

Influence of active compounds on the degradation of polylactide biocomposites

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Abstract: Biodegradable materials, which exhibit biocidal activity against microorganisms due to application of natural vegetable compounds, are presented. The effect of polylactide (PLA) modification, carried out by using bioactive compounds as mixtures form such as: carvacrol and eugenol, thymol and eugenol, thymol and carvacrol, on the thermal properties and biodegradation rate of this material was determined. The following sample features were determined: mass loss in time, thermal properties with the use of a differential scanning calorimeter (DSC) and thermogravimetry (TG) instrument, and morphology by the use of a scanning electron microscope (SEM). The use of active compounds in mixtures gives a synergistic effect. The natural vegetable compounds exhibit biocidal and fungicidal activities and, at the same time, no negative effect on the physicochemical properties of the prepared products and do not affect negatively the degradation rate of these products.

Keywords: polylactide, carvacrol, eugenol, thymol, active packaging, degradation.

Wpływ dodatku związków aktywnych na degradację biokompozytów polilaktydowych

Streszczenie: Przedstawiono biodegradowalny materiał, który dzięki zawartości naturalnych związków roślinnych wykazuje działanie biobójcze w odniesieniu do mikroorganizmów. Określono wpływ modyfikacji polilaktydu (PLA) związkami aktywnymi w postaci mieszanin, takich jak: karwakrol i eugenol, tymol i eugenol, tymol i karwakrol, na właściwości cieplne i szybkość biodegradacji tego materiału. Właściwości termiczne biokompozytu PLA określano metodą różnicowej kalorymetrii skaningowej (DSC) i termogravimetrii (TG), morfologię próbek zbadano za pomocą skaningowego mikroskopu elektronowego (SEM). Stwierdzono, że zastosowanie substancji czynnych w postaci mieszanin daje efekt synergiczny. Naturalne związki roślinne wykazują działanie biobójcze i grzybobójcze, a jednocześnie nie mają negatywnego wpływu na właściwości fizykochemiczne otrzymanych wytworów oraz nie wpływają negatywnie na szybkość ich degradacji.

Słowa kluczowe: polilaktyd, karwakrol, eugenol, tymol, aktywne opakowanie, degradacja.

Biodegradable materials are widely recognized as polymers of the future, first of all because they are the materials that undergo rapid biodegradation. Due to their biocompatibility and biodegradability, these polymers are being applied mostly in medicine. Nowadays, they begin to be used wider and wider in the packaging industry. At the same time, consumption of the plastic packaging radically increases. Therefore, it is vital to elaborate as soon as possible technical conditions for manufacture of packaging from biodegradable materials because of not only ecological issues but also because they are materials produced from natural raw materials that are valuable substitutes of mineral resources.

From among those materials, polylactide (PLA) is the polymer being the object of the most advanced scientific and technological studies. Production of PLA covers *ca.* 40 % of all the biodegradable polymers being manufactured.

Because packaging made of the biodegradable materials and meant for food, drugs, or medical instruments should be sterilized, compounds exhibiting biocidal activity are in the field of interest as additives to a polymeric matrix or deposited on a polymer surface as a coating [1–4]. In the field of food packaging, the increasing demand by consumers for safe, high quality, minimally processed and extended shelf life foods has been one of the main driving forces for innovation [5]. Active packaging (AP) technologies are being developed several years ago and involves the chemical interactions between package and packaged food or headspace atmosphere by the incorporation of certain additives into packaging film or within packaging containers [6]. Some examples of active packaging include

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oxygen and ethylene scavengers, antimicrobial and antioxidant films headspace atmosphere [7–11].

Manufacturing this food packages with antimicrobial (AM) capacity has to consider the release kinetics of the involved active compounds. Different applications of antimicrobial materials require different release rates of the antibacterial additive into the surrounding medium. In disposable medical devices or in some kinds of food packaging a fast release during a short time is suitable, whereas a slower release times can be convenient in other applications. In any case, the design of a suitable antibacterial plastic material requires a quantitative description of the release rate of active compound under different conditions [12–14].

The effectiveness of antimicrobial films can be partially determined by the release rate of the biocidal compounds (bioactive compounds). In recent years, the research interest has been oriented more towards on the use of efficient, eco-friendly and low-cost natural biocidal agents. Essential oils and their active compounds (for example thymol, carvacrol, *etc.*) have already been used as food additives, in food packaging or cosmetic industry [15]. In particular, thymol and carvacrol are present as major compounds in thyme and oregano essential oils and have received considerable attention because of its antimicrobial activity and antioxidant capacity [16]. Carvacrol shows antifungal, insecticidal, antitoxigenic and antiparasitic activities [17]. On the other hand, thymol has received considerable attention as an antimicrobial agent showing very high antifungal activity, being also an excellent food antioxidant [18, 19].

The popular and available in the market are packaging that use volatile gas form of biocidal agents such as ethylene, chlorine dioxide, ethanol, and sulfur dioxide. These biocidal agents are often enclosed separately in sachets that are attached to the internal part of the package. The AM agents will release in vapor form to the headspace of packaging to contact with food products [20]. Sometimes food packaging have biocidal agents in stickers or sheets form containing sodium chlorite and acid precursors [21].

The packaging for medical instruments and food is being sterilized by using the gamma radiation, plasma or by disinfection methods utilizing chemical agents. The polymeric materials are often not resistant against these factors and chemical agents being used may cause changes in properties and durability of the polymers. Moreover, remains of the disinfection agents being left on surfaces of devices used in the medicine (*e.g.*, medical instruments) or in the packaging industry essentially influence human health while the gamma irradiation is a technique that requires significant expenditure of money and time [22–25].

Therefore, it is justified to modify the biodegradable polymers with the natural vegetable compounds that exhibit biocidal and fungicidal activities and, at the same time, no negative effect on the physicochemical properties of the prepared products. Such agents have been used for ages in natural medicine. Thus, it is known that

when applied to sterilization of packaging for food and drugs or in medicine, these compounds will not affect negatively the consumer health.

There are different methods manufacturing biocidal films materials and the choice often depends on the biocidal agents properties and parameters processability of the polymeric material. The most commonly used processes consider the inclusion of the active additive into polymer matrices by melting extrusion [26] and coating process [27, 28]. The selection of the incorporation method of the active compound can be determined by its thermostability as well as its action mechanism such as diffusion or volatility [26]. One of the main drawbacks in the preparation of active materials with essential oils by traditional methods is related to the volatilization or degradation of the active components.

EXPERIMENTAL PART

Materials

Poly lactide (PLA) 2003 D (D-repeat units: 3.5 %, L-repeat units: 96.5 %) was provided by Cargill Down LLC, with the melt flow index of 4.2 g/10 min (2.16 kg, 190 °C), density $d = 1.24 \text{ g/cm}^3$ and molecular weight $M_w = 155.5 \text{ kDa}$.

Thymol ($\geq 99 \%$), carvacrol ($\geq 99 \%$) and eugenol ($\geq 99 \%$) were purchased by Sigma Aldrich (Poland). Particular samples were prepared by adding equal amounts (0.75 wt %) of (i) carvacrol (C) and eugenol (E), (ii) thymol (T) and eugenol, and (iii) thymol and carvacrol. Prepared samples were of molecular weight about 157 kDa.

Proteinase K ($\geq 30 \text{ units/mg}$) from *Tritirachium album* (Blirt, Poland), the reagents buffer 0.1 M Tris-HCl and sodium azide (NaN_3) were used in order to study enzymatic degradation.

Samples preparation

Granulated samples of the PLA containing biocidal agents were obtained using a single-screw extruder type Plasti-Corder (Brabender, Germany), equipped with screw of 20 mm diameter and L/D ratio of 25. The biocidal agents were dropped into zone I that resulted in a concentration of 1.5 % (w/w) with respect to PLA. The zone beneath the extruder hopper was cooled by blowing air. The temperatures of barrel heating zones I, II, and III and of the die head of the extruder were 180, 190, 200, and 200 °C, respectively. The screw rotational speed was constant (100 rpm). Subsequently, in order to produce specimens in the form of thin films, granules of the prepared blends were placed in a special compressing holder, attached to the dynamic mechanical analyzer (DMA). The samples were compressed at 160 °C under the pressure of 15 N, cut into pieces or strips of films. The specimens are denoted as follows: PLA, PLA+C+E, PLA+T+E, and PLA+T+C, PLA indicating non-modified polylactide, C – carvacrol, E – eugenol, and T – thymol.

Specimens were prepared as described also in [29, 30].

Methods of testing

Thermal properties

Measurements of glass transition temperatures and changes in the enthalpies of cold crystallization and melting were determined using a differential scanning calorimeter DSC type Q200 (TA Instruments, USA). The samples weighing from 6.7 to 7.4 mg were tested within the temperature range of 10–180 °C. All experiments were carried out under a purge of dry nitrogen. The glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m), melting enthalpy (ΔH_m) and cold crystallization enthalpy (ΔH_{cc}) were obtained from the DSC thermograms. DSC curves were recorded at three stages: first heating (10 °C/min), cooling (10 °C/min), and second heating (10 °C/min). In order to eliminate the thermal history of the samples, resulting from different times of incubation, the measurement results were analyzed based on the data from the second heating.

The thermogravimetric analyses (TG) were carried out in the atmosphere of nitrogen using thermogravimetric analyzer type Q500 (TA Instruments, USA). Specimens weighing 3–4 mg were examined within the temperature range of 0–600 °C at a heating rate of 10 °C/min.

Enzymatic degradation

Biocomposites were cut into strips of films weighing from 15 to 17 mg, and placed in test tubes with the reaction mixtures containing 2 mg of the enzyme proteinase K, 10 cm³ of 0.1 M Tris-HCl buffer, and 2 mg of sodium azide. Finally, the test tubes containing the investigated specimens were placed in an microbiological incubator type ILW 240 STD (Pol-Eko, Poland). Enzymatic degradation took place at the constant temperature of 37 °C.

The first measurements of mass loss were carried out after 48 hours, then after 5 and 7 days, and subsequently at weekly intervals for 2 to 7 weeks of incubation. After a specified time, the samples were withdrawn from the reaction mixture, washed in distilled water, and dried in a moisture analyzer MAX 60/NH (Radwag, Poland) to a constant weight. This enabled to determine the mass loss of each specimen. The loss of mass was calculated using the formula Eq. (1):

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

where: m_s – the initial mass [mg] of a specimen, m_f – the mass [mg] of the specimen after the specified period of incubation.

Scanning electron microscopy

Images reflecting changes in the geometric structure of the surface of the specimens were recorded by using

a scanning electron microscope (SEM) SU8010 Hitachi (Hitachi High-Technologies Co., Japan).

RESULTS AND DISCUSSIONS

The DSC curves for the studied samples are shown in Fig. 1 [31]. The data determined for the samples with and without modification using biocidal agents are summarized in Table 1.

Analysis of the curves corresponding to the second heating run indicates that addition of the biocidal agents to PLA causes reduction in T_g of the material from 60.9 °C for the non-modified PLA to 34.4–51.1 °C for the particular modified samples. A clear reduction of T_g values emphasizes the plasticizing effect of the active compounds in these samples. This behavior was more evident in the case of the PLA+T+E and PLA+C+E samples, showing the lowest values of T_g if compared with PLA+T+C (Table 1), underlining the synergic effect of carvacrol, thymol and eugenol on the thermal parameters of these multifunctional systems. Carvacrol, eugenol and thymol could act as plasticizer agents, increasing the chain mobility of the macromolecules in the PLA modified active compounds.

The temperature corresponding to the maximum of the cold crystallization peak decreases from 127.1 °C for the non-modified PLA to 117.1 °C for the PLA modified with the biocidal agents (T+E). The temperature corresponding to the maximum of the melting peak was *ca.* 149.5 °C for the non-modified PLA. Instead, T_m for the samples of PLA modified with the biocidal agents (T+E) clearly decreases,

Table 1. Thermal properties of the studied samples, derived from relevant DSC curves (for meaning of the symbols, see text)

Sample	T_g °C	T_{cc} °C	T_m °C	ΔH_{cc} J/g	ΔH_m J/g
PLA	60.9	127.1	149.5	4.90	5.04
PLA+C+E	45.5	127.6	148.1	0.50	0.06
PLA+T+E	34.4	117.1	141.8	1.40	0.30
PLA+T+C	51.1	127.2	140.5	0.01	0.02

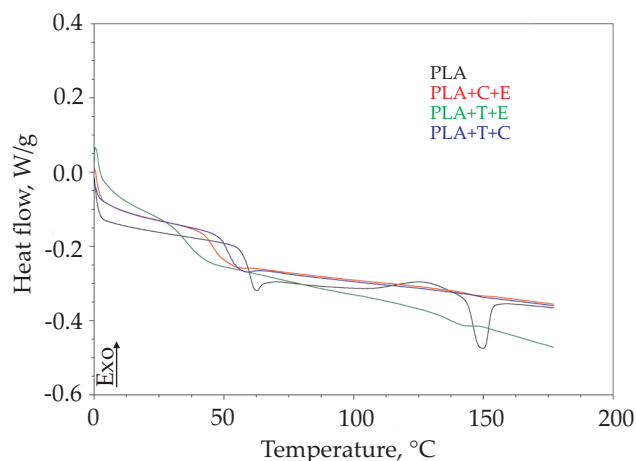


Fig. 1. DSC curves for samples non-modified and modified with biocidal agents

Table 2. Temperatures of decomposition (T_d) and temperatures ($T_{5\%}$, $T_{10\%}$, and $T_{95\%}$) corresponding to mass losses of 5, 10, and 95 %, derived from TG and DTG curves

Sample	T_d °C	$T_{d/dt}$ °C	$T_{5\%}$ °C	$T_{10\%}$ °C	$T_{95\%}$ °C
PLA	315.6	335.9	306.9	334.4	358.8
PLA+C+E	329.9	346.7	315.7	346.8	365.5
PLA+T+E	332.2	354.4	309.5	349.7	369.8
PLA+T+C	335.3	355.0	274.0	350.9	370.2

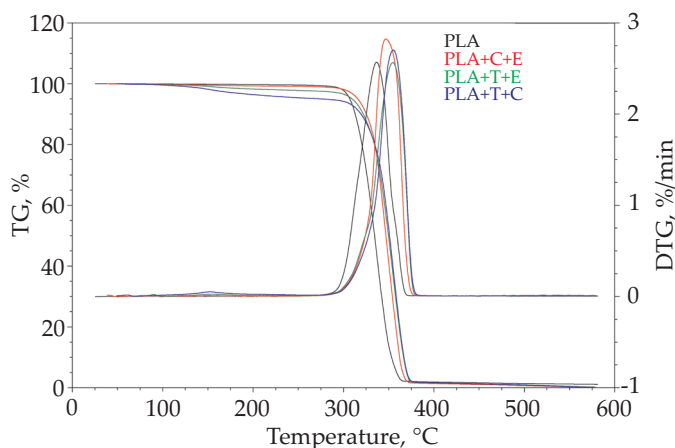


Fig. 2. TG curves for sample non-modified and modified with biocidal agents

mostly to 141.8 °C Thermal decomposition of polylactide modified with the biocidal agents is illustrated in Fig. 2 [31]. Temperatures of decomposition (T_d) and temperatures to mass losses of 5, 10, and 95 %, derived from TG and DTG curves are summarized in Table 2.

Table 3. Rates of degradation of the studied samples during 7 weeks

Sample	Δm , %
PLA	19.1
PLA+C+E	37.8
PLA+T+E	31.0
PLA+T+C	15.9

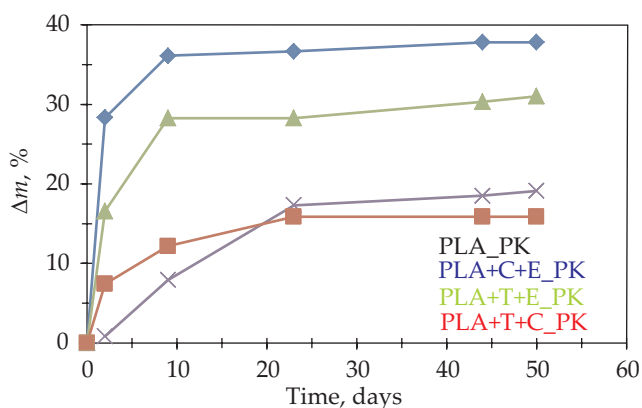


Fig. 3. Effect of proteinase K on degradation rate of the studied samples

In samples with biocidal agents two steps of thermal degradation can be identified. Samples (mainly PLA+T+C and PLA+T+E) showed a first degradation step at low temperatures (about 120 °C) and a second step corresponding to the thermal degradation of the polymer matrix.

Modification of polylactide by using the biocidal agents results in an increase in T_d from 315.6 °C (sample PLA) to 335.3 °C (sample PLA+T+C). A considerable rise in the degradation temperature due to modification of the samples is presumably caused by the fact that the biocidal agents increase durability of the antimicrobial products, which leads to the rise in the temperature at which thermal decomposition starts.

The effect of proteinase K on the mass loss of the studied specimens is presented in Fig. 3 and Table 3.

The extent and rate of the degradation of the studied samples depend on the kind of extracellular enzymes produced by microorganisms. The enzymes, being macromolecular substances, do not penetrate inside a material but they effectively cause decomposition of polymeric chains located on the material surface. Fragments of the material are absorbed by the microorganisms and undergo further degradation due to metabolic processes. It is accepted that aliphatic polyesters undergo the enzymatic degradation mainly by hydrolysis in which proteases, esterases, lipases, and cutinases are involved. Because of the mechanism of their action, these enzymes are considered as serine hydrolases, containing an active site in the form of a catalytic triad (Ser-His-Asp). Proteases (mainly serine ones) and esterases are the enzymes that are involved in the degradation of PLA [32].

The largest mass losses resulting from action of all the applied enzymes occur in the case of the samples containing carvacrol and eugenol as well as thymol and eugenol while the least mass losses appear in the case of the sample including thymol and carvacrol.

When comparing the extents of degradation of the non-modified PLA and PLA modified with the biocidal agents, one can notice that the use of mixtures of carvacrol and eugenol (C+E) as well as thymol and eugenol (T+E) as modifiers causes increase of the sample mass loss. The rate of the sample degradation occurs for proteinase K in the case of which the mass loss of the PLA+C+E sample varied from 28.3 % (after 2 days) to 37.8 % (after 7 weeks) and of the PLA+T+E sample, from 16.6 % (after 2 days) to 31.0 % (after 7 weeks). The mass loss of the non-modified PLA varied from 0.8 % (after 2 days) to 19.1 % (after 7 weeks).

Differences in the extents and rates of the sample degradation are associated with properties of the used enzymes, *i.e.*, their activity, durability, and structure. As can be expected, the higher the enzyme activity, the larger the rate and extent of the degradation. Proteinase K is the serine proteinase exhibiting a wide range of action and usually it shows the largest effect on the sample degradation. This high degree of degradation resulted from the fact that this enzyme, produced by *Tritirachium album*,

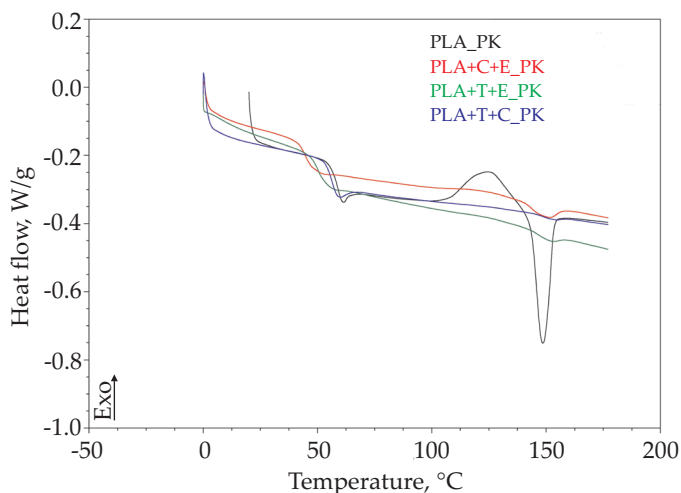


Fig. 4. DSC curves for degraded samples

Table 4. Thermal properties of the degraded samples, derived from relevant DSC curves

Sample	T_g °C	T_{cc} °C	T_m °C	ΔH_{cc} J/g	ΔH_m J/g
PLA_PK	59.0	125.2	148.5	17.60	18.36
PLA+C+E_PK	44.7	122.6	150.9	2.81	1.82
PLA+T+E_PK	56.5	127.8	154.1	0.96	0.29
PLA+T+C_PK	50.2	125.3	152.0	1.64	0.86

hydrolyses the amorphous phase of PLA faster than the crystalline phase. This process occurs by detachment of lactic acid units from chain ends as well as by chain scission that results in formation of oligomers. The larger content of L-lactic acid in the polymeric macromolecule is beneficial from the viewpoint of the PLA biodegradation [33–37].

The DSC curves for the degraded samples are shown in Fig. 4 [31]. The data determined for the samples are summarized in Table 4. The specimens are denoted as follows: PLA_PK, PLA+C+E_PK, PLA+T+E_PK, and PLA+T+C_PK; PK means proteinase K.

The degradation leads to the increase in the melting enthalpy of the PLA samples both non-modified and modified with the biocidal agents. In the case of the non-modified PLA, the ΔH_m value varies analogously as the mass loss does, *i.e.*, the melting enthalpy is the largest for the sample degraded upon proteinase K, for which the mass loss was also the largest one. The samples subjected to the degradation in the presence of proteinase K exhibit greater ability to crystallization since this enzyme when adsorbed on the PLA surface causes decomposition of the polymeric macromolecules to the greater extent as compared to the remaining enzymes. The resulting fragments of shorter chains are of greater mobility and can easier crystallize.

In the case of PLA modified with the biocidal agents, sample PLA+C+E_PK exhibits on the average the largest values of ΔH_m . The ΔH_m values successively decrease for samples PLA+T+E_PK and PLA+T+C_PK.

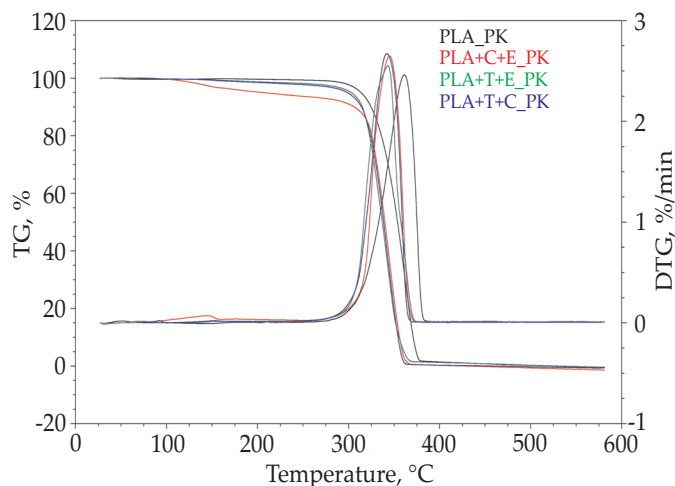


Fig. 5. TG curves for degraded samples

Table 5. Temperatures of decomposition (T_d) and temperatures ($T_{5\%}$, $T_{10\%}$, and $T_{95\%}$) corresponding to mass losses of 5, 10, and 95 %, derived from TG and DTG curves

Sample	T_d °C	$T_{d/dt}$ °C	$T_{5\%}$ °C	$T_{10\%}$ °C	$T_{95\%}$ °C
PLA_PK	334.4	361.0	313.6	353.9	374.2
PLA+C+E_PK	325.2	345.2	204.3	340.0	359.0
PLA+T+E_PK	319.8	343.8	302.9	337.0	360.8
PLA+T+C_PK	321.9	342.4	298.6	338.5	357.2

Thermal decomposition of the degraded samples is illustrated in Fig. 5 [31]. Temperatures of decomposition (T_d) and temperatures to mass losses of 5, 10, and 95 %, derived from TG and DTG curves are summarized in Table 5.

When considering the relevant results for the modified samples subjected to the enzymatic degradation, one can notice that T_d decreases in relation to the non-degraded modified samples. The samples degraded in the presence of proteinase K show the largest reduction in T_d . As indicated above, the same samples exhibited also the largest mass loss.

Images of the PLA surface, recorded by using a SEM, are shown in Figs. 6 and 7. The examined samples were subjected to the degradation in proteinase K for 7 weeks.

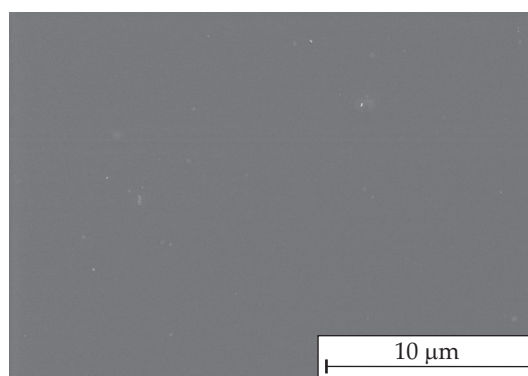


Fig. 6. SEM image of PLA sample

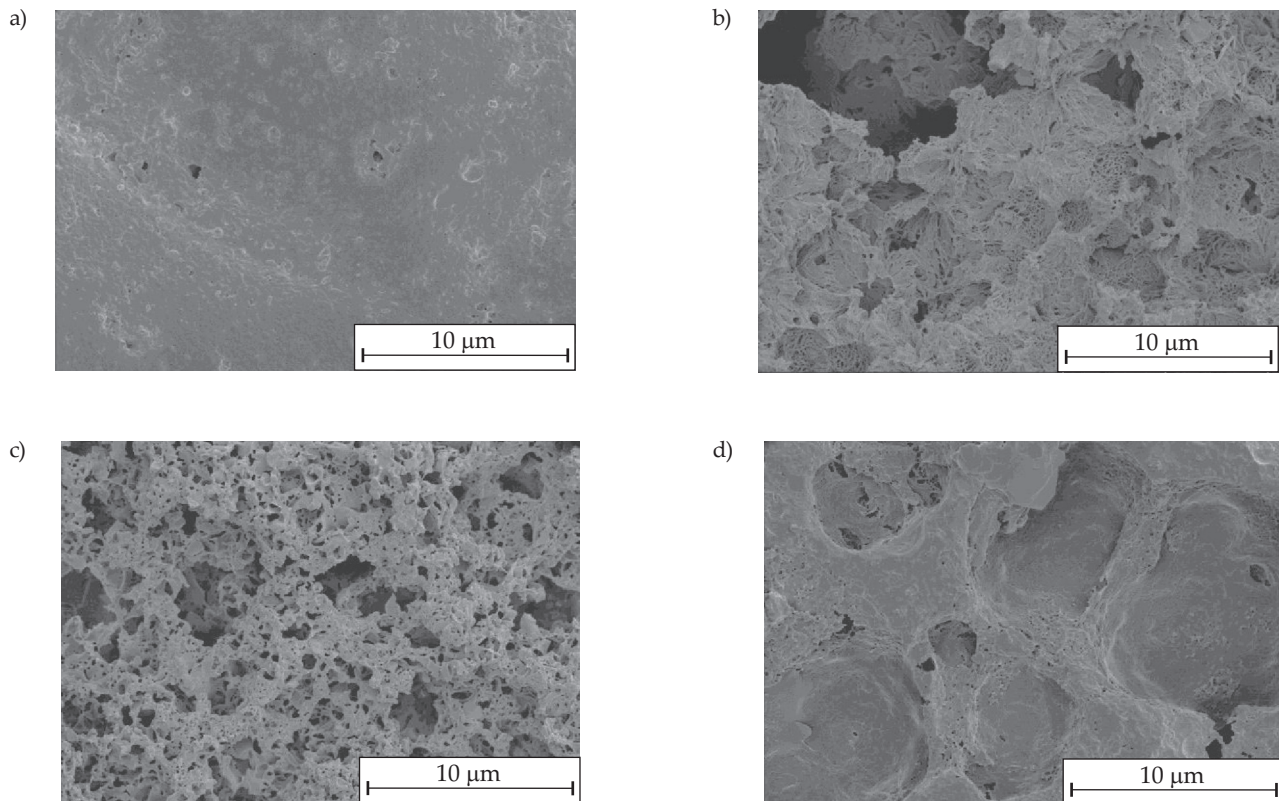


Fig. 7. SEM images of PLA samples subjected to degradation in proteinase K for 7 weeks: a) PLA_PK, b) PLA+C+E_PK, c) PLA+T+E_PK, d) PLA+T+C_PK

The largest changes in the sample surface were found for PLA modified with carvacrol and eugenol and somewhat smaller ones, for PLA modified with thymol and eugenol. The least changes occurred in the non-modified polylactide (PLA without biocidal agents) and somewhat larger ones, in PLA modified with thymol and carvacrol.

CONCLUSIONS

Determination of the effect of modification of the biodegradable materials with the biocidal agents on the degradation rate are the issues being in demand because they may be considered as a basis for development of novel methods for management of post-consumer waste. They contribute to quest for (i) new natural biocidal agents that do not affect negatively the degradation rate of antimicrobial products and (ii) enzymes exhibiting high affinity to biocomposites and causing noticeable degradation of them in a relatively short time.

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opracował ogólnokrajową

BAZĘ APARATURY DO OKREŚLANIA CHARAKTERYSTYKI I PRZETWÓRSTWA POLIMERÓW

będącej w posiadaniu uczelni, instytutów PAN i instytutów badawczych.

Baza jest wyposażona w funkcje umożliwiające wyszukiwanie wg zadanych parametrów: nazwy, typu lub modelu aparatu, roku produkcji, producenta, charakterystyki parametrów technicznych, zastosowania do badań, lokalizacji, słów kluczowych, sposobu wykonywania badań, numerów norm, wg których prowadzi się badania, oraz adresu i kontaktu z osobą odpowiedzialną za dany aparat.

Baza jest ciągle uaktualniana.

Dostęp do danych i wyszukiwanie informacji w bazie jest bezpłatne.

Instytucje i firmy zainteresowane zamieszczeniem w bazie informacji o posiadanej aparaturze prosimy o przesłanie danych na adres polimery@ichp.pl

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