DOI: 10.7251/JEPMEN1507027P
UDK:678.7:543.57
Scientific paper

THERMAL AGING STUDY OF BIODEGRADABLE POLYMER MATERIALS BY DIELECTRIC THERMAL ANALYSIS

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Abstract

Two different studies of the thermal aging of polyesters based on lactic and glycolic acids were compared. Thermal degradation of poly(L-lactic acid) (PLLA), poly(L-lactic acid-co-glycolic acid) (PLLGA) and poly(DL-lactic acid-co-glycolic acid) (PDLGA) was studied by the dielectric thermal analysis (DETA). The aging was performed at 37℃ in vacuum oven. The dielectric features i.e., dielectric permittivity,ε′, dielectric losses,ε″, and phase lag, tg δ, were determined by PL-DETA containing a parallel plate capacitance cell, from the room temperature to 80°, 150°, and 180 °C, at the heating rates of 2 and 3°Cmin^{-1}. Dielectric scans were obtained at a frequency of 1 kHz and a.c. signal of 200 mV. Different behavior of PLLA, PLLGA, and PDLGA during degradation was observed. As the aging of PDLGA proceeds, dielectric losses shift to the lower temperatures, indicating existence of lower molecular weights. ε′ - T, and tg δ - T dependences of PLLGA, as well as those for PLLA show two simultaneous processes occurring, crystallization and degradation.

Keywords: *poly(L-lactic acid), poly(L- (or DL-) lactic-co-glycolic acid), thermal aging, dielectric thermal analysis.*

INTRODUCTION

Characteristics, such as: biocompatibility, possibility of modeling in different shapes, ability to support the adhesion and proliferation of cell, ability to facilitate the diffusion of the nutritive materials to the cells and effluents from the cells, make polymers as very attractive materials for medical and pharmaceutical application. A continuous technology development aids the possibility of a synthesis of different polymers, as well as their mixing and combination, in order to gain the material with desired features for a certain application [1, 2]. Thus, the orthopedic devices should be prepared using very strong polymers, while materials which are used for the prevention of the adhesion should be prepared by soft membranes or films, and the polymers applied for rehabilitation of the skin damages should bear very big stresses. Besides the mechanical properties of polymers, the surface morphology, the porosity, and degradation properties are of a big significance too [1, 3].

A big number of scientists focus their research interest on preparation of different biodegradable and bio-absorptive polymer materials for medical application, but the most significant synthetic polymers are those based on aliphatic polyesters, such as lactic and glycolic acid [4, 5]. The importance of these polymers is based on their biodegradability. At this time, the various implants could be mentioned, which after accomplishment of their function are decomposed by the required degradation rate, to harmless low molecular weight compounds. Avoiding the repetitive surgical intervention for their removal, the total expenses for the whole treatment is reduced [6]. The other application area of the biodegradable polymers is the drug delivery systems [7], and lately as food packaging materials, as well [8].

Poly(glycolic acid) (PGA) is a highly crystalline polymer with a high values of mechanical strength, but the high stiffness restricts its application. PGA sutures in the period of two weeks loss 50% of their strength, 100% in the period of four weeks, and after 6 months they are completely absorbed [6]. The homopolymer of L-lactic acid (PLLA) is also a semi-crystalline polymer with large tensile, flexure strengths, and modulus of elasticity, and small values of tensile strains, enable the poly(L-lactic-*co*-glycolic acid) (PLLA) as suitable for the application at places with high loads [9]. On the other hand, poly(DL-lactic acid) (PDLLA) is an amorphous polymer with a random distribution of the two isomers of poly(lactic acid). Poly(DL-lactic acid) is an amorphous polymer composed of the two isomeric forms L(+) and D(-). Compared to PLLA, PDLLA holds lower values of the tensile strength, higher tensile strains, as well as a faster degradation. Copolymerization of lactic and glycolic acid enables preparation of polymers with different features. The copolymers could be amorphous or crystalline depending on the amount of the monomers included in the polymer.

Poly(DL-lactic-*co*-glycolic acid) (PDLGA) containing from 0 to 70% glycolic acid is amorphous, but if the content of glycolic acid in the copolymer of poly(L-lactic acid-co-glycolic acid) (PLLGA) varies between 25 to 70%, the resulting copolymer is crystalline [10].

It was shown that the thermal stability of aliphatic polyesters is small regarding: (1) a hydrolysis as a result of small amount of water existing; (2) ″zipper″-like de-polymerization catalyzed by the residual catalyst; (3) oxidative degradation leading to the random scission of the main backbone; (4) intramolecular transesterification of monomers and oligomers; and (5) intermolecular transesterification creating small molecular weight compounds (monomers and oligomers) [9].

The application of polyesters for biomedical purposes requires the fundamental knowledge of their stability in biomedical environment, but still there is poor information available regarding this type of hydrolysis [11].

It is known that ″bulk″ hydrolysis is characteristic for polymers based on lactic and glycolic acid, addressed to the random scission of the ester bonds in the polymer chain, accompanied by the slump of the molecular weight and at the same time insignificant decrease of the masses. In the interior of the polymers autocatalytic degradation occurs, and it is more pronounced in PDLLA [12], but also in nonporous PLLA membranes [13] and PDLLA and PLGA microspheres with large diameters [14, 15]. The degradation products are disabled to diffuse trough nonporous structures or higher diameter microspheres in the external medium, so that they decrease the local pH value, and thus facilitate the bonds' scission.

The time of the hydrolytic degradation of PLLA ranges between several months up to 60 years for the highly oriented fibers [9], depending on the molecular weight, molecular weight distribution, crystallinity and the chains' orientation. On the other hand, poly(glycolic acid) is very hydrophilic, so that it can degrade in a week [14].

As it was already mentioned, the diverse degradation rates could be achieved by the application of different amounts of lactic and glycolic acid in their copolymers [16, 17].

In this study, an attempt was made to create a comparison of our two previous researches regarding the thermal degradation of a homopolymer of L- lactic acid and the influence of the glycolic acid on the degradation behavior of its' copolymers with L- and DL-lactic acids. As a study technique a dielectric thermal analysis (DETA) was used.

The synthesis of poly(L-lactic acid) (PLLA), the preparation of films, and the conditions of the analysis was explained in our previous researches [18, 19], as well as the procedure for the preparation of copolymers of lactic and glycolic acid [20].

Thermal degradation of poly(L-lactic acid), poly(L-lactic-*co*-glycolic acid) and poly(DL-lactic-*co*-glycolic acid)

All the samples were kept in a vacuum oven at 37 °C, as the typical hydrolytic degradation is usually performed in the buffer simulating the fluids in the living bodies, at 37 °C. After a given time all the samples were analyzed by DETA.

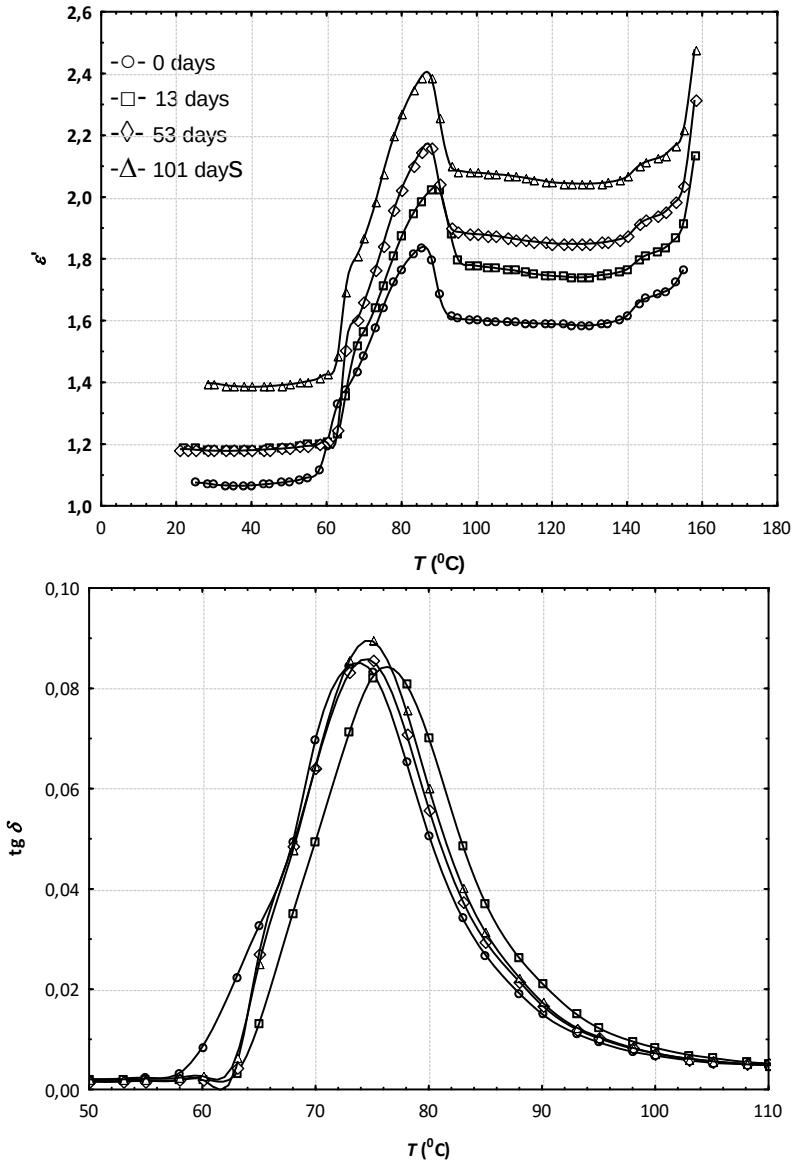

Figure 1. *ε′-T and tg δ - T dependences of PLLA aged 0, 13, 53, and 101 days, at 37 °C; heating rate 2 °C/min*

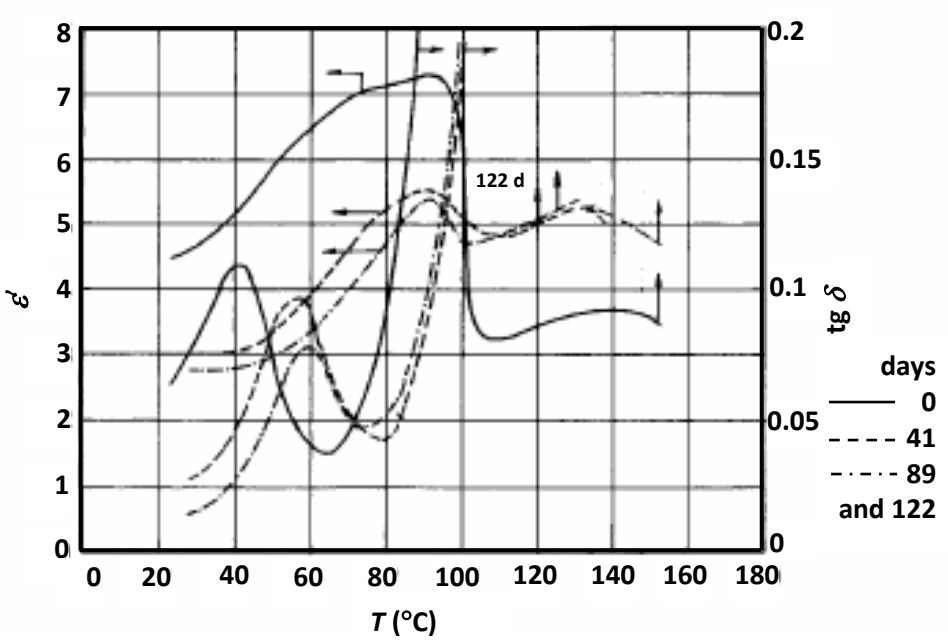

Figure 2. *ε' – T and tg δ – T dependences forPLLGA samples, aged 0, 41, 89 and 122 days, at 37 °C; heating rate 3 °C/min*

Graphs representing ε'-T and tg δ – T dependences of poly(L-lactic acid) (PLLA) are given in Fig. 1. A cold crystallization process could be observed in the ε' – T curves, by the characteristic peak appearing between 64° and 96°C for all samples, unaged and aged as well. The shoulder appearing between 62° and 66°C, on the tg δ – T relationship of an untreated sample, corresponds to the glass transition temperature (T_g). Glass transition temperature is slightly higher than those reported in the literature of about 55°-60°C [6], most probably as a result of the preparation technique of the films [18, 21].

At the beginning of aging, ε' - T and tg δ - T curves are shifted toward higher temperatures, and lower values of the dielectric permittivity and phase lag, respectively, which is typical for highly organized structures. It is considered that initially heating at 37 °C enables reorganization of the polymer chains. As degradation time increases, both, ε' and tg δ peaks are slightly moved to the lower temperatures and takes higher values, which could be attributed to the higher flexibility of the macromolecules [19]. The degradation time of ~100 days is not enough to achieve significant degradation of PLLA, as the temperatures at which the "thresholds" at the tg δ – T dependences appear at almost the same temperature of ~160 °C.

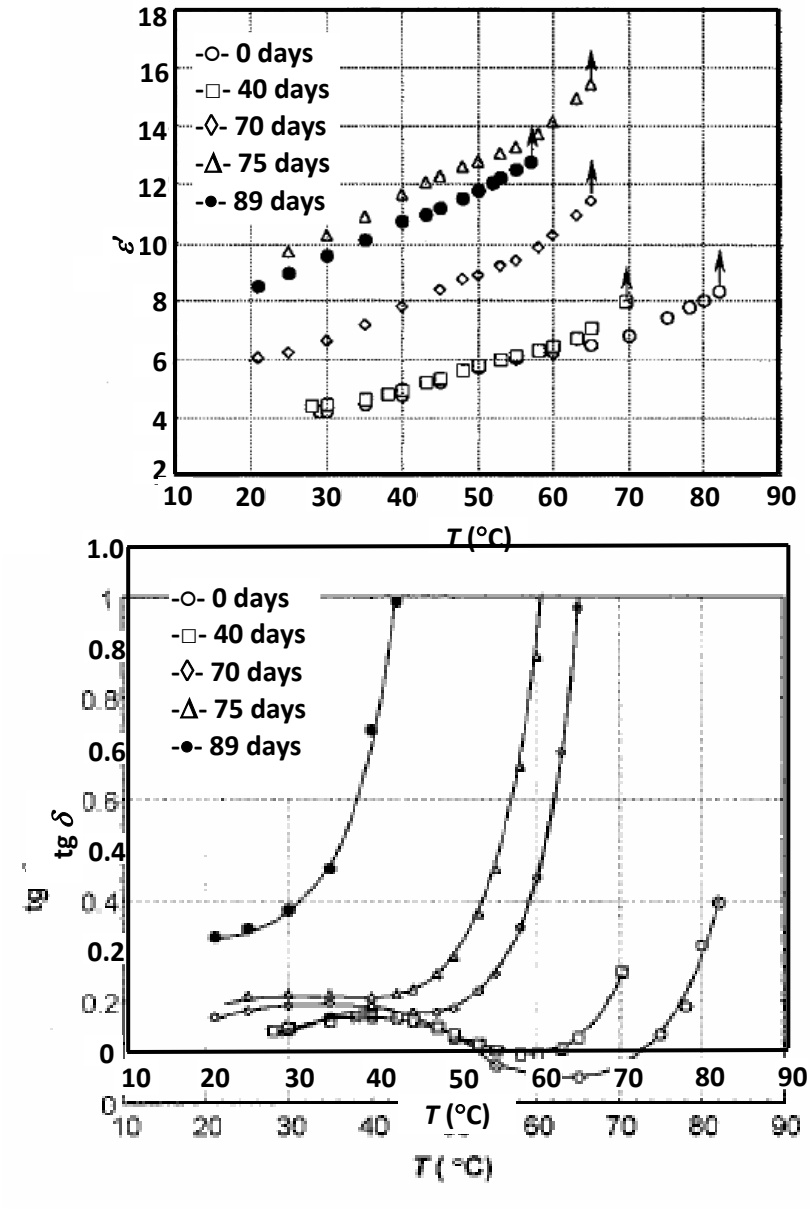

Figure 3. *ε' - T and tg δ - T dependence for of PDLLGA aged 0, 40, 70, 75 and 89 days, at 37 °C; heating rate 3 °C/min*

Preparation of a copolymer of L-lactic and glycolic acid decreases the T_g to a value of ~ 40 °C compared to a glass transition temperature of a homopolymer, Fig. 2. The aging spectra of poly(L-lactic-*co*-glycolic acid) (PLLGA) indicate a behavior similar to that of PLLA, at the beginning of the degradation process. But, as the degradation proceeds, additional change of ε' and tg δ curves to lower values and shift toward higher temperatures could be noticed.

Fig. 2 clearly indicate two coinciding processes occurring, a cold crystallization process addressed to the abrupt decrease of ε' after 80 °C and degradation indicated by the dislocation of the "thresholds" at tgδ- T curves from ~150 °C to lower temperatures of ~120 °C. Including the glycolic monomer in the PLLA chain, it is obvious that the homopolymers disturbed so that the degradation proceeds faster [20].

Even more facilitated degradation is observed in the copolymer of DL-lactic acid and glycolic acid (PDLLGA), Fig. 1, so that in just 89 days the samples became too sticky, so that they cannot be analyzed by DETA, which is designated by the tails on the tg δ - T dependences. The cold crystallization process in these samples was absent, so that only degradation process occurs. Both, dielectric permittivity and losses takes higher values during aging, and are located at lower temperatures, which is characteristic for systems with lower molecular weights and/or amorphous structures [20].

CONCLUSIONS

A comparison of a thermal degradability of a nonporous PLLA, PLLGA, and PDLLGA films at 37 °C, analyzed by DETA was given.

Treatment of PLLA at 37 °C in a period of 100 days is not enough for a degradation of the homopolymer, so that the extended aging is required. Restructuring of the polymer chains, at the beginning of aging, and later slight increase of the chain flexibility was observed [19].

Disrupting the regularity of poly(L-lactic acid) by the addition of a glycolic acid, leads to a facilitated degradation of the copolymer, and also two parallel occurring process were observed: cold crystallization and degradation [20].

The fastest degradation was observed in PDLLGA copolymers [18], which coincide with the literature data [16, 17].

Dielectric thermal analysis (DETA) could be considered as a very helpful technique in determination of structure altering as a result of thermal aging.

REFERENCES

[1] Seal, B. L., Otero, T. C., Panctch, A. Mater. Sci. Eng. 2001, R34, 147-230.

[2] Thomas, Ch. B., Burg, K. J. L. Tissue Engineering systems, In: Absorbable and Biodegradable polymers, Sh. W. Shalby, K. L. Burg: CRC Pres, Boca Raton, Florida, 2004, pp 159-176.

[3] Mano, J. F., Sousa, R. A., Boesel, L. F., Neves, N. M., Reis, R. L Compos. Sci. Technol. 2004, 64, 789-817.

[4] Porjazoska, A., Cvetkovska, M., Karal Yılmaz, O., Baysal, K. B., Kayaman Apohan, N., Baysal, B.M. *Bull. Chem.Technol. Macedonia*, 2004, 23**,** 147-156.

[5] Porjazoska, A. Goracinova, K. Mladenovska, K. Glavaš, M. Simonovska, M. Janjević, E.I. Cvetkovska, M. *Acta Pharmaceutica*, 2004, 54, 215-229.

[6] Middleton, J., Tipton, A. Biomaterials, 2000, 21, 2335-2346.

[7] Ramchandani, M., Robinson, D. J. J. Control. Release, 1998, 54, 167-175.

[8] Fukushima, K., Fina, A., Geobaldo, F., Venturello, A., Camino, G. Express Polym. Lett. 2012, 6, 914–926.

[9] Sodergard, A., Stolt, M. Prog. Polym. Sci., 2002, 27, 1123-1163.

[10] Gilding, D. K., Reed, A. M., Polymer, 1981, 22, 494-498.

[11] Tsuji, H., Miyauchi, Sh., Polymer, 2001, 42, 4463-4467.

[12] Tsuji, H. Polymer, 2002, 43, 1789-1796.

[13] Luciano, R. M., Zavaglia, C. A. C., Duek, E. A. R., Alberto-Rincon, M. C. J. Mater. Sci.-Mater. Med., 2003, 14, 87-94.

[14] Hurrell, S., Cameron, R. E., J. Mater. Sci.-Mater. Med., 2001, 12, 811- 816.

[15] Andreopoulos, A. G., Hatzi, E. C., Doxastakis, M. J. Mater. Sci.-Mater. Med., 2000, 11, 393-397.

[16] Miller, R. A., Brady, J. M., Cutright, D. E. J. Biomed. Mater. Res., 1977, 11, 711-719.

[17] Grijpma, D. W., Pennings, A. J. Macromol. Chem. Phys., 1994, 195, 1633-1647.

[18] Kujundziski, A.P., Chamovska, D., Marra, A., Duraccio, D., Silvestre, C. Proceedings of International Conference 15 YUCCOR, 17-20 September, 2013, Tara, Serbia, 252-260.

[19] Chamovska, D., Porjazoska-Kujundziski, A. Zaštita materijala i životne sredine, in press.

[20] Porjazoska, A., Grchev, T., Cvetkovska, M., Karal-Yilmaz, O., Baysal, B. M. Bull. Chem. Technol. Macedonia, 2002, 21, 199–206.

[21] Chen, Ch.-Ch., Chueh, J. Y., Tseng, H., Huang, H. M., Lee, Sh. Y. Biomaterials, 2003, 24, 1167-1173.

DOI: 10.7251/JEPMEN1507027P
UDK: 678.7:543.57
Naučni rad

SLEDENJE NA TERMIČKATA DEGRADACIJA NA BIORAZGRADLIVITE POLIMERNI MATEREIJALI SO DIELEKTRIČNA TERMIČKA ANALIZA

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Izvod

Napravena e komparacija na dve istražuvanja koi se odnesuvaat na termičkoto stareenje na poliesteri na mlečnata i glikolnata kiselina. Termičkata degradacija na poli(L-mlečna kiselina) (PLLA), poli(L-mlečna-ko-glikolna kiselina) (PLLGA) i poli(DL-mlečna-ko-glikolna kiselina) (PDLGA) beše ispituvana so pomoš na dielektrična termička analiza (DETA). Stareenjeto na primerocite beše izvedeno na 37 ℃ vo vakuum sušara. Dielektričnite svojstva, t.e. dielektričnata konstanta, ε′, dielektričnite zagubi, ε″ i tg δ, bea oderedni so pomoš na PL-DETA instrument, so kapacitetna ćelija so paralelni ploči, od sobna temperatura do 80 ℃, 150 ℃ i 180 ℃, primenuvajći brzina na zagrevanje od 2 i 3 ℃ min^{-1}. Dielektričnite spektri bea dobieni pri frekvencija od 1 kHz i a.c. signal od 200 mV. Vo tekot na termičkata degradacija, beše zabeležano različno odnesuvanje na PLLA, PLLGA i PDLGA. Vo tekot na stareenjeto na PDLGA, dielektričnite zagubi se pomestuvaat kon poniski temperaturi, ukažuvajći na namaluvanje na molekulskite masi. ε′ - T, and tg δ - T zavisnostite za PLLGA, kako i tie dobieni za PLLA, ukažuvaat na postoenje na dva simultani procesi, kristalizacija i degradacija

Ključne riječi: *poli(L-mlečna kiselina), poli(L- (ili DL-) mlečna kiselina-ko-glikolna kiselina), termičko stareenje, dielektrična termička analiza.*