



# Influence of polydopamine and tannic acid coatings on thermal properties of polylactide

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## Abstract

In this paper, the research findings about the impact of polydopamine and tannic acid coatings on specific thermal properties of polylactide are discussed. The influence of deposited coatings on the resistance to oxidation, heat resistance, and the temperatures of phase transitions was determined. Therefore, the oxidation induction temperature, thermogravimetry, and differential scanning calorimetry studies were carried out. To gain a deeper understanding of the findings, mass measurements for the samples before and after the deposition process were conducted, as well as scanning electron microscopy studies. Studies have shown that the application of coatings can improve the resistance of polylactide against oxidative and thermal degradation. However, these coatings have minimal impact on the intensity and temperature of phase transformations. The polylactide showed increased thermal resistance when coated with polydopamine, whereas tannic acid coating was found to be more effective in increasing oxidation resistance. The differences observed were likely caused by variations in the structure of the coatings applied, impacting the level of oxygen diffusion and heat transfer within the material.

**Keywords** Polylactide · Polydopamine · Tannic acid · Thermal properties

## Introduction

Due to their properties, polymeric materials are one of the most important groups of engineering materials. Density oscillating around  $1 \text{ g cm}^{-3}$ , high mechanical strength about mass, ease of shaping finished products, or resistance to weather conditions and active environment, allowed them to be used in the broadly understood industry.

Recently, biodegradable plastics obtained from renewable raw materials have become particularly popular. The most popular example of such a material is polylactide (PLA)—thermoplastic polyester, made of cornmeal, used in the textile and packaging industry—also in contact with food [1–3]. Due to its non-toxicity and biodegradability, PLA is also used in medicine, including scaffolding, drug delivery systems, bone fixation devices, such as screws and plates, sutures, and surgical meshes [4–8].

Polylactic acid has been extensively studied in terms of properties—both in pure and doped form. It has been

discovered that PLA can undergo crystallization through stretching, temperature treatment, and copolymerization. PLA can be easily processed on a wide range of equipment. Additionally, doping the PLA with natural compounds can lead to enhanced thermal, mechanical, and conductive properties [9–13]. Mixtures of PLA with other biodegradable polymers such as polycaprolactone (PCL) can create composites with enhanced thermal or mechanical properties compared to the individual polymer components while maintaining biodegradability [14, 15].

Furthermore, the study of PLA included an examination of how modifying the surface layer affects changes in functional and technological properties. It was found that the laser, corona, plasma, or chemical modification cleans the surface, changes the geometric structure, and increases the roughness and consequently the adhesive strength of the plastic-coating connection. It is particularly important in the case of coated plastics characterized by high resistance to external factors and the best possible adhesion to the substrate [16–19].

When biodegradable polymers are covered with coatings—which can be protective, decorative, or technical—they gain extra properties from the coating material. Particularly important are coatings that improve selected technical

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properties. Coatings are applied to enhance different properties, such as thermal, electrical, mechanical, adhesive, biocidal, and biological. They may also be used to achieve catalytic properties, such as depositing a conductive metallic coating. [20, 21]. A new way to modify surfaces involves using biomimetic chemical compounds that are inspired by plants and animals, such as polyphenols and catecholamines.

Among the catecholamines, dopamine is the most commonly used substance. The use of dopamine in coating formation was inspired by the adhesive nature of catechols and amines observed in mussel adhesive proteins [22]. Dopamine has the capability to create nanoscale coatings through auto-polymerization. This results in the formation of a thin layer of polydopamine (PDA) on the coated material's surface. The PDA layer exhibits adhesion-increasing, complex-forming, and antibacterial properties and participates in the process of removing free radicals [23–25]. In recent years, due to the biocompatibility of PDA, research has been carried out on its application in medicine, mainly in the implementation of bioelectronics, performing tumor ablation, imaging, or drug delivery [26–34]. The research also showed that it is beneficial to use PDA as a modifier of the thermal properties of composites. It was found that the modification of PDA of various fillers of polymeric materials increases the stability and thermal conductivity of the obtained composites [35–38].

Polyphenols, including tannic acid, are also used in the surface coating process. In the process of auto polymerization, a layer of poly(tannic acid) (PTA) is formed on the surface of the coated material. PTA is used as a supramolecular or chemical crosslinking agent to provide versatile functional polymer networks for a variety of applications. In addition, used in medicine, it provides bone regeneration, is used to create skin adhesives, wounds, and dressings, as well as deliver drugs and photothermal conversion [39–43]. The use of PTA in the manufacture of sensors is also known. A group of Chinese scientists [44] have developed new fluorescent PTA nanoparticles in a self-polymerization reaction. This nanomaterial has excellent intrinsic fluorescent properties. The method of producing this type of nanomaterial is of high importance due to its excellent sensitivity and selectivity and low cost of production. Research is also conducted on the use of PTA as anode materials for high-performance lithium–sodium batteries [45]. The studies on the influence of PTA on the thermal properties of composites show that its use as a functionalizer of additives introduced into the polymer matrix improves the thermal conductivity and thermal stability of composites [46, 47].

Previous studies extensively examined and described the impact of polydopamine and tannic acid coatings on various physicochemical properties of different materials. However, these studies rarely addressed the impact of directly applied

coatings on the thermal properties of the coated materials. This study aims to investigate how the application of polydopamine and tannic acid coatings affect the thermal properties of polylactide. By applying tested coatings on polylactide, this polymer can acquire entirely new properties that are useful for both simple and complex applications. It is important to investigate the impact of applied coatings on the thermal properties of polylactide, as most methods of obtaining these elements and their applications involve heat in some form.

## Materials and methods

### Materials

Polylactide (PLA) 2003D (Cargill Down LLC, USA) was used as a substrate for deposited coatings. Dopamine hydrochloride ( $C_8H_{12}ClNO_2$ ) (Sigma Aldrich, Poland), tannic acid ( $C_{76}H_{52}O_{46}$ ) (Sigma Aldrich, Poland), and 0.1M Tris–HCl buffer with pH 8.5 (Chempur, Poland) were used in the coating deposition process.

### Methods

The test samples were produced by injection molding with parameters typical for PLA. Samples in the form of small cylinders weighing 6–15 mg were cut out of 60 × 60 mm plates and then covered with polydopamine or tannic acid coating.

A simple immersion method was used in the deposition process using a pre-prepared solution. The deposition solution was obtained by dissolving dopamine hydrochloride or tannic acid in the amount of 5 mg mL<sup>-1</sup> in a Tris–HCl buffer. The coating deposition process was carried out at room temperature (approx. 23 °C). Samples were immersed in the deposition solution for 24 or 72 h. After the deposition process, the samples were dried in a laboratory dryer for 24 h. As a result of the deposition of the coating, a sample in the form of a core–shell was created. The samples obtained for further tests were marked as PLA\_PD\_X or PLA\_TA\_X, where PD means a polydopamine coating, TA means a tannic acid coating, and X means deposition time, respectively, 1 for 24h deposition, 3 for 72h deposition.

Oxidation induction temperature (OOT) was determined using a Q500 differential scanning calorimeter (DSC) (TA Instruments, USA). Samples weighing about 14 mg were heated in an oxygen atmosphere from 20 °C to the temperature of the beginning of the oxidation process. The scanning rate was 10 °C min<sup>-1</sup>. The OOT value was determined as the onset of the DSC curve.

The change in sample mass ( $\Delta m$ ) was determined with the WAS 160X (Radwag, Poland) laboratory scale using Eq. 1:

$$\Delta m = \frac{m_2 - m_1}{m_1} \cdot 100\% \quad (1)$$

where:

$m_1$ —sample mass before the deposition [mg],

$m_2$ —sample mass after the deposition [mg].

Microscopic images of the surface of the samples were taken using a scanning electron microscope Hitachi SU8010 (Hitachi High-Technologies Co., Japan). The tests were carried out in a high vacuum of 0.1Pa, with various magnifications from 250x to 5000x, accelerating voltage of 5kV, in the mapping mode using a backscattered electron detector (BSD). Before imaging, the surface was covered with a layer of gold using a low-vacuum sputtering machine MCM100P (SEC, South Korea).

Thermogravimetric analysis was performed using the Q200 thermobalance (TA Instruments, USA). Samples weighing about 12 mg were heated in the temperature range from 20 to 700 °C with a scanning rate of 10 °C min<sup>-1</sup>. The test was carried out in a nitrogen atmosphere. From the obtained thermogravimetric curves, the values of  $T_{5\%}$ ,  $T_{50\%}$ , and  $T_{95\%}$  were determined, corresponding to the loss temperature of 5, 50, and 95% of the initial sample mass. From the differential thermogravimetric curve (DTG) (the first derivative of the TG curve), the  $T_{\max}$  value was also determined, indicating the temperature of the fastest mass loss. The results include a full cross-section of the degradation kinetics of the tested materials, to show its course. However, the description of the test results focuses primarily on the  $T_{5\%}$  value, which is the most important parameter determining the thermal stability of materials.

Differential scanning calorimetry (DSC) studies were performed using the Q200 differential scanning calorimeter (TA Instruments, USA). Samples weighing about 10 mg were heated in the temperature range from 0 to 700 °C with a temperature change rate of 10 °C min<sup>-1</sup>. The test was carried out in a nitrogen atmosphere. Based on the DSC study, the glass transition temperature ( $T_g$ ), cold crystallization temperature ( $T_{cc}$ ), cold crystallization enthalpy change ( $\Delta H_{cc}$ ), melting point ( $T_m$ ), melting enthalpy change ( $\Delta H_m$ ), and degree of crystallinity ( $X_c$ ) were determined.  $X_c$  values were calculated from formula 2:

$$X_c = \left( \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{m100\%}} \right) \cdot 100\% \quad (2)$$

where:

$\Delta H_{m100\%}$ —melting enthalpy change value of 100% crystalline PLA; 93 J g<sup>-1</sup> [48].

## Results and discussion

### OOT

The first thermal parameter determined in the conducted research was the oxidation onset temperature (OOT). This parameter is an indicator of the material's resistance to oxidative decomposition. OOT is the temperature at which oxidation reactions begin and designates the beginning of the material degradation process.

The OOT value of pure PLA was 224.4 °C and was consistent with the values observed in the literature [49, 50]. The applied coatings showed an oxidation-reducing effect, as the obtained OOT values were significantly higher than those obtained for pure PLA. The OOT of the PLA\_PD\_1 sample was 242.1 °C (Fig. 1). Therefore, the polymer's thermal resistance increased by approximately 20 °C after a 24-h deposition of the polydopamine coating.

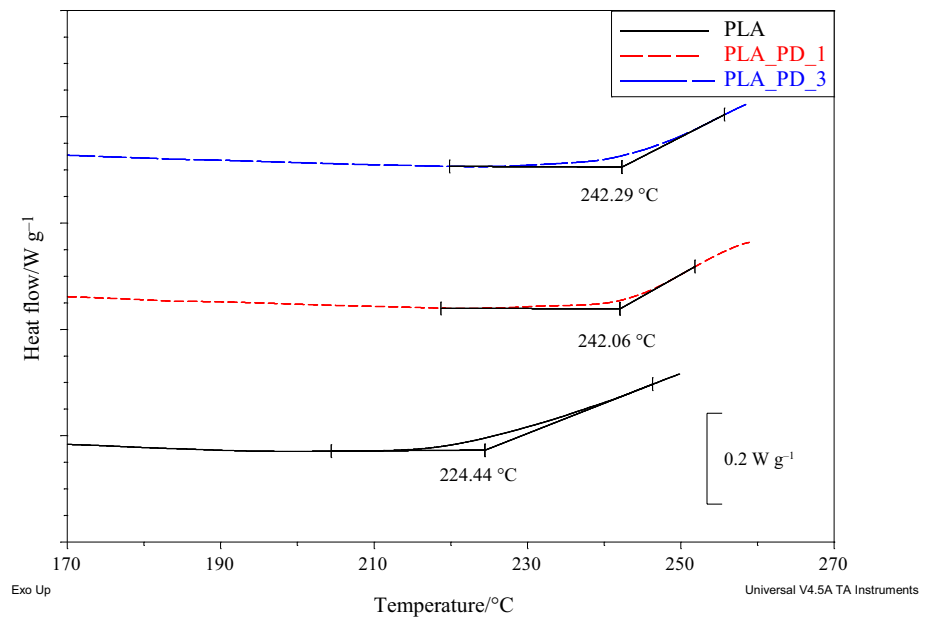
Increasing the deposition time did not cause significant changes in the thermal resistance of the material, because the OOT of the PLA\_PD\_3 sample was practically identical (242.3 °C).

When comparing the heat resistance of the tannic acid and polydopamine coatings, it was found that the initial increase in heat resistance was lower for the tannic acid coating. After 24h of deposition, the OOT of the PLA\_TA\_1 sample was 230.2 °C, so the increase compared to pure PLA was only about 6 °C (Fig. 2). However, a large increase was observed after 72h of coating deposition. For the PLA\_TA\_3 sample, the OOT was 253.7 °C, so it was almost 30°C higher than the value obtained for pure PLA and almost 10 °C higher than the value obtained for the PLA\_PD\_3 sample.

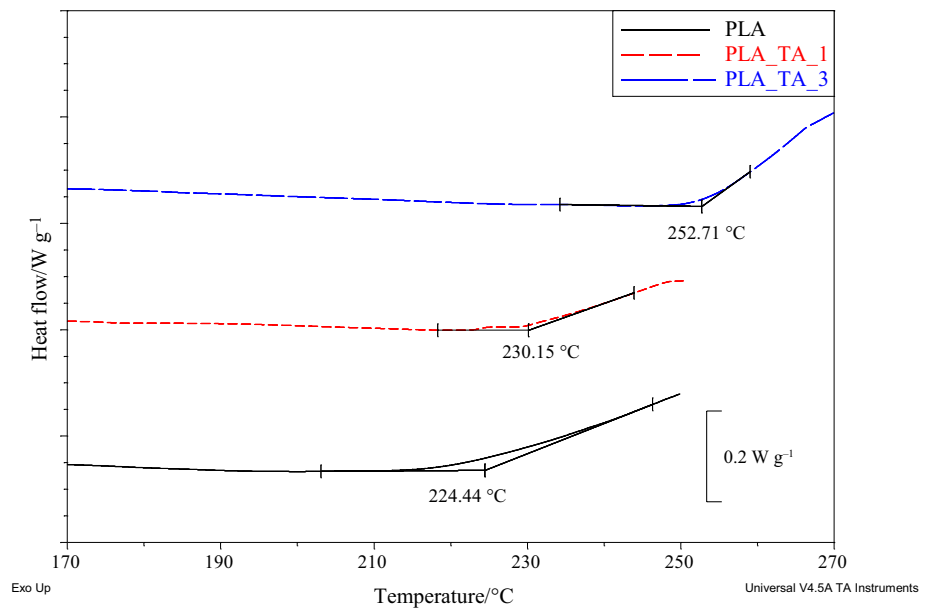
The reason for the increase in resistance to oxidative degradation was probably the limitation of diffusion of oxygen molecules into the polymer through the coatings [49]. The barrier properties of tannic acid coatings have already been described in the literature [51], but there is no such information regarding polydopamine. It can be inferred that a comparable process takes place with polydopamine coating. Therefore, if these compounds have similar film-forming properties, a similar mechanism may occur when polydopamine coating is applied. The barrier effectiveness depends on the structure of the polydopamine or tannic acid coating and the thickness and/or packing density of these coatings. This was indirectly confirmed by the analysis of SEM images (Fig. 3) and the analysis of the mass change of samples before and after the coating deposition process ( $\Delta m$ ) (Fig. 4).

As can be seen in the SEM images, both coatings differ significantly in structure. The polydopamine coating is characterized by high heterogeneity and discontinuity,

**Fig. 1** Oxidation induction temperature (OOT) of samples with a deposited polydopamine coating



**Fig. 2** Oxidation induction temperature (OOT) of samples with a deposited tannic acid coating



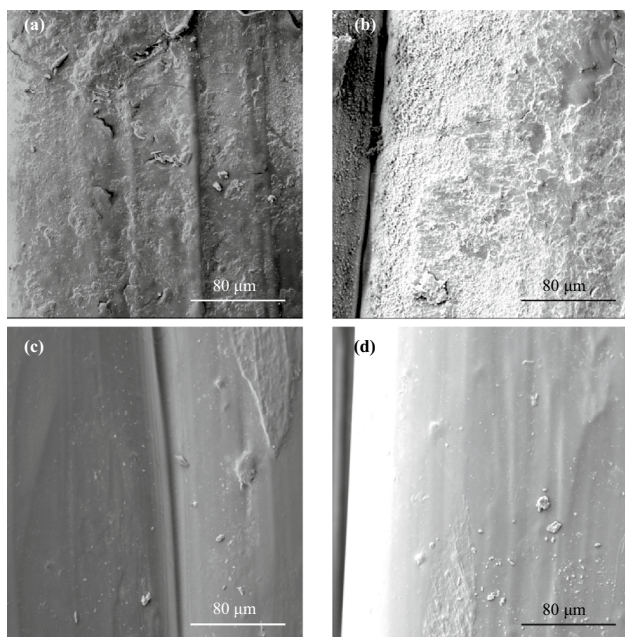
which deepen with increasing deposition time. After 72h of deposition, the coating additionally appears to be significantly porous. The tannic acid coating, on the other hand, is smooth, uniform, and continuous regardless of the deposition time, which explains the overall better ability to limit oxidative degradation. The dense tannic acid coating better reduces the diffusion of oxygen to the PLA under the coating than the polydopamine coating full of voids, which is particularly noticeable after 72h of deposition, where the difference in the structure of both coatings is the greatest.

The obtained  $\Delta m$  results are consistent with the observed OOT changes. The largest increases in OOT correlate with

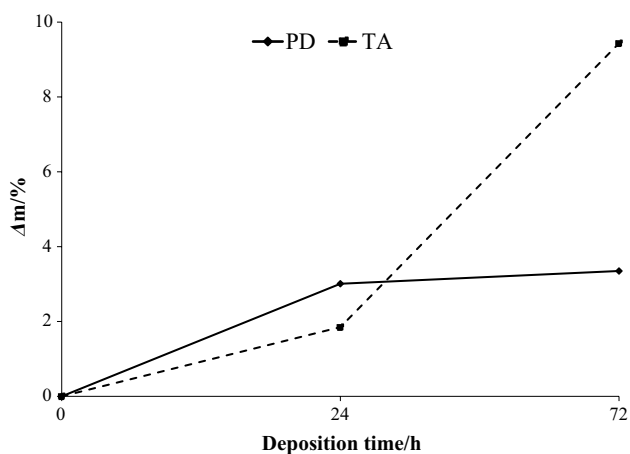
the largest increases in sample mass, i.e., after 24h for the polydopamine coating (mass increase of 3.0%) and after 72h for the tannic acid coating (mass increase of 9.4%). Thus, it can be seen that as the deposition time increased, the thickness and/or packing density of the coatings increased, limiting the possibility of oxygen reaching the underlying polymer and increasing the resistance to oxidative degradation.

### Thermogravimetric analysis

The thermal stability of the tested materials in a wider range of temperatures along with the study of the thermal degradation process was determined by thermogravimetric



**Fig. 3** SEM images of the surface of the samples **a** PLA\_PD\_1, **b** PLA\_PD\_3, **c** PLA\_TA\_1, **d** PLA\_TA\_3



**Fig. 4** Sample mass as a function of deposition time; PD—solid line, TA—dashed line

analysis. Since the thermogravimetric analysis was carried out in an inert atmosphere (nitrogen), the main role in this study is played by heat and its transport to the material. The results of the thermogravimetric analysis of the tested materials are presented in Table 1.

The observed degradation process of pure PLA was typical for this material. One observed single large mass loss in the range of 300 to 380 °C due to thermal degradation of the polymer material. Thermal resistance determined based on the temperature of 5% mass loss ( $T_{5\%}$ ) was approx. 310 °C

**Table 1** The results of the thermogravimetric analysis

Sample	$T_{5\%}/^{\circ}\text{C}$	$T_{50\%}/^{\circ}\text{C}$	$T_{95\%}/^{\circ}\text{C}$	$T_{\text{max}}/^{\circ}\text{C}$
PLA	310.2	349.2	370.6	358.8
PLA_PD_1	323.0	353.2	370.9	361.2
PLA_PD_3	324.7	356.3	373.3	363.1
PLA_TA_1	315.5	348.0	365.9	355.4
PLA_TA_3	317.3	353.5	371.3	360.7

and the degradation process was the most intensive ( $T_{\text{max}}$ ) at approx. 359 °C.

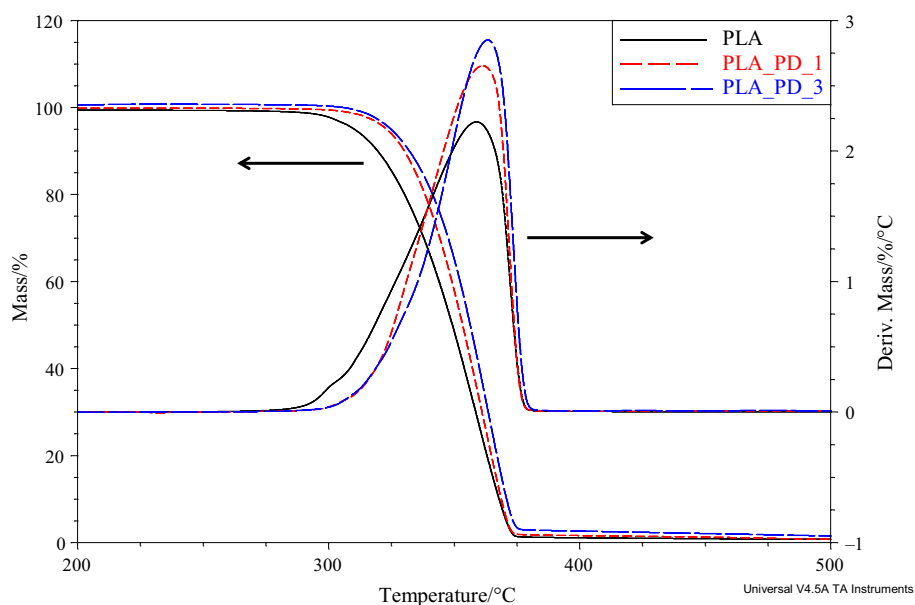
Deposition of a polydopamine coating on PLA improved the thermal resistance of the material (Fig. 5). After 24h of coating deposition, the  $T_{5\%}$  of the PLA\_PD\_1 sample increased to 323.0 °C. However, increasing the deposition time to 72h no longer resulted in significant changes. Although the  $T_{5\%}$  of the PLA\_PD\_3 sample increased to 324.7 °C, but the difference in values was too small to be considered an improvement in thermal resistance. Therefore, the deposition of the polydopamine coating caused an increase in thermal resistance by approx. 14 °C, regardless of the deposition time.

Also, the deposition of the tannic acid coating improved the thermal resistance, but the change was not as large as in the case of the polydopamine coating (Fig. 6). The  $T_{5\%}$  value after 24h of coating deposition (sample PLA\_TA\_1) was 315.5 °C, and after 72h of deposition (sample PLA\_TA\_3) it slightly increased to 317.3 °C. Thus, it can be seen that the application of a tannic acid coating improves the thermal resistance of PLA by approx. 6 °C.

The reason for increasing the thermal resistance of materials with deposited coatings may result from the occurrence of two phenomena. The first is simply applying a coating to the PLA surface, which is characterized by greater thermal resistance, consequently increasing the thermal resistance of the entire system. The high thermal resistance of polydopamine was described in [52], where it inhibited the degradation of another biodegradable polymer—polycaprolactone (PCL).

The second is the change in the intensity of heat transfer to the PLA after the coatings are applied. Heat conduction through a polymer is a complicated process that depends on many parameters, such as crystallinity, temperature, or orientation of macromolecules. As described in the literature, heat transfer in polymers and polymer composites can be well explained by phonon propagation or the flow of lattice vibrational energy, i.e., mechanical vibrations in general [53]. Phonons are usually thought of as heat carriers in polymers because there are only a small amount of free electrons in these materials, and the exact mechanism for this phenomenon can be found in [54].

**Fig. 5** TG curves of samples with a deposited polydopamine coating



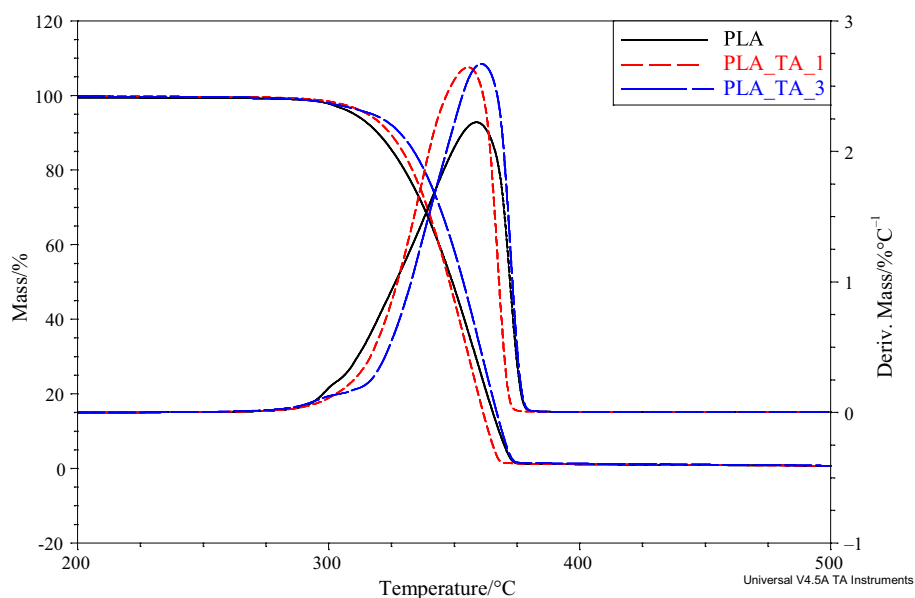
The appearance of the polymer/coating interface may limit the propagation of phonons and the deterioration of thermal conductivity, which is manifested by higher recorded  $T_{5\%}$  values of samples with deposited coatings than of pure PLA. At the same time, the observed differences in the thermal resistance of samples with individual coatings may result from a different structure of those coatings. The polydopamine coating is more irregular, and has more damage and voids (especially after a longer deposition time) than the smooth and compact tannic acid coating (Fig. 3). All imperfections present in the polydopamine coating lead to phonon scattering and poorer thermal conductivity,

which led to higher  $T_{5\%}$  values of PLA\_PD\_X samples than PLA\_TA\_X.

### Differential scanning calorimetry

The influence of polydopamine and tannic acid coatings on the kinetics and temperatures of PLA phase transitions was checked. For this purpose, differential scanning calorimetry (DSC) was performed. Based on obtained heating curve, the influence of the coatings on the observed phase transformations was determined. The results of differential scanning calorimetry are presented in Table 2.

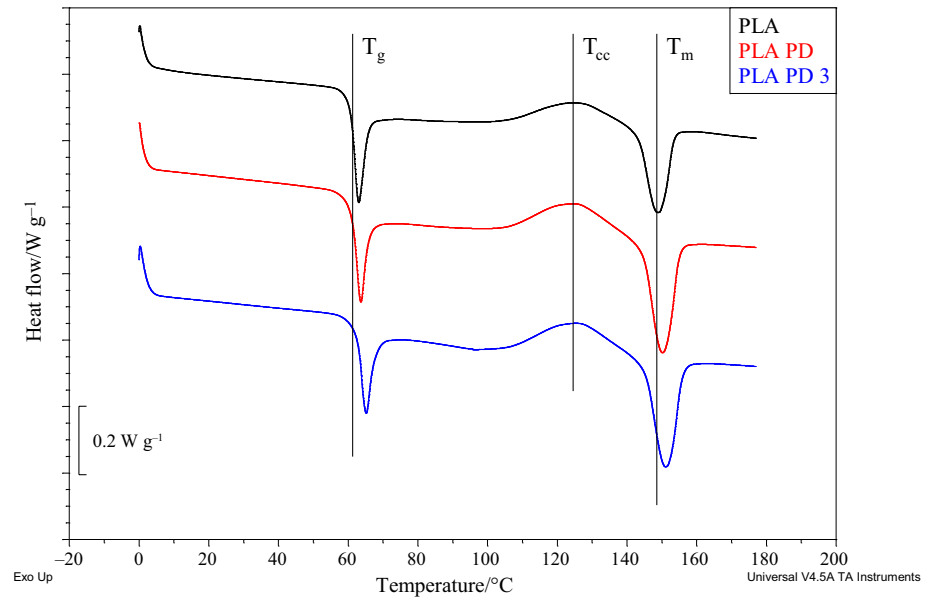
**Fig. 6** TG curves of samples with deposited tannic acid coating



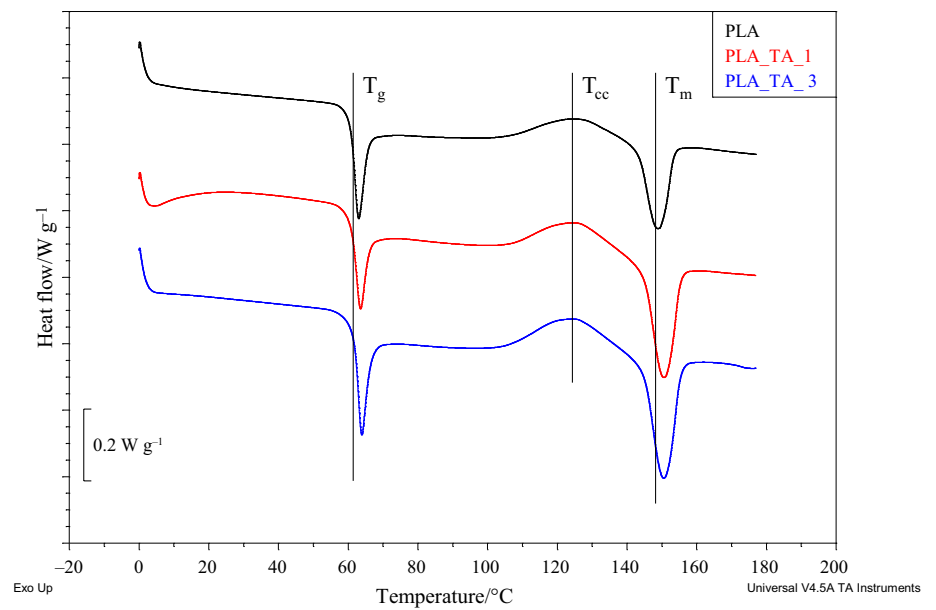
**Table 2** The results of differential scanning calorimetry

Sample	$T_g/^\circ\text{C}$	$T_{cc}/^\circ\text{C}$	$\Delta H_{cc}/\text{J g}^{-1}$	$T_m/^\circ\text{C}$	$\Delta H_m/\text{J g}^{-1}$	$X_c/\%$
PLA	62.0	125.5	9.6	148.8	9.9	0.3
PLA_PD_1	62.7	125.2	13.5	150.0	13.6	0.1
PLA_PD_3	63.8	125.9	12.8	151.0	14.0	1.3
PLA_TA_1	62.5	125.5	13.9	150.6	14.1	0.2
PLA_TA_3	63.0	124.7	14.1	150.4	15.4	1.4

**Fig. 7** DSC curves of samples with a deposited polydopamine coating



**Fig. 8** DSC curves of samples with deposited tannic acid coating



The heating curve of pure PLA was typical for this polymer. A step change at 62.0 °C due to the glass transition ( $T_g$ ) of PLA, an exothermic cold crystallization peak with a maximum at 125.5 °C ( $T_{cc}$ ), and an endothermic melting peak with a maximum at 148.8 °C ( $T_m$ ) was observed. The calculated degree of crystallinity ( $X_c$ ) of the tested sample was 0.3%, therefore the tested PLA is amorphous.

The deposition of polydopamine and tannic acid coatings does not change the number of observed phase transitions (Figs. 7, 8). Glass transition, cold crystallization, and melting were still observed in heating curve 1. A slight increase in  $T_g$  and  $T_m$  was obtained after the deposition of the coatings, however, the differences did not exceed 2 °C even after 72h of deposition. Despite small changes, still, an evident effect of the deposition time on the transition temperatures could be observed. For longer deposition times, the  $T_g$  and  $T_m$  values were slightly higher. Larger differences were observed in the thermal effects of transitions. The deposition of polydopamine and tannic acid coatings increased the values of  $\Delta H_{cc}$  and  $\Delta H_m$  by 4–5 J g<sup>-1</sup>, regardless of the deposition time.

A typical cause of the increase in  $T_g$  is the change in the degree of crystallinity. Higher crystallinity limits the mobility of macromolecules. The mere application of coatings in mild conditions of the deposition process could not increase the degree of crystallinity of the base material, which is confirmed by the calculation of  $X_c$ . The lack of limitation of the mobility of macromolecules due to the increase in the content of the crystalline phase is also confirmed by the same values of the cold crystallization temperature [55]. The increase in  $T_g$  must therefore be due to the already described limitation of heat transfer to the base material after the application of the polydopamine and tannic acid coatings. The same phenomenon must also cause an increase in the value of  $T_m$ .

The observed increase in the intensity of the melting process and  $\Delta H_m$  is only a consequence of the change in the kinetics of the cold crystallization. The entire melting crystalline phase is formed in the process of cold crystallization, which is confirmed by the results of calculations of the degree of crystallinity.

## Conclusions

The study presents the impact of polydopamine and tannic acid coatings on selected properties of polylactide. It was found that the deposition of coatings:

- Increases polylactide resistance to oxidative degradation. The highest increase was observed after 72h of coating deposition. The maximum increase in resistance to oxidation was approx. 20 °C for the

polydopamine coating and approx. 30 °C for the tannic acid coating.

- Increases polylactide resistance to thermal degradation. The greatest increase was observed after 72h of coating deposition, although it was not significantly greater than after 24h of deposition. The obtained maximum increase in resistance to thermal degradation was approx. 14 °C for the polydopamine coating and approx. 6 °C for the tannic acid coating.
- Does not significantly affect the temperature and kinetics of phase transitions of polylactide. Only a slight increase in the glass transition temperature by approx. 2 °C (on heating curve 1) and an increase in the intensity of the cold crystallization process by approx. 5 J g<sup>-1</sup> (on heating curves 1 and 2) were observed, regardless of the type of deposited coating and the deposition time.

**Authors' contributions** Conceptualization: KM; Methodology: KM; Formal analysis and investigation: KM, KS; Writing—original draft preparation: KM, KS; Writing—review and editing: KM; Resources: KM; Supervision: KM.

## Declarations

**Conflict of interest** The authors did not receive support from any organization for the submitted work. The authors have no relevant financial or non-financial interests to disclose.

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