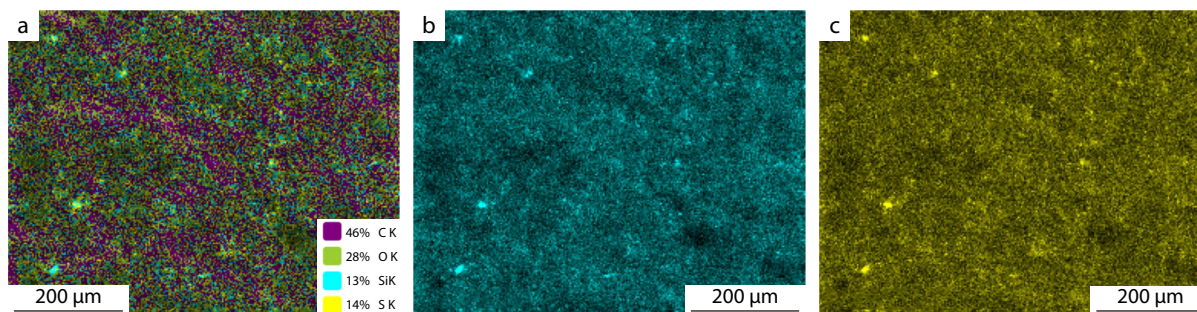


Fig. 4 EDS mapping of fractured samples 5% SSQ-SH (a) all elements, (b) Si mapping, (c) S mapping.

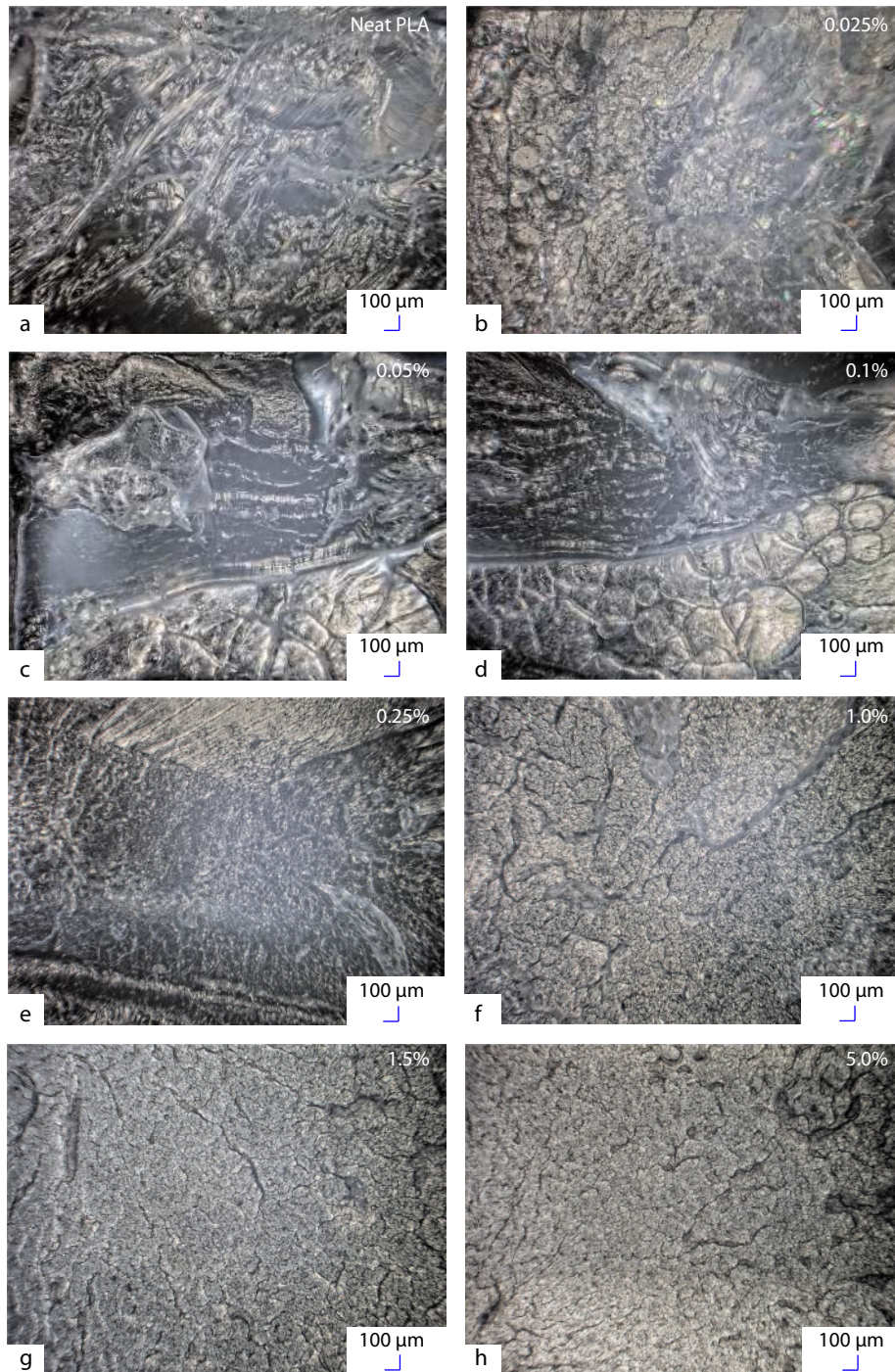


Fig. 5 Microscopic images of fractured samples (a) neat PLA, (b) 0.025% modifier, (c) 0.05% modifier, (d) 0.1% modifier, (e) 0.25% modifier, (f) 1.0% modifier, (g) 1.5% modifier and (h) 5.0% modifier.

modifier.^[32]

Observations based on polarized optical microscopy images of the composite materials reveal the presence of spherulitic structures across a range of modifier concentrations, spanning from 0.025% to 1% (Fig. 6). Notably, for lower concentrations of the SSQ-SH modifier within the polymer matrix, larger spherulitic structures exhibiting irregular shapes were identified. Contrastingly, in systems with higher concentrations (0.25%, 0.5% and 1%), the dimensions of the

spherulitic structures were clearly smaller and amounted to 64 ± 19 , 69 ± 25 , 57 ± 14 μm, respectively (Table 2), concurrently accompanied by an increased nucleation density. Upon analyzing microscopic images, it has been observed that the polylactide modified with silsesquioxane compounds exhibits the development of spherulitic structures in the shape of a Maltese cross, which is a characteristic feature of this type of modification.^[33,34] The increased number of spherulitic structures simultaneously with the decreased diameter indi-

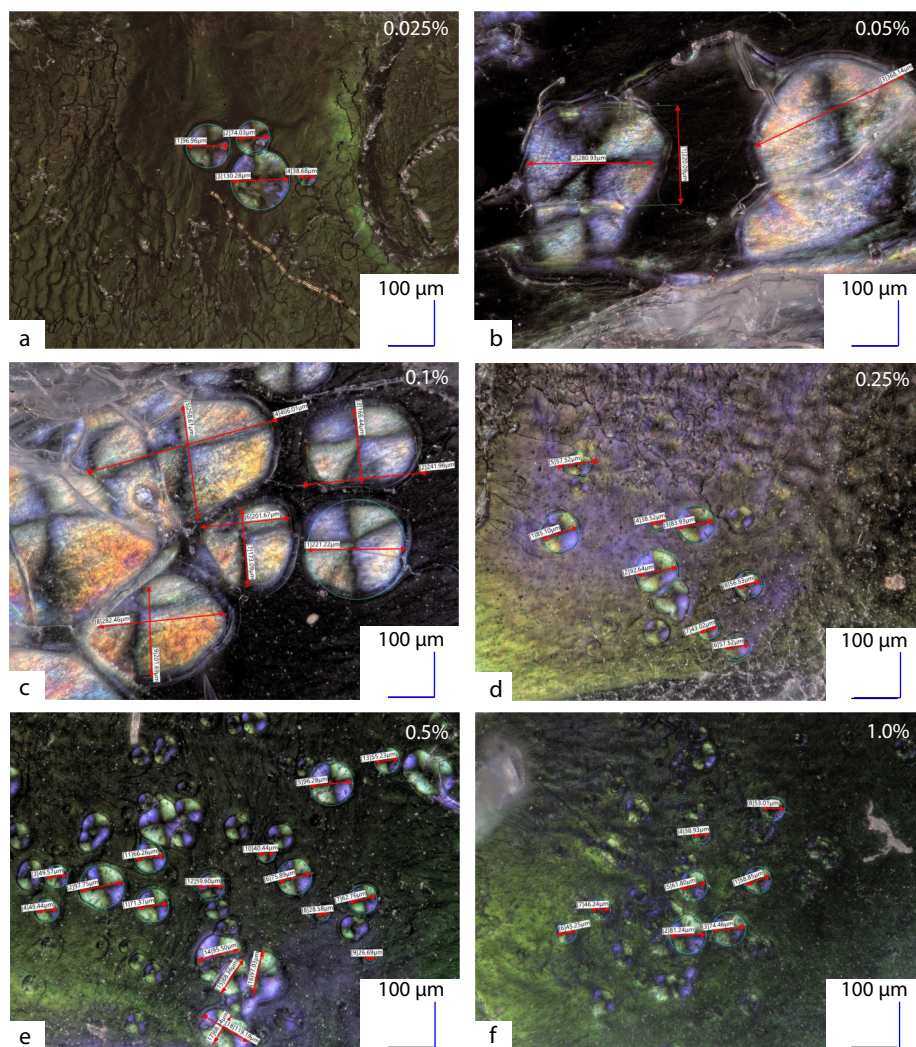


Fig. 6 Polarized optical microscopy images of composites: (a) 0.025% modifier, (b) 0.05% modifier, (c) 0.1% modifier, (d) 0.25% modifier, (e) 0.5% modifier, (f) 1.0% modifier.

Table 2 The size of spherulites in material with different modifier concentrations.

Modifier concentration (%)	Size distribution of spherulites (diameter) (μm)	Average diameter of spherulites (μm)
0.025	(38.68–130.28)	85 \pm 33
0.05	220.00; 280.00; 386.00	290 \pm 61
0.10	(166.00–406.00)	239 \pm 69
0.25	(38.52–92.64)	64 \pm 19
0.50	(26.69–119.19)	69 \pm 25
1.00	(38.92–81.24)	57 \pm 14

icates that the addition of silsesquioxane to polylactide enhances the process of forming the PLA crystalline nucleus.^[22]

Differential Scanning Calorimetry (DSC)

Fig. 7 displays DSC curves for both the unmodified polymer and the composites. These charts reveal three distinct temperature regions. The temperature range between 40 and 70 °C corresponds to the glass transition temperature, the range from 85 °C to 125 °C represents the cold crystallization temperature, and the range between 130 °C and 180 °C indicates the melting point. These phase transitions are characteristic of semi-crystalline polymers, including PLA 2003D.

For the composite material with a concentration of 5% of SSQ-SH, during the first heating cycle, two peaks are observed at temperatures 56.8 and 66.8 °C, respectively, which are located in the T_g region of the polylactide. However, the visible separation of peaks, which is not observed for other systems, may be due to the high amount of modifier concentration and incomplete interfacial miscibility.^[35] Fig. 8 presents DSC curves for neat PLA and the highest concentration of SSQ-SH (5%). In the case of the modified samples, a significantly sharper cold crystallization peak is noticeable in comparison to the reference sample. It can be inferred that SSQ-SH acts as a plasticizing agent, leading to increased mo-

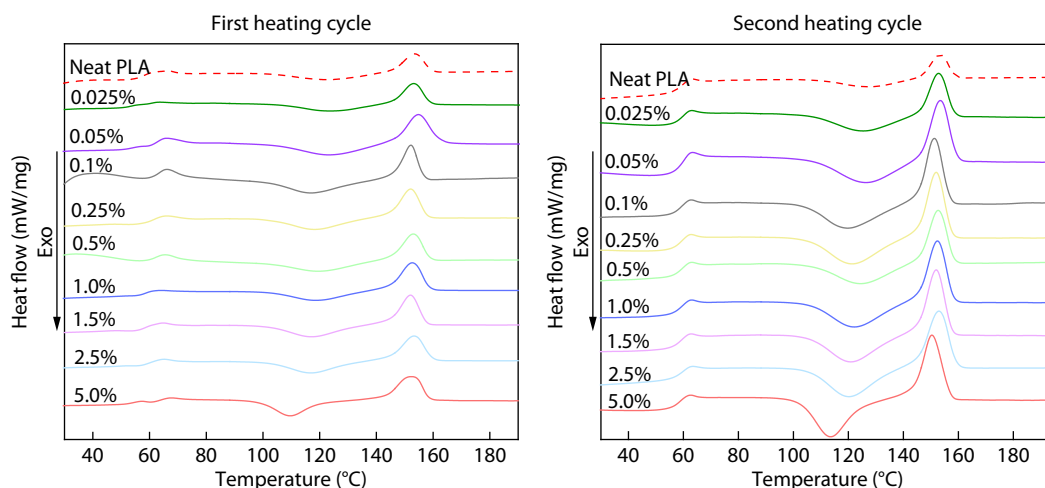


Fig. 7 DSC curves recorded for the first heating cycle (left) and the second heating cycle (right).

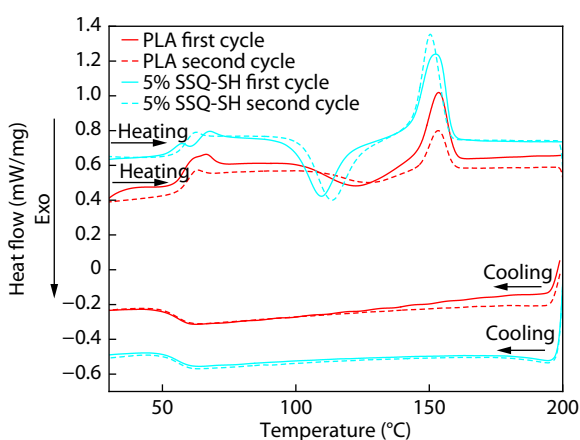


Fig. 8 DSC curves for neat PLA (red) and the highest concentration of SSQ-SH (5%) (blue).

bility of polymer chains in the amorphous phase, reorganization of aggregates within the material, and subsequent alterations in the internal structure, impacting crystallization. As the concentration of the modifier in the sample rises, a decrease in the cold crystallization temperature is observed (neat PLA T_{cc} =128.0 °C, 5% SSQ-SH T_{cc} =113.4 °C during the second heating cycle) (Table 3). The alteration of T_g (glass transition temperature) and T_{cc} (cold crystallization temperature) in polymers, specifically PLA, following the addition of

silsesquioxane, is well-documented in the literature due to the role of SSQs as a nucleating agents.^[36,37]

Degree of Crystallinity

The heat of fusion (ΔH_m) was determined from the DSC thermograms for each sample in both cycles and was determined from the area between the peak contour and the baseline. Knowing ΔH_m , the degree of crystallinity (w_c) can be determined from the formula presented in Eq. (1).^[38]

$$w_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \quad (1)$$

where w_c is degree of crystallinity [%]; ΔH_m is the heat of fusion [J/g]; ΔH_m^0 is the heat of fusion of 100% crystalline polymer (w_c =100%) (J/g). Based on literature data, ΔH_m^0 for neat PLA is 93.6 J/g.^[22]

The degree of crystallinity of PLA and composites are presented in Fig. 9. Calculations were performed according to Eq. (1), based on data resulting from DSC analysis. The obtained results clearly indicate a significant impact of the addition of silsesquioxane on increasing the degree of crystallinity of the polymer compared to the reference sample. The measurement process reveals that the introduction of silsesquioxane is crucial for the crystal structure of the polymer, which is reflected in a significant increase in the degree of molecular order.

In the amorphous product SSQ-SH, characterized by a com-

Table 3 DSC analysis results.

Concentration of modifier (%)	T_g (°C)		T_{cc} (°C)		T_m (°C)	
	First	Second	First	Second	First	Second
Neat PLA	61.8	62.2	121.9	128.0	153.7	153.4
0.025	63.2	62.2	124.2	124.8	153.5	152.9
0.05	65.0	62.6	123.3	126.4	154.8	153.6
0.10	66.4	62.1	117.1	119.3	152.1	147.3
0.25	64.8	62.1	118.7	120.9	152.4	152.1
0.5	65.0	62.2	120.0	123.7	153.5	152.9
1.0	62.5	62.0	119.0	121.4	152.9	152.6
1.5	64.5	61.9	116.8	121.1	152.2	152.1
2.5	64.4	62.5	117.3	120.4	153.5	153.3
5.0	66.8	61.7	109.5	113.4	152.8	150.4

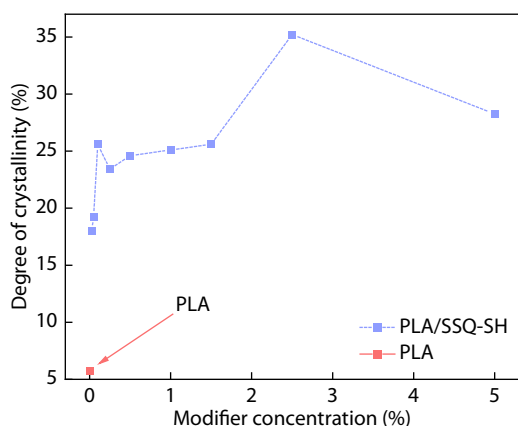


Fig. 9 Degree of crystallinity based on DSC analysis.

combination of cage structures and incompletely condensed silanols, the presence of proton donors is observed, both in the form of $-SH$ and $-OH$ groups. Their presence enables the formation of hydrogen bonds between the carbonyl groups in polylactide (PLA) and the thiol and hydroxyl groups contained in the SSQ-SH modifier. Though the thiol groups form weaker interactions with the carbonyl groups, the hydroxyl groups are capable of forming strong hydrogen bonds with the molecule matrix. Hydrogen bonds increase the ability to initiate the cold crystallization process. Strengthened interactions between the functional groups of the modifier and the PLA polymer structure through hydrogen bonds affect the mobility of polymer segments. This effect leads to the intensification of the nucleation process, which is crucial for the crystallization of the polymer at low temperatures.^[39] Fig. 10

shows the possible hydrogen interactions between the PLA matrix and the SSQ-SH mixture.

Thermal Analysis Results (TGA)

The thermal stability of composite materials is a pivotal consideration in both their application and processing. Through thermogravimetric analysis (TGA) conducted in a nitrogen atmosphere, it was revealed that the incorporation of an organosilicon modifier does not compromise the stability of the systems, regardless of the quantity of the modifier utilized (Fig. 11, Table 4). The derivative thermogravimetric (DTG) curves displayed a single peak at the Maximum Rate of Mass Loss, with a temperature of 362.1 °C observed for neat PLA and ranging from 359.9 °C to 363.0 °C for the composites. For the composites with the highest modifier concentration (2.5% and 5%), the residual mass at temperature 500 °C is 0.003% and 1.398%, respectively, which indicates a silica originating from the silsesquioxane core.

The presented data show that the introduction of an organosilicon modifier does not have a negative effect on the thermal stability of the composites. This means that even with different modifier concentrations, the overall thermal properties of the composite materials remain comparable to neat PLA. These observations are important in the context of ensuring that the improved properties obtained by the addition of the organosilicon modifier will not have a negative impact on the thermal stability of the composite materials.

Mechanical Test

Impact strength

The impact tests have confirmed the significant influence of the SSQ-SH modifier on the tested samples, as shown in Fig. 12. The impact strength of the neat PLA sample measures 17.1 kJ/m²

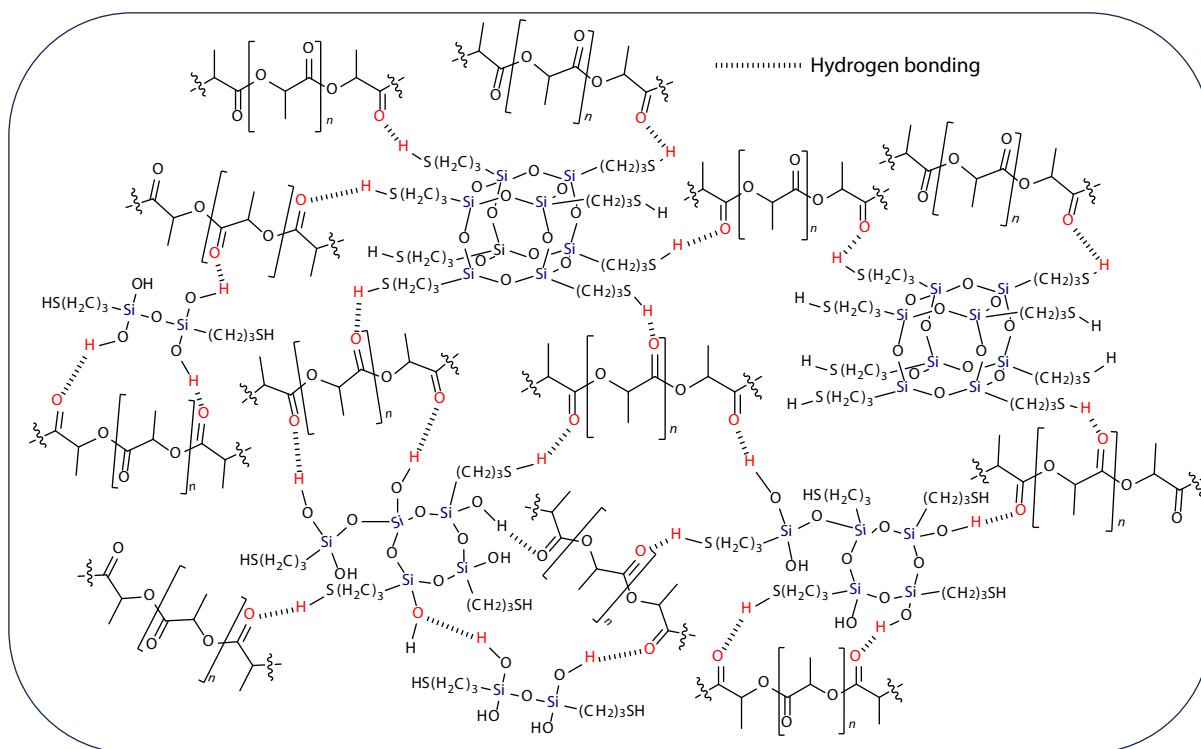


Fig. 10 Possible hydrogen interactions between the PLA matrix and the SSQ-SH mixture.

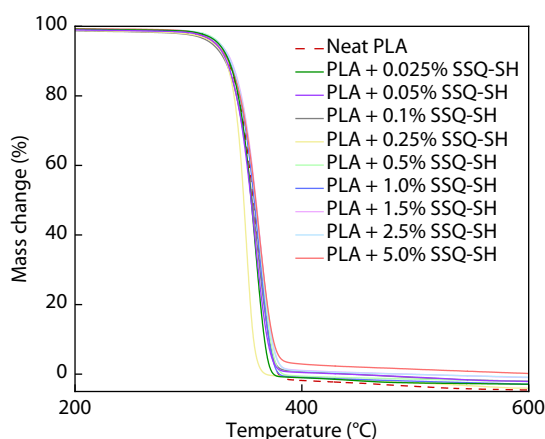


Fig. 11 TGA curves recorded in N₂ atmosphere.

Table 4 Results of thermogravimetric analysis.

Concentration of modifier (%)	Temperature at 5% mass loss (°C)	Onset temperature (°C)	Temperature at the maximum rate of mass loss (°C)	Residual mass at 500 °C (%)
Neat PLA	342.2	342.2	362.1	0
0.025	327.1	342.6	359.9	0
0.05	325.6	342.1	360.4	0
0.10	321.1	340.4	360.9	0
0.25	323.2	340.4	361.1	0
0.5	328.3	343.4	362.9	0
1.0	327.2	343.9	362.5	0
1.5	327.8	344.7	363.5	0
2.5	328.1	343.8	363.0	0.003
5.0	311.8	342.2	363.6	1.398

(red line). Even the addition of low concentrations of the modifier (0.025% and 0.05%) enhances impact resistance by 3.7 and 5.8 kJ/m², respectively, which translates to a 21.6% and 33.9% improvement compared to neat PLA. There is a clear linear trend of increasing impact strength with higher modifier concentration for tests after 4 weeks. The graph shows that the tested samples after one week are characterized by large deviations and a non-linear increase in the parameter. The linear trend occurring for the tested materials after 4 weeks may be due to structural stabilization in the polymer, which may lead to a reduction in the number of defects in the material structure. The highest impact strength was achieved with the 5% SSQ-SH/PLA composite, exhibiting a remarkable improvement of 32.0 kJ/m² compared to PLA, which represents an increase of 187%. Similar to the findings in the earlier rheological tests, the modifier acts as a plasticizer, reducing the brittleness of the polymer. The impact strength of composites is influenced by a significant change in the crystal structure of the polymer. As described in DSC and degree of crystallinity sections above, the addition of oil to the matrix increases the degree of crystallinity. The increase in impact strength observed with higher degree of crystallinity can be attributed to the increased energy dissipation resulting from the deformation of the crystallites. As crystallinity progresses, the material exhibits greater ability to absorb and dissipate energy during deformation, thereby increasing its overall impact resistance.^[40,41] The influence of the size and ar-

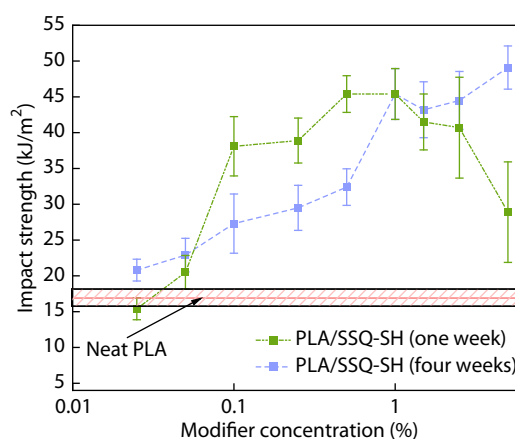


Fig. 12 Impact strength of composites.

range of spherulitic structures on impact strength can also be observed. The higher nucleation density that occurs at higher concentrations reduces the radius of the spherulitic structures, which is one of the causes of the increased impact strength.^[41] This phenomenon highlights the correlation between crystallinity and impact strength, emphasizing the role that the structural arrangement of crystallites plays in influencing the mechanical properties of the material. Additionally, the organosilicon compound particles, constituting the dispersed second phase within the polymer matrix, can serve as a barrier in the system, increasing the energy required to fracture the sample during impact.^[42] This phenomenon aligns with the model proposed by A.G. Evans, which posits that when a crack interacts with the second dispersed phase, more energy is needed to propagate secondary cracks compared to a pure material. As the concentration of SSQ-SH increases, the distance between the particles decreases, consequently raising the energy threshold required for fracture. Second-phase dispersions typically enhance strength, which may be related to the phenomenon equivalent to the "line tension effect" observed for dislocation motion.^[43]

Tensile strength

The results of static tensile strength tests indicate an increase in the elasticity of composite materials caused by the addition of SSQ-SH to the PLA matrix, without a significant reduction in tensile strength (Fig. 13). The tensile strength values for the composites are generally comparable to those of unmodified PLA, with the exception being the 5% SSQ-SH composite. Notably, the elongation at break is significantly higher for the modified samples, with neat PLA exhibiting an elongation of 3.45%, whereas the 5% SSQ-SH composite shows an elongation of 7.32%, which also confirms the plasticizing nature of the additive used. The incorporation of a modifier, acting as a plasticizer, leads to increased "mobility" within the polymer phase. One of the factors that influences the change in mechanical properties is the penetration of the plasticizer between the macromolecular polymer chains, reducing the intermolecular forces acting along them.^[44] Additionally, the interactions created between the functional groups of the modifier and the PLA polymer structure can lead to local cross-linking and interpenetrating network structure in the PLA matrix, thus increasing the chain entanglement and flexibility of PLA.^[45] From the tests carried

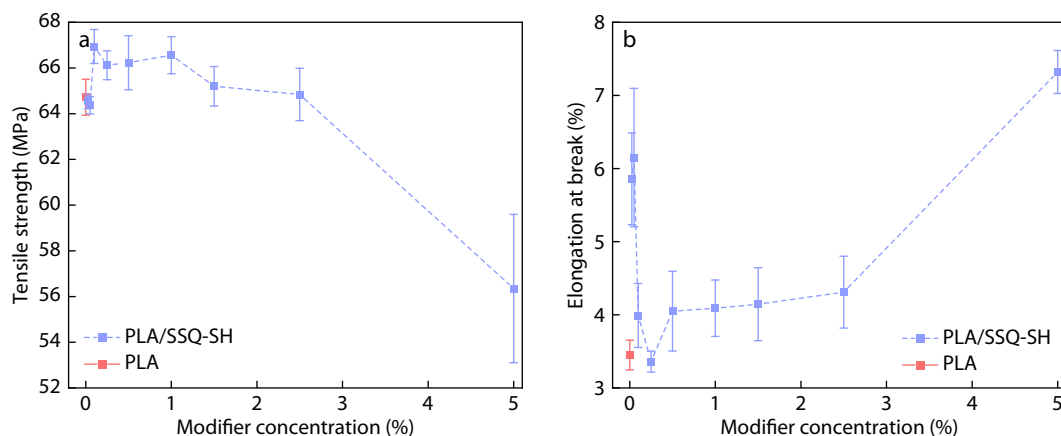


Fig. 13 (a) Tensile strength of composites; (b) Elongation at break of composites.

out, it can be concluded that samples containing 0.025% and 0.05% SSQ-SH are in the optimal concentration range, where a beneficial plasticization effect is achieved, improving the elasticity of the material while minimizing the impact on tensile strength.

The introduction of the organosilicon compound, SSQ-SH, has a discernible effect on the structure and microstructure of the polymer. The observed phenomenon could be due to the interaction between SSQ-SH and polylactide, influencing its mechanical characteristics. These factors are important in the context of composite material design and have the potential to make a substantial contribution to contemporary polymer research.

CONCLUSIONS

In the present work, SSQ-SH, an amorphous hydrolytic condensation product derived from 3-mercaptopropyl(trimethoxy) silane, was introduced into a polylactide (PLA) matrix using a conventional melt mixing method. Test samples were obtained by injection moulding. Detailed thermal and mechanical characterization of the composites was carried out, as well as a rheology test, which showed a significant increase in the MFR index for the obtained composites (compared to neat PLA). Their morphology was also characterized using SEM-EDS, X-ray diffraction, and optical microscopy methods. SEM microscopic images with EDS mapping showed effective dispersion of the modifier in the polymer matrix, which could be attributed to the thiol groups present. This dispersion led to improved crystallization, as evidenced by a decrease in the cold crystallization temperature (T_c) and an increase in the degree of crystallinity. The formation of spherulite structures was observed in microscopic images. The thermal tests performed showed that SSQ-SH acts as a nucleating agent in the PLA matrix. Additionally, an increase in mechanical parameters was observed for samples containing an organosilicon additive.

Particularly noteworthy is the fact that SSQ-SH significantly improves the impact strength of the composite, which is extremely important in the case of brittle PLA. Even at low concentrations, its addition increased impact strength. The composite containing 5% SSQ-SH showed the highest impact strength, showing a remarkable improvement of 187% compared to neat PLA. These findings suggest that SSQ-SH may act as a cost-effective polylactide modifier, significantly im-

proving its properties.

Patents

The results of this publication have been patented with Polish patent application no. P.446764, 17.11.2023r.

Conflict of Interests

The authors declare no interest conflict.

Data Availability Statement

The data presented in this study are available on request from the corresponding author. The data are not publicly available: bogdan.marciniak@amu.edu.pl (B.M.), robert.przekop@amu.edu.pl (R.E.P.)

ACKNOWLEDGMENTS

This work was financially supported by the Smart Growth Operational Programme (No. POIR.04.02.00-00-D003/20-00); European Funds (No. RPWP.01.01.00-30-0004/18) and Ministry of Science and Higher Education (No. 21/529535/SPUB/SP/2022).

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