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ENVIRONMENT FRIENDLY POLYMERIC MATERIALS – IDENTIFICATION OF THEIR BIODEGRADABILITY ON BASE OF THERMOMECHANICAL COUPLING PHENOMENON

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Environment friendly polymeric materials were investigated using an infrared camera in order to identify the relationship between their structure and properties including biodegradability. The experimental technique, based on the thermomechanical coupling phenomenon, was applied to investigation of polymers. Three samples of biodegradable polymers, i.e. the reference one and the modified two, were subjected to tensile and relaxation tests, according to a special program. The temperature changes were measured by a contact less method and related to mechanical characteristics. In the modified material, the temperature decrease, related to the thermoelastic effect, was observed in almost the whole range of the tensile tests. It means that the deformation does not exceed the limit of elasticity, and next, highelasticity – the stage of polymer deformation that follows the elasticity. The temperature measurements seem to be a useful tool for the investigation of biodegradable polymers: thermal characteristics may define a material according to its fragility related to biodegradability.

Key words: biodegradable polymers, tension test, mechanical characteristics, thermomechanical coupling, thermoelastic effect

1. Introduction

Environmental challenges and scientific imperatives call for special interest in environment friendly materials. The primary objective of this work, which covers a range of biodegradable polymers, was to devise simple and reliable experimental techniques of investigation of the biodegradability. To this end, thermoelastic and thermoplastic stress analysis consisting in the detection of a temperature change caused by a change in stress conditions was applied. The main task was to get the stress and temperature values for the critical load conditions important in terms of the recognition and investigation of mechanical and thermal material properties of biodegradable polymers. Effects of the thermomechanical coupling, which are of frequent occurrence in nature have had a long history in both theoretical and experimental works. The problem was developed by Thomson (Lord Kelvin) (1857), Taylor and Quinney (1934), Bever *et al.* (1973), Beghi *et al.* (1986), Chrysochoos and Martin (1989), Pieczyska (1997, 1999). Thermoelastic effects, i.e. the change in temperature in elastic range of elongation, according to the Kelvin Law (Kelvin, 1857): $\varDelta T = -k\varDelta\sigma_{ii}$ was worked out. According to this law, the change of temperature is a linear function of the first invariant of the stress tensor σ_{ii}. It can be negative in the case of a tension test, positive for a compression test and equal zero during torsion or shear tests. Plastic deformation of all materials and all kinds of deformation is always accompanied by the increase in temperature due to dissipation processes.

As far as polymers are concerned, there are not many works concerning thermomechanical studies on them. However the material behaviour is similar, the observed thermoelastic effect in polymers is greater in comparison with that in metals and, generally, the impact of temperature variation caused by mechanical testing is even stronger, since the melting temperature of polymers is rather low (Gadaj *et al.*, 1999; Pieczyska *et al.*, 2002a,b,c). Furthermore, highelasticity – a reversible but rather not linear stage that occurs during polymer deformation also has to be taken into the consideration. The highelastic deformation is not accompanied by energy conversion but is related to the entropy decrease. This thermodynamically uncomfortable situation causes easy reversibility of highelastic strains, often observed in polymers.

In this approach, the phenomenon of the negative temperature increment in the elastic range of deformation and the positive increment during plastic deformation is applied in order to investigate polymers with respect to material biodegradability. Taking into account the fact that simultaneous heat transfer accompanies the process of deformation, registered temperature variations related to mechanical characteristics obtained during tests provoke an additional insight into thermomechanical and visco-elasto-plastic behaviour of biodegradable polymers. Nevertheless, that requires further studies, especially those concerning the evolution of the material microstructure due to loading.

2. Methodology

The following investigations were realised with 3 samples of biodegradable polymers – the reference one: natural crystalline poly (R-3-hydroxybutyrate) of molecular weight Mn=125000; Mw/Mn=2.9 (a product by Biomer, Germany; sample denoted "Co") and two samples modified towards the increase of its biodegradability (denoted as S1 and S2). The glass transition temperature of reference sample Co was $T_g \approx 5°\mathrm{C}$ and the melting temperature $T_m = 179°\mathrm{C}$. Samples S1 and S2 were blends of natural PHB containing c.a. $35w\%$ of synthetic amorphous poly (R, S-3-hydroxybutyrate) (a-PHB) (Scandola *et al.*, 1997) of various molecullar weights (sample S1: a-PHB of Mn=15600, Mw/Mn=1.3; sample S2: a-PHB of Mn=4600, Mw/Mn=1.7). A small depression of the melting point of the crystallizable component was observed in these blends (for S1 $T_m = 178°\mathrm{C}$ and for S2 $T_m = 174°\mathrm{C}$), which resulted in approximately the same temperature of the maximum crystallization rate for the blends as pure polymers (Abe *et al.*, 1994). The studied polymeric materials were processed by injection molding at the Biomer Co.

The sheet samples ($6\,\mathrm{mm}\times 3\,\mathrm{mm}\times 115\,\mathrm{mm}$) of the biodegradable polymer were subjected to a special program of tensile deformation by means of a testing machine; see Fig. 1 and the photograph (Fig. 2). The testing was carried out with a constant rate of loading and unloading, equal to $10^{-2}\,\mathrm{s}^{-1}$ (strain rate). The gauge length (G.L.) was equal to $25 \pm 5\,\mathrm{mm}$. An infrared camera was used in order to measure temperature changes of the sample in a contact less way with high accuracy. The temperature was taken as an average from the sample surface $\sim 2\,\mathrm{cm}^2$. The mean-square error of temperature evaluation was about 0.1 K.

3. Results and discussion

In order to investigate thermomechanical behaviour of the biodegradable polymers, the following investigations were done:

- A tensile test for the three kinds of polymers – the reference one, denoted as Co, and two modified types of increased biodegradability, denoted as S1 and S2 (the last digits at the curves denote the number of a sample)
- A 1-stage and 2-stage relaxation test for polymer S2.

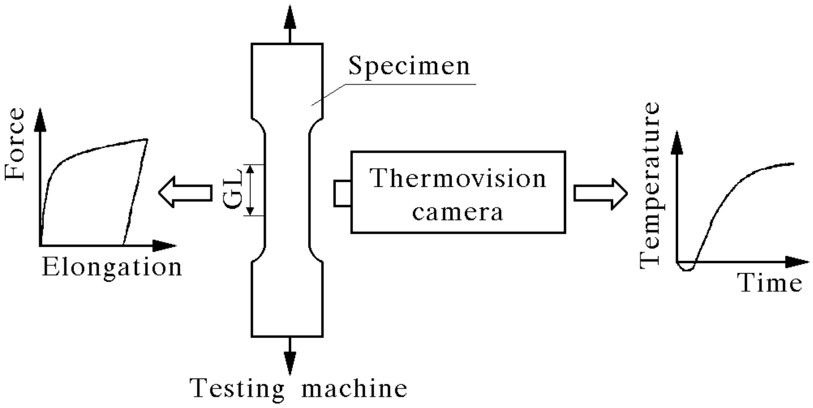

Fig. 1. Scheme of experimental set-up

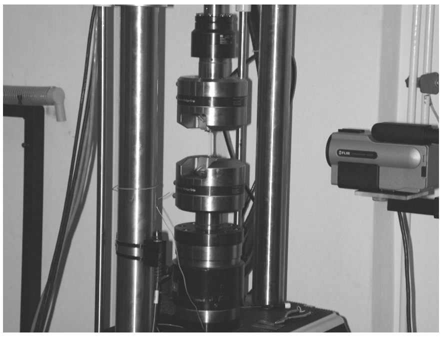

Fig. 2. Experimental equipment

3.1. Tensile tests

The mechanical data and the temperature distribution registered during the test enabled us to derive stress-strain characteristics (Fig. 3) and temperature variations of the sample subjected to deformation (Fig. 4 and Fig. 5). Two satisfying results were obtained for each group of samples. Looking at the stress-strain curves, one could notice very good repeatability of the obtained results.

The mechanical characteristics are smooth and there are no significant discrepancies between them, however they differ both by the stress values and by the maximum values of deformation obtained before cracking of the specimens. The reference material (Co) achieves a higher strain. After modification, the two polymers were more fragile; the modification increases their fragility. Furthermore, the modified polymer S1 becomes more resistant than polymers S2 and Co; its stress-strain characteristics are significantly higher.

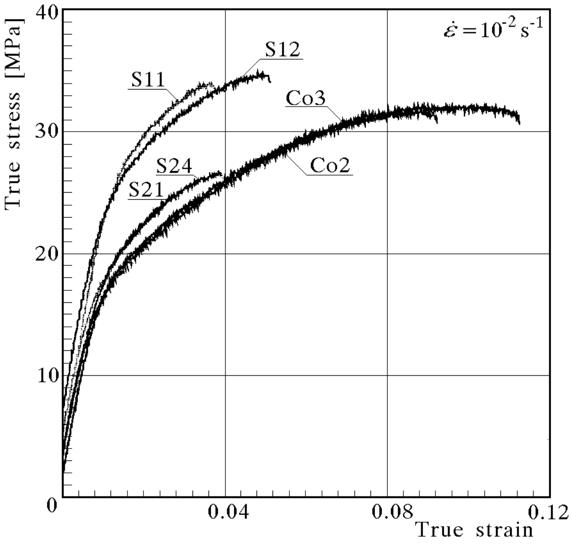

Fig. 3. Stress-strain curves and temperature variations obtained during tensile test on three kinds of biodegradable polymers

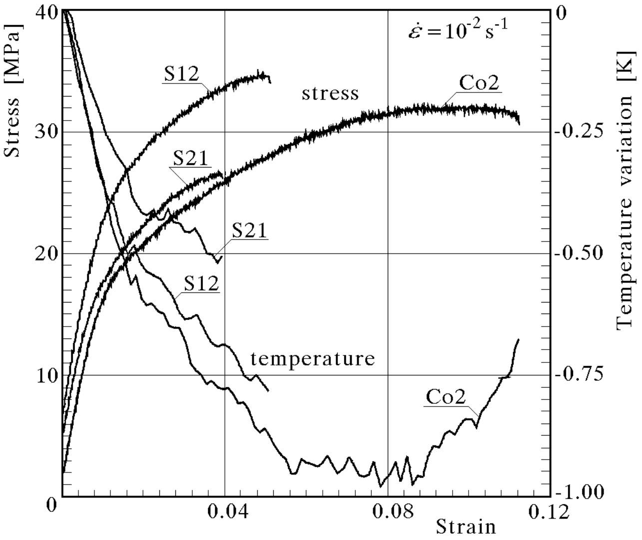

Fig. 4. Stress-strain and temperature variation curves obtained during tensile test on three kinds of biodegradable polymers

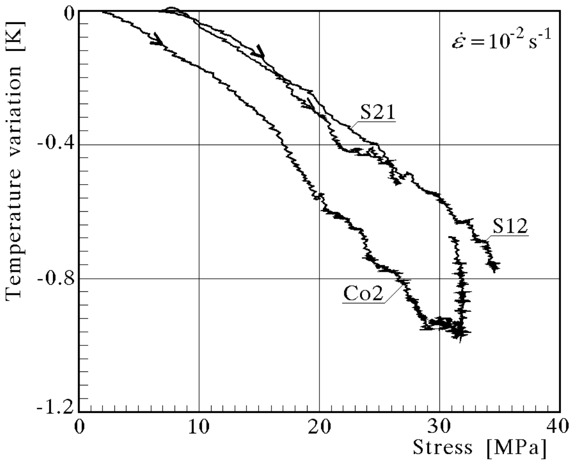

Fig. 5. Temperature variations versus stress obtained during tensile test on three kinds of biodegradable polymers: reference polymer Co and modified ones S2 and S1

A comparison of chosen mechanical and temperature characteristics is shown in Fig. 3. In the initial range of the tension test, the temperature of all samples decreases as a result of the thermomechanical effect. In the reference polymer, Co, at the strain 0.05, an equal level of the temperature value is observed, followed by temperature increase, typical for plastic deformation. On the contrary, in the modified material, the temperature decrease is observed up to the material break. It manifests that the modified polymers S1 and S2 do not reach the plastic range of their deformation. Furthermore, the temperature decrements obtained for these materials are lower. Analyzing the mechanical and temperature characteristics, one can notice that the temperature decrease occurs not only in the elastic but also in the highelastic range of polymer deformation (Pieczyska *et al.*, 2002a,b,c).

The temperature variations presented as a function of stresses are shown in Fig. 5. The temperature characteristics are linear only within the short initial range (Fig. 5), which indicates high fragility of the polymers. Next, a higher degree of the temperature decrease, followed by a plateau and temperature increase was observed for the biodegradable reference material. The modified polymers did not exceed the elastic region, which confirmed their fragility related to higher biodegradability.

3.2. Relaxation tests

Two programs for testing relaxation effects in the biodegradable material S2 were proposed:

Relaxation 1 – straining upto $\Delta l = 1.1\,\mathrm{mm}$ ($\varepsilon = 2.35\%$), stopping at this level of deformation, 3 min waiting with instantaneous registration of stress and temperature, unloading with the same rate of straining $\dot{\varepsilon} = 10^{-2}\,\mathrm{s}^{-1}$.

Relaxation 2 – straining upto $\Delta l = 1.1\,\mathrm{mm}$ ($\varepsilon = 2.35\%$), stopping at this level of deformation, 3 min waiting with instantaneous registration of stress and temperature, straining again by another $\Delta l = 1\,\mathrm{mm}$, 3 min waiting, unloading with the same rate of straining $\dot{\varepsilon} = 10^{-2}\,\mathrm{s}^{-1}$.

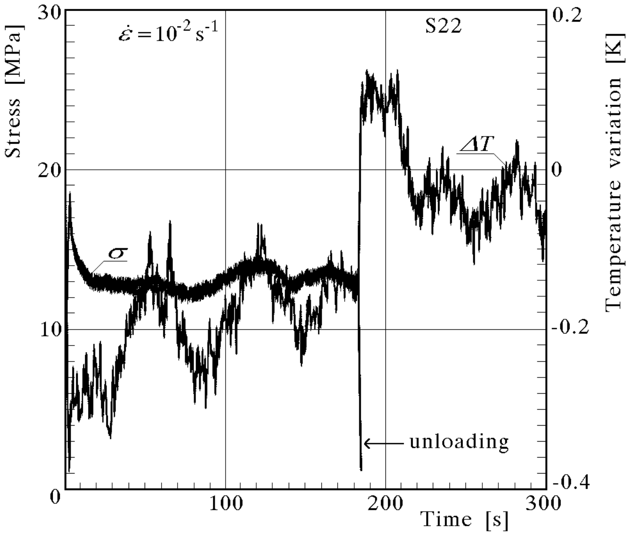

Fig. 6. Stress and temperature versus time during test relaxation 1 of biodegradable polymer S2

The mechanical and thermal characteristics were measured both in elastic and plastic ranges as well as after the process. The obtained results are shown in Fig. 6 - Fig. 9.

During the relaxation (Fig. 6), namely within the 3 min waiting, the stress decreases by about 18 upto 13 MPa (about 28% of the loading); then it oscillates on a similar level in all the tests. A smooth temperature increase, related first of all to the heat exchange, accompanies the process of relaxation. A sudden drop in the temperature was observed at the moment of unloading (effect of thermoelastic unloading), followed by the temperature decrease due to the heat exchange (Gadaj *et al.*, 1999; Pieczyska *et al.*, 2002a,b,c).

During the first step of relaxation 2, the stress decrease and the temperature increases as a result of the heat exchange (Fig. 7). Unfortunately, the sample cracked during the second step of loading, so the experiment was not

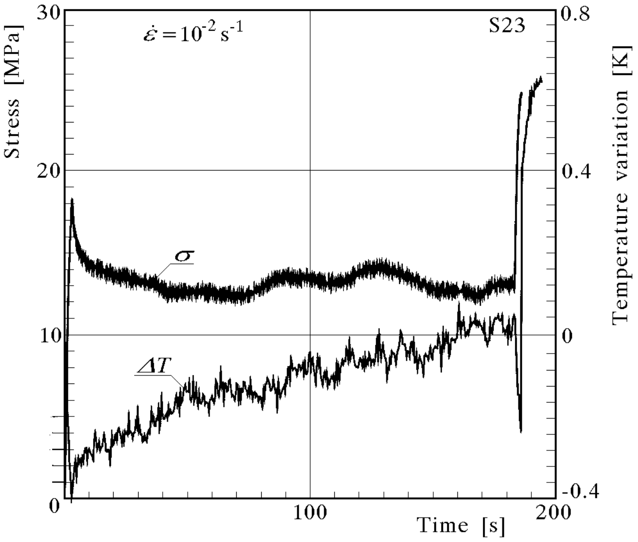

Fig. 7. Stress and temperature versus time during test relaxation 2 of biodegradable polymer S2

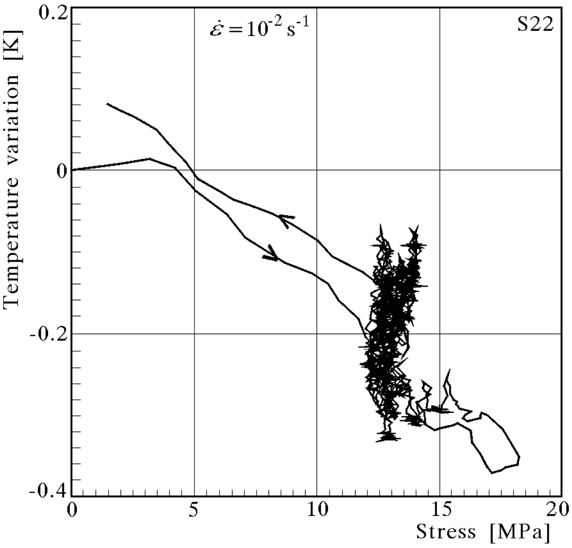

Fig. 8. Temperature as function of stress during test relaxation 1

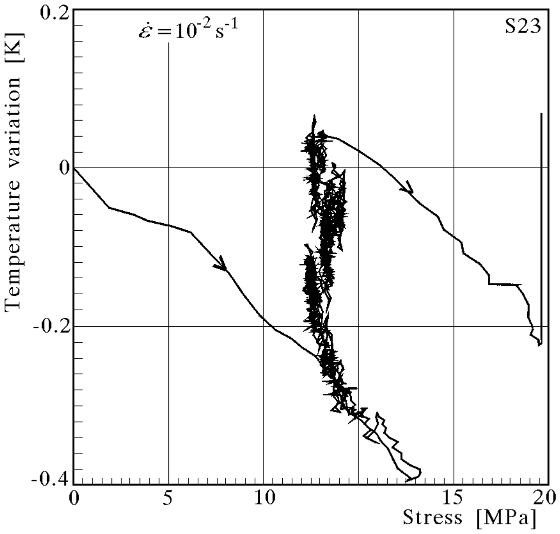

Fig. 9. Temperature as function of stress during test relaxation 2

completed according to the initial plans. A significant temperature increase was observed after the cracking.

The temperature variations measured during the relaxation tests are presented as a function of stresses in Fig. 8 and Fig. 9.

The characteristics differ slightly both in shape and in values, however their general run is similar. The same thermoelastic effect during loading as well as the same inclination of the first part of ΔT versus stress characteristics like those obtained during unloading and during the second stage of loading in test II, were observed and registered. The decrease in temperature still accompanies the second stage of loading (to the end of the experiment caused by damage), which manifests that the fracture occurred in the pure elastic range of the straining. An urgent drop in the temperature observed at the moment of unloading was brought about by the effect of thermoelastic unloading (Pieczyska, 1999). Then, the temperature decreased due to heat exchange with the surrounding.

4. Concluding remarks

- A qualitative change of the nature of temperature behaviour in biodegradable polymers in elastic and plastic ranges enables one to identify their biodegradability.

- In the elastic regions of deformation, the thermo-elastic effect is registered during loading in the form of a significant drop in temperature by $-1\,\mathrm{K}$ due to elasticity. This value is much higher in comparison with metals but similar to other polymers, like polyamide or copolimers.
- The weaker thermoelastic effect manifests material fragility, particularly high in biodegradable polymers after modification.
- During 3 min of relaxation of biodegradable polymers, the stress decreases by about 28% and the temperature increases by about 0.4 K.
- High fragility of the modified polymer makes it impossible to realize the complete program of relaxation tests, however all results confirm the applicability of infrared methods to the investigation of polymer properties in terms of their biodegradability.

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Polimery przyjazne środowisku – identyfikacja ich biodegradawalności na podstawie efektów sprzężeń termomechanicznych

Streszczenie

W pracy badano charakterystyki mechaniczne oraz efekty sprzężeń termomechanicznych w biodegradawalnych polimerach. Trzy rodzaje próbek polimeru, tzn. materiał odniesienia oraz modyfikowany w kierunku podwyższonej biodegradawalności, poddano badaniom rozciągania oraz badaniom relaksacyjnym. Temperaturę deformowanych próbek mierzono w sposób bezstykowy za pomocą kamery termowizyjnej. Stwierdzono, że odkształcaniu materiału modyfikowanego aż do zerwania towarzyszy spadek temperatury zwany efektem termosprężystym. Oznacza to, że deformacja nie

przekracza zakresu sprężystego i tzw. wysokoelastycznego, nieliniowego chociaż odwracalnego etapu występującego w procesie odkształcania polimerów. Pomiar temperatury może być przydatny do badań tych polimerów – charakterystyki temperaturowe pozwalają zidentyfikować kruchość materiału związaną z jego biodegradawalnością.

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