

Effect of surface layer modification method on thermal stability of electroless metallized polylactide

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Abstract: The effect of different methods of surface layer modification on the thermal stability of electroless metallized polylactide (PLA) was investigated. The modification of polylactide was carried out by chemical or plasma methods, using acidic KMnO_4 or alcoholic NaOH solutions. The oxidation induction temperature (*OIT*) and thermogravimetric properties of the metallized samples were determined. The study showed that the surface layer of the modified PLA was only slightly changed when using KMnO_4 solution, which did not significantly influence the thermal stability of the samples. On the other hand, alcoholic NaOH solution clearly etched the surface of the examined samples with consequent deterioration of their thermal stability.

Keywords: polylactide, electroless metallization, thermal stability.

Wpływ metody modyfikowania warstwy wierzchniej na odporność termiczną metalizowanego polilaktydu

Streszczenie: Zbadano wpływ wybranych metod modyfikowania warstwy wierzchniej na odporność termiczną bezprądowo metalizowanego polilaktydu (PLA). Modyfikację prowadzono metodą plazmową lub chemiczną, za pomocą kwasowego roztworu KMnO_4 lub alkoholowego roztworu NaOH . Oznaczano temperaturę indukcji utleniania (*OIT*) i właściwości termogravimetryczne metalizowanych próbek. Stwierdzono, że roztwór KMnO_4 tylko w niewielkim stopniu zmieniał warstwę wierzchnią modyfikowanego PLA, co nie miało dużego wpływu na zmianę odporności termicznej próbek, natomiast alkoholowy roztwór NaOH wyraźnie trawił powierzchnię badanych próbek, a w konsekwencji wpływał na pogorszenie ich odporności termicznej.

Słowa kluczowe: polilaktyd, bezprądowe metalizowanie, odporność termiczna.

The degradation of materials is a universal phenomenon common for all types of processing and applications areas. The universality of this phenomenon makes it the main subject of numerous research projects, both from the point of view of knowledge of aging mechanisms and its effect on the properties of different materials [1, 2].

Increasing demands for polymeric materials, that often are indispensable in the construction of machines, equipment and products of daily use are the reason that research work is focused on the explanation of complex mechanism of aging and degradation processes. Many studies have been carried out to determine aging effect on the physical and chemical properties of materials, as well as to assess the impact of processing conditions on the progress of degradation processes [3–5].

The degradation of polymeric materials is defined as the overall physical and chemical changes occurring in the structure during processing, storage and use. These changes take place due to the prolonged exposure to ex-

ternal factors such as heat, oxygen and ozone or light radiation. Adverse changes can be also caused by moisture, chemicals, active organic material and mechanical stress, resulting in a deterioration of material initial properties. Degradation of polymer material is most often recognized in the first place by changes in the physical appearance, followed by degradation of mechanical properties. A common effect of degradation is change in color, embrittlement, loss of gloss, and surface cracking, which make the polymer product unusable [6].

Thermal degradation occurs when the polymer material changes its properties due to the heat at elevated temperature. Heat treatment of polymers can affect chemical bonds present in the main or side chains of macromolecules or substituent atoms present in macromolecule structure. Most models of thermal degradation describe this phenomenon as a multistage process. The conventional model for thermal degradation assumes autoxidation reaction, which involves such major steps as initiation, propagation, branching, and termination.

Polymeric materials are rarely chemically homogeneous. Usually they contain components such as dyes, fillers or stabilizers as well as contaminants from differ-

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ent stages of material processing. In addition, the surface of polymers is often subjected to gluing, printing, decorating or metallization. Additional components contained in the material or deposited on its surface may react with a polymer at elevated temperature increasing the rate of oxidation and reducing the thermal stability [7].

One of such substances is copper. This element often acts as catalyst of oxidation reaction of polymer materials significantly reducing their thermal stability. Decrease of thermal stability can be also caused by the high thermal conductivity of copper, which results in an improved heat transfer to the interior of the heated polymer. The efficiencies of catalyst and heat transfer processes are related to contact surface area of copper layer and substrate. With the increase of the surface area efficiency of the catalysis process and the amount of transferred heat increases. The effectiveness of copper as a promoter of degradation process depends also on the type of polymer with which it is in contact and location of copper atoms [7–10].

The proper preparation of metallized surface is one of the most important steps in the process of autocatalytic metallization of polymeric materials. This step has a significant impact on the quality of the deposited metal layer. The properties and structure of the deposited copper layer depend on the structure of metallized surface [11]. Metal layers deposited on a non-conductive material in which the catalyst is present are characterized mostly by grain structure. Grains tend to form larger structures with increasing thickness of deposited metal layer. Grain structure is obtained because the catalyst is highly dispersed on the metallized surface. Initially, the metallization takes place on the surface of the catalyst. With increase of metallization time the dimensions of the individual grains increase and form a uniform layer of metal.

In recent years there has been growing interest on polylactide (PLA) also as a polymer for the production of printed circuit boards [12–16]. In recent years, several papers describing metallization process of PLA were published [17, 18]. Those studies involved the use of chemical or plasma methods in the preparation of the surface layer of PLA prior to autocatalytic metallization. The methods used for surface modification successfully enabled the deposition of copper layer on PLA surface. The basic properties of the deposited copper layer, such as adhesive strength and electrical conductivity were investigated. However, no investigations of thermal properties of metallized PLA have been conducted. In particular, the effect of copper on the thermal stability of metallized PLA is not known.

The aim of this study was to determine the effect of modification method on the thermal stability of metallized PLA. Because the process of metallization of this polymer is not fully examined, the obtained results may significantly extend the knowledge regarding this process as well as the knowledge on the properties of deposited copper layer and metallized PLA.

EXPERIMENTAL PART

Materials

Polylactide (PLA) type 2002 D (Cargill Down LLC, USA) with weight average molecular weight of about $155.5 \cdot 10^3$, melting point of 150 °C, containing 3.5 % structural units D and 96.5 % structural units L was used.

All aqueous solutions have been made using distilled water – Aqua purificata (Maggie Co., Poland). In chemical modification, potassium permanganate KMnO_4 pure p.a. (POCH S.A., Poland), nitric acid 65 % HNO_3 pure p.a. (POCH, Poland) with density 1.40 g/cm³, sodium hydroxide NaOH pure p.a. (POCH S.A., Poland) and retail ethanol 96 % (PPS Polmos Warszawa, Poland) were used.

In activation process, pure p.a. palladium(II) chloride PdCl_2 (POCH S.A., Poland) and pure tin(II) chloride SnCl_2 (Chempur, Poland) were used.

In acceleration process, pure p.a. hydrochloric acid HCl 35–38 % (Chempur, Poland) with density 1.19 g/cm³ was utilized.

The metallization process has been conducted in autocatalytic copper plating bath M-Copper 85 (MacDermid, USA) containing pure formaldehyde HCHO 36 % (POCH, Poland) with density 1.09 g/cm³ as a reductor.

Specimen preparation

The specimens for studies were made using injection molding machine Tederic TRX 80 ECO 60 (Tederic Machinery Manufacture Co. Ltd, Taiwan). Temperatures I, II and III of the injection molding machine cylinder zone, head and mold were: 170 °C, 180 °C, 190 °C, 190 °C and 30 °C, respectively.

Sample modification

Chemical modification of PLA surface was performed using two solutions. The first was acidified solution of potassium permanganate (KMnO_4) composed of 0.17 mol/dm³ KMnO_4 and 1.24 mol/dm³ HNO_3 (further referred to as solution 1). Modification with this solution was carried out at room temperature for 40, 50 or 60 minutes. The second solution was composed of 0.25 mol/dm³ sodium hydroxide (NaOH) in water and ethyl alcohol with volume ratio of 1 : 1 (further referred to as solution 2). Modification with this solution was carried out at 50 °C for 1, 5, or 10 minutes. Conditions of modification varied depending on the applied solution and were chosen based on literature data to ensure the best results of modification [19]. Samples were designated as PXY, where X symbol denotes type of the solution (M – solution 1, N – solution 2) and Y denotes time of modification.

Plasma modification was performed using the Femto plasma generator (Diener electronic GmbH, Germany), with nominal plasma power of 100 W. Samples were placed in plasma generator chamber on metal slab and exposed to the effect of a plasma discharge generated in

oxygen under lowered pressure (20 Pa). The samples were modified for 2.5, 10 or 30 minutes with a plasma power of 50 W. Previous studies have shown that the best quality copper layer was deposited on samples modified with that power [17]. Samples were designated as PX, where X symbol denotes time of modification.

Autocatalytic copper plating was carried out through multistep process including activation, rinsing, acceleration, autocatalytic metallization, rinsing, and drying. Surface activation was conducted by a one-step process.

The one-step activation process was conducted by immersing the samples into an aqueous solution containing 0.25 g/dm³ PdCl₂, 12 g/dm³ SnCl₂ and 60 cm³/dm³ 38 % HCl at 25 °C for 5 minutes. The specimens were subsequently immersed into acceleration solution containing 32 cm³/dm³ 38 % HCl at 25 °C for 5 minutes. It was necessary to treat the activated surface with an accelerator in order to selectively remove the stabilizing tin ions, exposing the catalytically active Pd(0). After acceleration processes the samples were rinsed in deionized water to prevent contamination of the plating bath.

The activated samples were consequently immersed in autocatalytic copper plating bath at 46 °C for 5 minutes. The pH value of the bath at a temperature of 46 °C was 12.8. Following the recommendations of the manufacturer, the bath was continuously aerated during the metallization. In the post-treatment stage, the samples were dried in a laboratory oven.

Methods of testing

The images of modified PLA surface were made with Hitachi SU8010 scanning electron microscope (Hitachi High-Technologies Co., Japan), at the accelerating voltage of 2 kV, current from 6 to 10 μA (depending on the type of the sample), with the working distance of 4 mm. Before testing, samples were covered with a gold layer about 3 nm thick.

Oxidation induction temperature (OIT) was determined using Q 500 calorimeter (TA Instruments, USA) as an onset temperature of increase in measured heat flow. Samples were heated from 20 to 250 °C in an oxygen atmosphere with heating rate of 10 °C/min. The OIT values were determined according to ISO 11357-6:2008 standard.

The thermogravimetric (TG) measurements were performed using Q200 thermogravimetric analyzer (TA Instruments, USA) in the nitrogen atmosphere. The TG measurements were carried out according to ISO 11358-1:2014 standard in the temperature range from 25 to 600 °C with heating rate of 10 °C/min. The TG plots were used to determine the temperature of thermal degradation considered as the $T_{5\%}$ temperature corresponding to the 5 % mass loss of the samples and the T_{max} corresponding to a maximum rate of mass change.

RESULTS AND DISCUSSION

The effects of modification and metallization process of selected samples are shown in Fig. 1.

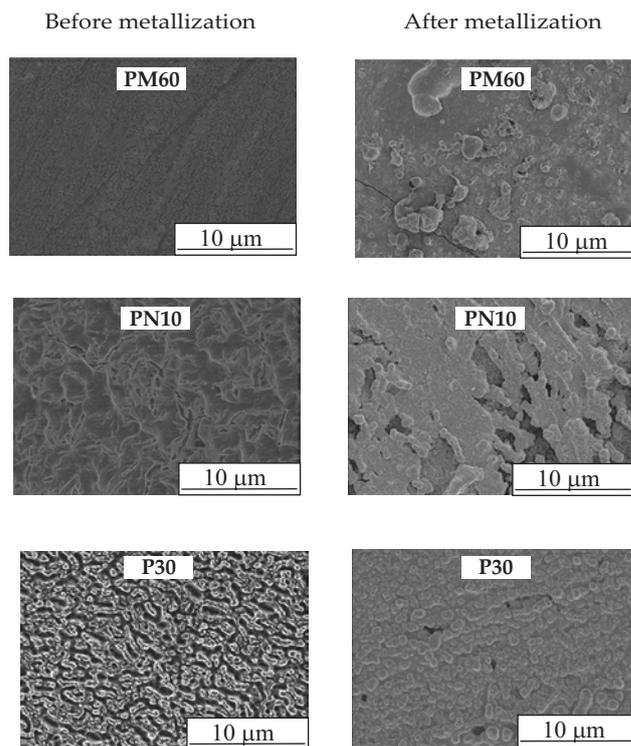


Fig. 1. SEM images of surface of selected modified and metallized samples

Detailed characteristics of the changes caused by modification and metallization of PLA surface layer have been given in [12, 17, 18], therefore only brief description of modification results has been presented. The figure presents SEM images of the surface of the samples modified with the highest applied modification time. The effects of modification and metallization of the samples using a shorter treatment time are similar, but not so intense.

The modification with solution 1 (PM60 samples in Fig. 1) did not result in major changes in the surface structure of modified samples. The main changes caused by modification with solution 1 are associated with an increased content of oxygen atoms in the surface layer of the polymer.

Surface changes caused by chemical modification with solution 2 (PN10 samples in Fig. 1) resulted from hydrolytic degradation. PLA is aliphatic polyester whose ester bonds undergo hydrolytic degradation in the presence of water. The rate of degradation process depends, however, on the pH value of solution. In case of solution 2 hydrolytic degradation is catalyzed by hydroxyl ions derived from NaOH. A high concentration of hydroxide ions significantly accelerates the process of hydrolytic degradation of PLA. During the hydrolytic degradation water-soluble, low molecular weight oligomers and monomers are formed, and then washed away leaving fractures and grooves in the polymer surface layer.

Changes in the surface structure of PLA modified with plasma (P30 samples in Fig. 1) are caused by plasma etching. Initially, at short modification times, degradation products form on PLA surface. When the treatment time

Table 1. Results of oxidation induction temperature (*OIT*) and thermogravimetric analyses of neat and metallized polylactide samples

Modification level	Sample	<i>OIT</i> , °C		$T_{5\%}$, °C		T_{max} , °C	
		Before metallization	After metallization	Before metallization	After metallization	Before metallization	After metallization
0	PLA	224.7	–	321.1	–	361.7	–
1	PM40	223.9	221.8	323.5	311.8	360.5	351.5
2	PM50	224.8	221.5	320.6	305.0	360.9	349.2
3	PM60	224.3	218.8	321.8	301.0	360.3	349.8
1	PN1	224.0	219.3	322.2	297.9	362.3	348.8
2	PN5	224.5	215.5	321.7	297.4	361.9	347.2
3	PN10	224.6	213.9	319.9	293.9	361.1	345.1
1	P2.5	224.9	220.9	321.4	301.4	361.8	350.3
2	P10	223.6	220.2	321.9	296.6	362.2	348.3
3	P30	224.4	216.7	322.8	294.1	362.1	347.5

increases, more degradation products form and merge into large drops with irregular edges. After the maximum modification time (P30 sample), the degradation products are completely removed and a rough surface of PLA is exposed.

Copper layers obtained after PLA metallization had a characteristic, grain structure typical for metallized non-conductive materials. The best results of metallization process were obtained for samples chemically modified with solution 2 [17, 18]. However, depending on the modification method, the structure of deposited copper layer was different. It can be seen that the structure of that layer is similar to the underlying modified polymer surface.

To determine the effect of modification method, and thereby the effect of structure of deposited copper layer,

on the process of PLA thermal degradation, an *OIT* and TG tests were conducted. The DSC thermogram of *OIT* determination and TG curves of neat PLA and PN10 sample are shown in Fig. 2.

Test results for individual samples together with assigned values of modification level are shown in Table 1.

To check if the modification process itself does not influence the thermal stability of PLA, the *OIT* and TG studies were also conducted for modified but non metallized samples. The obtained results indicated that modification processes did not change significantly *OIT*, $T_{5\%}$ and T_{max} values compared to neat PLA. It can be therefore stated that all changes in studied parameters of metallized samples are the effect of copper deposition and the influence of that element on the thermal stability of PLA. Since the modification process did not affect the values of *OIT*, $T_{5\%}$ and T_{max} , all results of further investigations have been compared to neat PLA. A single reference point allowed easier interpretation and comparison of obtained data.

In case of all metallized samples, deposition of copper layer reduced the *OIT* values. The lowest values were obtained for samples with the highest level of modification. However, depending on the method of surface layer modification, the individual curves had different characteristics (Fig. 3).

The lowest decrease in the values of *OIT* has been observed for the samples chemically modified with solution 1. The *OIT* decreased from 224.7 °C (PLA) to 218.8 °C (PM60 sample). Very similar decrease in *OIT* values has been observed for plasma modified samples. However, *OIT* value at each modification level was lower than that determined for the samples modified with solution 1. The largest decrease in the *OIT* has been observed for the samples modified with solution 2. As the level of modification increased a significant decrease of *OIT* value was found. The total decrease of *OIT* values after modification with solution 1, plasma and solution 2 was 5.9 °C

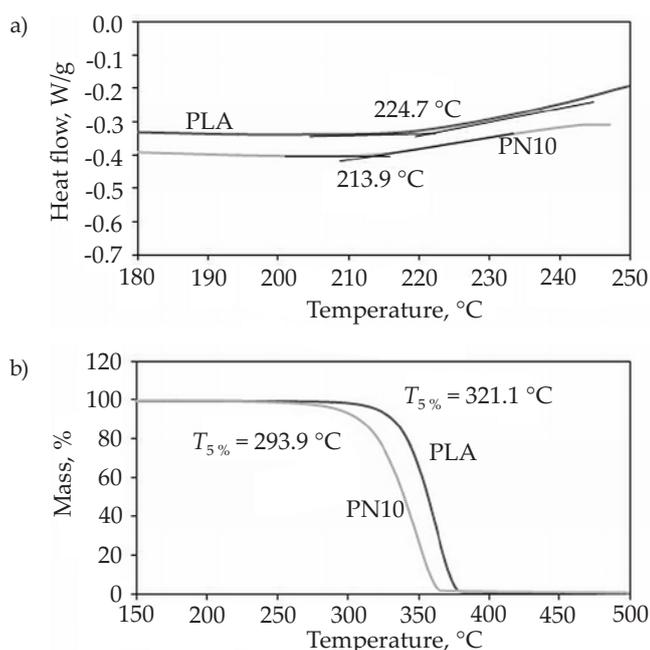


Fig. 2. a) DSC thermogram for *OIT* determination, b) thermogravimetric curves of polylactide (PLA) and PN10 samples

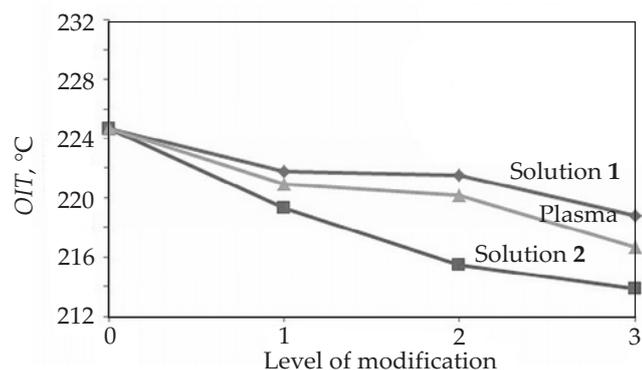


Fig. 3. Influence of level of modification on oxidation induction temperature (OIT) of metallized polylactide samples (solution 1 – 0.17 mol/dm³ KMnO₄, solution 2 – 0.25 mol/dm³ NaOH)

(PM60 sample), 8.0 °C (P30 sample) and 10.8 °C (PN10 sample), respectively.

The deposition of copper layer on the surface of PLA resulted in a reduction of $T_{5\%}$. The lowest $T_{5\%}$ values were obtained for samples with the highest level of modification (Fig. 4).

As in the case of OIT studies, the smallest decrease in $T_{5\%}$ values has been observed for the samples chemically modified with solution 1. The $T_{5\%}$ decreased with increasing level of modification. The $T_{5\%}$ value decreased from 321.1 °C (PLA sample) to 301.0 °C (PM60 sample). A much larger reduction has been observed for the samples chemically modified with solution 2 or plasma. In addition, the changes in $T_{5\%}$ for the samples modified by those methods were very similar. In both cases, after the first level of modification a large decrease in $T_{5\%}$ occurred. However, the $T_{5\%}$ value was slightly lower for the samples modified with solution 2. Further increase in the level of modification did not cause a significant reduction in $T_{5\%}$. The values after maximum modification level were also similar regardless of the used modification method. The lowest values observed in both cases were 294.1 °C for plasma (P30) and 293.9 °C for solution 2

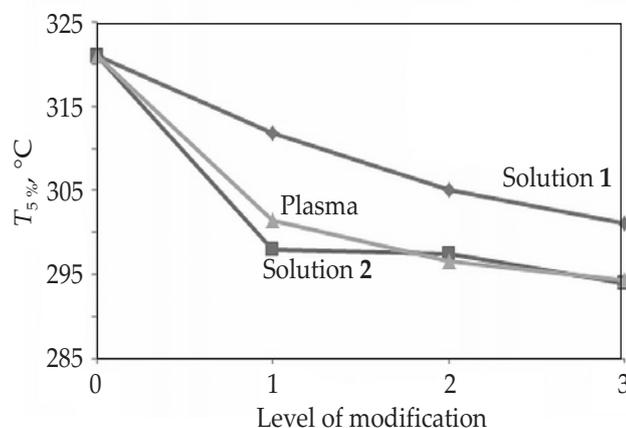


Fig. 4. Influence of level of modification on temperature corresponding to the 5% mass loss ($T_{5\%}$) of metallized polylactide samples (solution 1 – 0.17 mol/dm³ KMnO₄, solution 2 – 0.25 mol/dm³ NaOH)

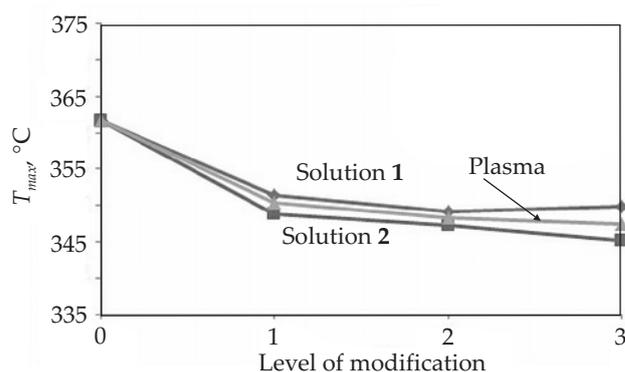


Fig. 5. Influence of level of modification on temperature corresponding to a maximum rate of mass change (T_{max}) of metallized polylactide samples (solution 1 – 0.17 mol/dm³ KMnO₄, solution 2 – 0.25 mol/dm³ NaOH)

(PN10). The total decrease in $T_{5\%}$ value after modification with solution 1, plasma and solution 2 was 20.1, 27.2 and 27.0 °C, respectively.

The method of surface modification had no effect on the curve characteristic of T_{max} changes of metallized PLA samples (Fig. 5).

Regardless of the modification method, initially a significant decrease in the value of T_{max} has been observed. After the first level of modification the obtained results were similar. Further modification did not result in a significant reduction of T_{max} values. The results obtained after the second level of modification were also similar regardless of the modification method. Only after the third level of modification bigger differences in the obtained results have been observed. The highest T_{max} value of 349.8 °C was determined for the sample chemically modified with solution 1 (PM60). The lowest value of 345.1 °C was obtained for the sample chemically modified with solution 2 (PN10).

Clearly, the presence of copper layer lowers the thermal stability of metallized PLA compared to the neat polymer. Analyzing SEM images of the surface of modified samples and the surface of samples after the metallization process it may be noted that the rate of thermal stability reduction depends on the structure of the modified surface and the structure of the deposited copper layer.

The modification process with solution 1 had the lowest impact on the thermal stability of metallized PLA. The surface structure of this sample after modification has undergone the smallest changes in comparison with the unmodified sample. Atomic force microscopy studies presented in [18] showed only a slight increase in surface roughness from 0.7 nm for the sample of unmodified PLA to 4.3 nm for the sample PM60. Additionally, visual assessment of the copper layer after the metallization process and the analysis of SEM images of metallized surface showed that deposited copper layer had the worst quality. It can thus be concluded that among all used modification methods, the contact area of copper layer and the substrate was the lowest, resulting in the smallest decrease of thermal stability of metallized PLA.

The mid decrease in thermal resistance among tested samples has been observed in case of plasma modification. The surface structure after modification has undergone a much larger changes than in the case of samples modified with solution 1 [17]. The surface roughness after the modification process has increased to 45.8 nm for the P30 sample. The increase in surface roughness caused an increase in contact surface area of copper layer and substrate, resulting in a larger decrease in thermal stability than for the samples modified with solution 1.

The largest reduction in thermal stability has been observed in the case of samples modified chemically with solution 2. This modification resulted in the biggest changes of the PLA surface structure [18]. A significant increase in the roughness up to 700 nm for the sample PN10 has been observed. The large increase of surface roughness caused a large increase in contact surface area with deposited copper layer and substrate. The deposited copper layer had the best quality among all the samples modified with utilized methods. Visual assessment of the quality of metallized samples showed that the copper layer was deposited on the entire metallized surface, while the analysis of SEM images showed that the layer was uniform and thick. In addition, numerous cavities penetrating into the bulk of the sample have been formed after modification. The deposited copper layer filled those cavities, enabling better and more efficient heat transfer to the inner layers of the polymer. The described effects of modification and metallization consequently caused the greatest decrease in thermal stability of the samples modified chemically with solution 2.

CONCLUSIONS

The study showed that the deposition of copper layer lowers the thermal stability of polylactide. However, the rate of decrease in thermal stability depends on the method of surface layer modification prior to metallization process.

The relation between the increase in surface roughness after modification and decrease in thermal stability of metallized polylactide can be observed. The increment in surface roughness increases the contact surface area of copper layer and substrate, increasing the negative effect of copper on the thermal stability of polylactide. This relationship has been confirmed by obtained results.

The lowest reduction of thermal stability was observed for the samples modified with acidified solution of potassium permanganate (KMnO_4) (solution 1), where the structure of the surface after the modification process underwent the smallest changes. The increase of surface roughness after the modification process was not significant, and therefore the contact surface area of the copper layer and substrate was the smallest among the tested samples. This resulted in the smallest decreases in the values of the oxidation induction temperature and temperature corresponding to 5 % mass loss.

The largest decrease in thermal stability has been observed for the samples modified with aqueous-alcoholic solution of sodium hydroxide (NaOH), where the structure of the surface layer after modification process has undergone significant changes and the deposited copper layer had the best quality. The modification caused a very large increase in a surface roughness. The complex structures formed after modification and metallization yield a large surface area of contact of copper layer and substrate, enabling better and more efficient heat transfer to the inner layers of the polymer. This increases the negative effect of copper, causing a large decrease in thermal stability of polylactide.

Despite the fact that there is a lot of papers in the literature about the metallization of polymeric materials, there is little information on the autocatalytic metallization of polylactide and no information about the properties of deposited copper layer on that polymer. This fact was the ground for undertaking research presented in the article. The study allowed a closer examination of the effect of copper layer on the thermal stability of polylactide. It was also important to examine the effect of the modification method and parameters of that process on that characteristic. Knowledge gained in this way will have a novel character, because in case of PLA these phenomena are rarely studied or unstudied at all.

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