THERMAL AND DIELECTRIC PROPERTIES OF BIODEGRADABLE POLY(BUTYLENE SEBACATE-*CO*-BUTYLENE DILINOLEATE)

A. Kozłowska[1], M. Orłowski[2] and J. Majszczyk[2]

[1]Szczecin University of Technology, Institute of Polymers, Pulaskiego 10, 70-322 Szczecin, Poland
[2] Szczecin University of Technology, Institute of Physics, Al. Piastów 17, 70-310 Szczecin, Poland

Abstract. A new biodegradable copolymers: poly(butylene sebacate-*co*-butylene dilinoleate) modified by different (0 – 10 wt.%) content of buthylene terephtalate were synthesized and their thermal and dielectric properties were investigated in a wide temperature range. There was find that melting temperature T_m decreases from 338 to 316K and glass temperature increases from 206.5 to 216.5K with the increase of the buthylene terephtalate content. Two dielectric relaxations: α at about 250K and β near 200K were observed in dielectric spectra; also melting process is explicitly seen there in a form of rapid increasing of dielectric constant value. Good coincidence between values of melting temperatures estimated by DSC and dielectric measurements was observed. A reason of such a behaviour is disscused with respect to degree of crystallinity changes caused by buthylene terephtalate presence in the copolymer.

1. INTRODUCTION

The wide use of polymers in various applications because of their versatility and mass-production ability is considered as a serious source of environment pollution. The use of biodegradable polymers as an alternative to conventional nonbiodegradable plastics could contribute to the solution of the environmental problem. Aliphatic polyesters made from dicarboxylic acids and diols are expected to be one of the most economically competitive biodegradable polymers [1,2]. The biodegradability of these polymers depends mainly on their chemical structure and especially on the hydrolysable ester bond in the main chain, which is susceptible to microbial attack. Other factors such as molecular weight, degree of crystallinity,

stereoregularity and morphology also affect the rate of polymer biodegradation.

Dielectric spectroscopy has proven to be a very useful tool to study the structure and the dynamics of polymeric systems [2–6]. This knowledge is important for the development of new materials and also to understand the eventual degradability of those materials.

The complex dielectric function, $\varepsilon^* = \varepsilon' - i\varepsilon''$, is a material's property depending on frequency, temperature, and structure. ε' is related to the electric field energy stored in the material, whereas ε'' is proportional to the energy that is dissipated in each cycle of the electric field change. These quantities are quite important for the technical characterization of the material and its possible application;

Corresponding author: A. Kozłowska, e-mail: agak@ps.pl

study of its dependence on frequency and temperature could be useful in the phase structure determination of complex polymeric systems [7].

In this study synthesis, thermal (DSC), and dielectric properties of biodegradable, aliphatic, and aliphatic-aromatic copolyesters are presented. Biodegradation tests are in progress in our laboratory and results will be published in near future.

2. EXPERIMENTAL

Materials

Dilinoleic acid –DLA (dimerized fatty acid –DFA), trade name Pripol 1009, molecular weight ~570 g/mol, C36 was kindly provided by Uniqema BV, The Netherlands; 1,4-butanediol –BD (BASF, Germany); sebacic acid –SA (Aldrich Chemie); dimethyl terephthalate –DMT (ZWCH Elana, Poland) were used as received.

Synthesis

Copolyesters were prepared by typical melt polycondensation method. The esterification reaction between sebacic, dilinoleic acids and 1,4-butanediol (BD) in molar ratio 1:2,2 was carried out in the presence of magnesium-titanate organometallic complex (Mg-Ti) as catalyst using intensive stirring and upon programmed temperature raising from 373 to 473K.

The transesterification between dimethyl terephthalate (DMT) and 1,4-butanediol (BD) in molar ratio 1:2 was carried out in the presence of Mg-Ti catalyst with intensive stirring and a programmed temperature rise from 423 to 483K at a heating rate of 1.5 deg/min. The reaction was finished after more than 90% of the stoichiometric amount of methanol had been evaporated.

The polycondensation reaction was carried out at 528-533K, ~ 0.4 hPa and in the presence of Mg-Ti catalyst. The process was considered complete when the observed power consumption of the stirrer motor signalled that the polymer of highest melt viscosity had been obtained. The reaction mass was extruded by means of compressed nitrogen.

The schematic formula of the final products is presented below.
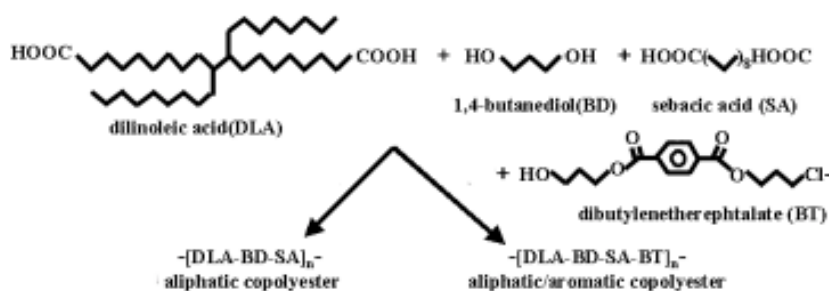
Measurements

Melting point temperature (T_m) measurement was conducted by optical method with Boethius apparatus (Franz Kunster Nacht KG, type HKM). Thin scrap of polymer was located between glass sheets on heating plate of microscope; heating rate was 4 deg/min.

Differential scanning calorimetry (DSC) measurements were performed using 910 DSC Du Pont Instruments set, in the cycle of heating-cooling-heating, with the heating rate of 10 deg per minute in the temperature range from 173 to 473K.

Dielectric measurements. Dielectric spectroscopy measurements were performed using the Hewlett-Packard Impedance Analyser type HP 4192A within the frequency range from 1 to 1000 kHz. The sample was placed into a nitrogen thermostat, where the temperature was changed from about 80K until the melting point of the investigated copolymer with step of 5 deg. Samples in a form of a thin, flat disc were covered with aluminium electrodes disposed by hot pressing method, for more details see our previous work [8]. All results are presented in the *temperature domain* with the frequency as a parameter.

3. RESULTS AND DISSCUSION

The designation of samples and their composition are presented in the Table 1. Five samples with different contents of the BT-component varying from 0 to 10 wt.% and equal parts of the DLA and AS were investigated by the DSC and dielectric spectroscopy methods. Some selected results are listed in Table 1.

Differential scanning calorimetry (DSC) thermograms are shown in Fig. 1. Only one glass temperature T_g varying from 206,7K (for BT= 0) to 216.8K (BT = 10 wt.%) is seen for each samples; this fact indicates that one homogeneous, amorphous phase exists here.

Dielectric spectra of the all samples exhibit the same character. As an example, temperature dependence of the ε' and ε'' at some selected fre-

dilinoleic acid(DLA) + 1,4-butanediol(BD) + sebacic acid (SA)

+ dibutylenetherephtalate (BT)

-[DLA-BD-SA]$_n$-
aliphatic copolyester

-[DLA-BD-SA-BT]$_n$-
aliphatic/aromatic copolyester

Table 1. Specification of samples and their thermal and dielectric properties as well as fitting parameters.

Sample	DLA/SA/BT wt.%	T_m Boet. [K]	T_m diel. [K]	T_g DSC [K]	T_o diel. [K]	C	D [K]	E_b kJ/mol
A85	50/50/0	338	329	206.5	200.7	14	381	55.3
A86	48.75/48.75/2.5	333	323	205.54	203	12.9	340	54.3
A87	47.5/47.5/5	323	313.5	210.3	208	12.3	334	55
A88	46.25/46.25/7.5	318	313.1	211.1	219	9.2	321	54.1
A89	45/45/10	316	311	216.5	226	8.8	299	51.7

DLA- content of dilinoleid acid,

SA- content of sebacic acid,

BT- content of butylene terephtalate,

T_m Boet. and T_m diel. – melting temperature as measured by the *Boethius* or dielectric method, respectively,

T_g DSC- glass temperature by DSC-method,

T_o diel.- extrapolated (Vogel) glass temperature: fitting with the Eq. (2),

C, D- constant parameters from fitting with Eq. (2),

E_b - activation energy of the b-process, from fitting with Eq. (1).

quencies for the A87 sample are shown in Figs. 2a and 2b, respectively. There are two relaxations within investigated temperature and frequency regions: one at about 193K denoted as β and second- at some –293K, as α. Note the rapidly increas-

Fig. 1. DSC- thermograms of the poly(butylene sebacate-*co*-butylene dilinoleate) samples with different additions of butylene terephtalate. Numerical data are listed in Table 1.
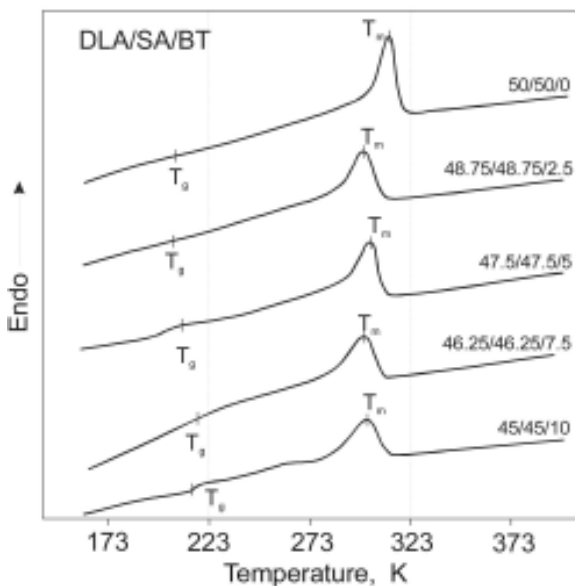
ing value of ε' at certain temperature (Fig. 2a), which can be attributed to melting process of crystalline phase of this material. No similar behavior was observed for the ε'' values (Fig. 2b). It means that during melting process a number of polar molecules are relased, but not any free charge carriers appear.

Melting temperatures T_m revealed for all samples by either *Bethius* or dielectric method are compared in Table 1.
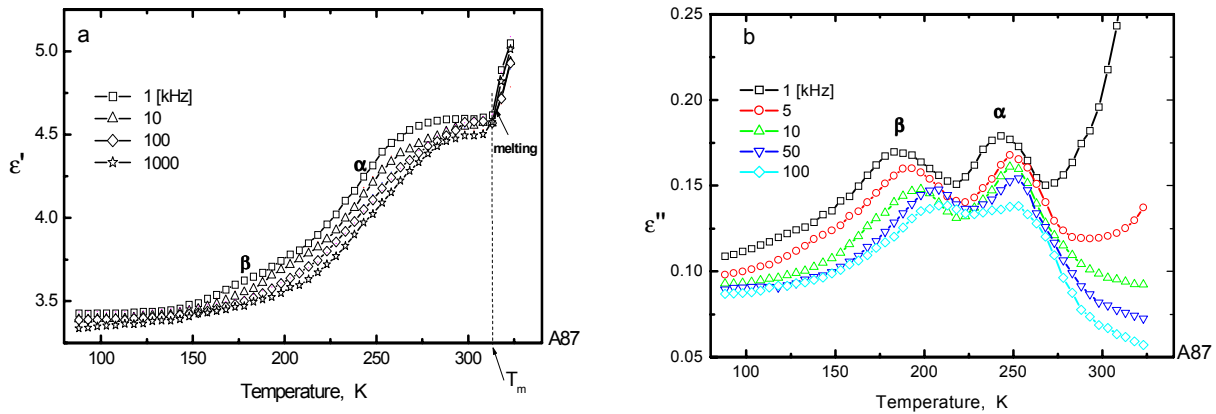
The comparison of dielectric spectra of samples with different composition shows a slight shift of the both relaxation peaks toward higher temperatures (at constant frequency) with incresing of the BT-contents in the copolymer. These phenomena could be seen in Fig. 3 where curves of ε''(T) at 10 kHz for the all samples are presented.

Taking respective data from the Fig. 2b and the same for the others samples (not presented here), a relaxation plot was constructed and presented in Fig. 4. for three selected samples: two extremal and one central with respect of BT-content. One can see here two different dependencies: linear for the $\tilde{\beta}$-relaxation and nonlinear for the $\tilde{\alpha}$-one. The $\tilde{\beta}$-relaxation fulfil the Arrhenius equation (1):

$$\log(f_{max}) = A - E_b / RT, \tag{1}$$

Fig. 2. Temperature dependence of: a) dielectric constant ε' and b) dielectric loss ε'' for the A87 sample at different frequencies.

where: f_{max} – frequency corresponding to the maximum of ε'', A – constant, E_β – activation energy of the β-process, R – gaseous constant and T – absolute temperature. The nonlinear a-relaxation dependence can to be fitted by the Vogel-Fulcher equation (2);

$$\log(f_{max}) = C - D / (T - T_o), \qquad (2)$$

where: C, D – constants and T_o – extrapolated (Vogel) glass temperature. Fitting the experimental results with the above equations a number of parameters were estimated and shown in Table 1.

The values of the activation energies of the β-relaxation for the all samples are approximately equal; they could be described as $E_\beta = (50 \pm 5)$ kJ/mol. It means that the β-relaxation mostly runs in the DLA and/or AS components of the investigated copolymers. The apparent activation energy

of the α process, i.e. obtained from linear approximation of the nonlinear data, shows values within 200 and 250 kJ/mol which is typical for relaxations near glass transition.

The Vogel-Fulcher parameters obtained by fitting of Eq. 2 depend on the BT-content. They are listed in Table 1 and presented in Fig. 5. The values of glass temperatures T_g taken from DSC results and dielectric strength Δε extrapolated from the dielectric spectra are also shown in the same Table 1 and Fig. 5. Note the very good agreement between T_g and T_o for all samples.

An interesting feature of the materials studied in this work is the increase of glass transition temperatures T_g (and T_o) with the increase of the BT-content, whereas the melting temperatures T_m are shifted down. It is well known that polyesters (e.g. PBT) have high T_g and should elevate the glass
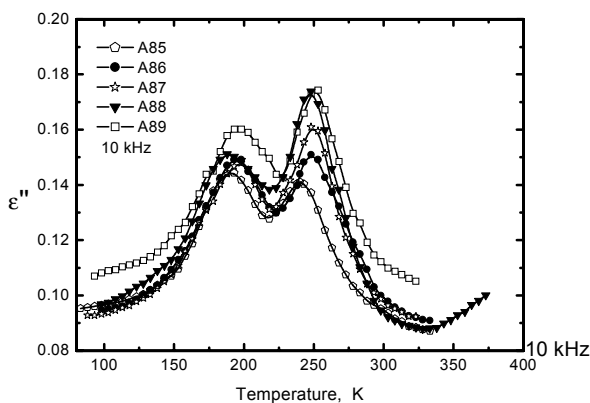
Fig. 3. Temperature dependence of ε'' of all samples measured at the frequency of 10 kHz.
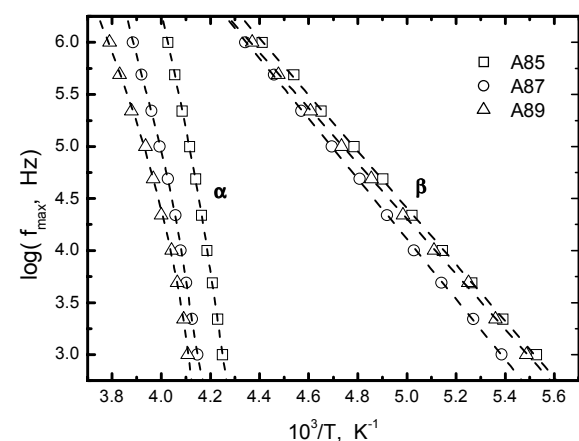
Fig. 4. Relaxational plot: log(f_{max}) versus reciprocal temperature $10^3/T$ for three selected samples.
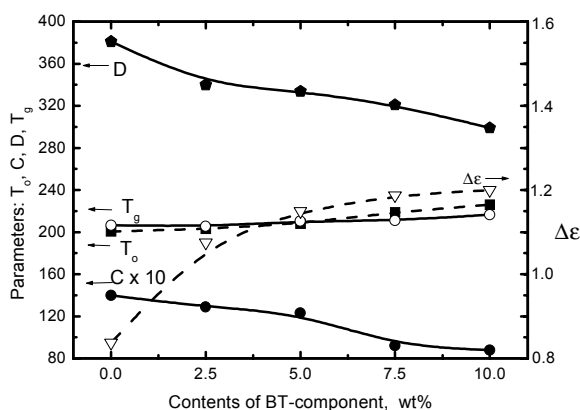
Fig. 5. Fitting and calculating parameters from experimental data (presented in Table 1) as a function of the butylene terephtalate content.

temperature of copolymer [9]. In order to explain this problem, values of dielectric strength $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ were extrapolated from experimental data. Here ε_s is the value of dielectric constant at very low frequency, and ε_∞ at very high one. The $\Delta\varepsilon$ value is proportional to the number of dipoles involved into a given relaxation process. The dependence of $\Delta\varepsilon$ on the BT-content is shown in Fig. 5. On the basis of this dependence one can suppose that number of dipoles increases therefore addition of the BT-component decreases degree of crystallinity of these copolymers and their melting temperatures T_m. On the other hand, addition of highly polar ester molecules shifts up the glass temperatures T_g and T_o.

4. CONCLUSION

The investigated poly (butylene sebacate-*co*-butylene dilinoleate) copolymers are semicrystalline materials with melting temperatures about 323K and glass temperatures about 213K. Two relax-

ation processes: α and β were observed within the whole temperature range used in the experiments, i.e. from 80 to 370K.

Evident influence of the content of *dibutylene terephtalate* (BT) component in the samples upon the T_g and T_o temperatures was observed. Shift up of the above mentioned temperatures as well as shift down of the melting temperature T_m with the content of BT could be a result of a competitive crystallisation processes of the aliphatic SA and aromatic BT components. It leads to a reducing of the crystallinity degree of these copolymers.

ACKNOWLEDGEMENT

REFERENCES

[1] M. Kim, K. Kim, H. Jin, J. Park and J. Yoon // *Eur. Polym. J* **37** (2001) 1843.

[2] H. Jin, B. Lee M. Kim and J. Yoon // *J. Appl. Polym. Sci.* **38** (2000) 1504.

[3] G. Williams, *Keynote lectures in selected topics of polymer science* (1997, CSIC, Madrid).

[4] J. Runt and J. Fitzgerald, *Dielectric spectroscopy of polymeric materials* (1997, American Chemical Society, Washington).

[5] A. Blythe, *Electrical properties of polymers* (1979, Cambridge University Press, Cambridge).

[6] P. Hedvig, *Dielectric spectroscopy of polymers* (1977, Adam Hilger, Bristol).

[7] A. Kozłowska, J. Majszczyk and M. Orłowski // *Rev. Adv. Mater. Sci.* **12** (2006)139.

[8] J. Majszczyk, A. Kozłowska and J.Słonecki // *Macromol.Chem.Phys.* **202** (2001) 1207.

[9] J. Runt, L. Du, L.M. Martynowicz, M.E. Hancock, D.M. Brezny and M. Mayo // *Macromolecules* **22** (1989) 3908.