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Dynamic stress relaxation of thermoplastic elastomeric biomaterials

Judit E. Puskas [a,*], Miroslawa El Fray [b], Matthew Tomkins [a,c,d], Lucas M. Dos Santos [a], Frank Fischer [d], Volker Altstädt [d]

[a] Department of Polymer Science, The University of Akron, Goodyear Polymer Center, Akron, OH 44325-3909, USA
[b] Division of Biomaterials and Microbiological Technologies, Polymer Institute, Szczecin University of Technology, Pulaskiego 10, 70-322 Szczecin, Poland
[c] Department of Chemical Engineering, The University of Western Ontario, London, ON, Canada
[d] Department of Polymer Engineering, University of Bayreuth, Universitätstr. 30, 95447 Bayreuth, Germany

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ABSTRACT

In this paper we present the results of comparative dynamic stress relaxation studies performed with poly(styrene-*b*-isobutylene-*b*-styrene) (SIBS), polyurethane (PU) and polyester (PED) biomaterials in air and simulated body fluid (SBF) at 24 °C and 37 °C. SIBS showed the highest value of relieved stress under constant strain (24.1% after 100,000 cycles in air) with PED and PU having similar relative change (12.2% and 10.5%). In spite of its softness (Shore A 56 vs. 80), the dynamic modulus (E_{dyn}) and stiffness of SIBS were in between PED and PU. The behavior of the materials was correlated to their structure: SIBS is an amorphous block copolymer with a long elastomer midblock, while PU and PED are semicrystalline segmented copolymers with much shorter soft blocks, and hydrogen bonding. SIBS and PED were relatively insensitive to SBF and temperature changes, while PU experienced the largest changes in physical properties *in vitro* (simulated body fluid, 37 °C).

1. Introduction

Polymeric biomaterials offer a wide range of valuable physical properties for various applications [1–6]. The extended range of physical properties available for polymers while retaining their biocompatibility makes them desirable as biomaterials. Even though polymers represent the largest class of biomaterials currently in use, there is still a constant driving force to find new biomaterials with suitable physical properties, or to apply known polymeric biomaterials to new applications. Polymers can be tailor-made for special applications. High performance thermoplastic elastomers (TPEs) with good solvent resistance, elasticity, tear strength and fatigue properties have found a wide range of medical applications [7]. Polyisobutylene (PIB)-based block copolymers are among those TPEs, and are gaining increasing popularity for biomedical applications [4,7–11]. These materials consist of a soft elastomeric PIB midblock, capped with hard polystyrene (PS) segments. The first linear triblock poly(styrene-*b*-isobutylene-*b*-styrene) (SIBS) copolymers with good mechanical properties were introduced in the early 1990's, and were made by living carbocationic polymerization [7–10]. SIBS resembles medical-grade silicone rubber, but does not need reinforcing fillers and chemical crosslinkers. SIBS has been used as the drug-eluting coating on the Taxus® coronary stent under the trade name of Translute™, since the FDA approval of this stent in 2004 [5]. Previous reports have shown that SIBS is biocompatible in ultra-long-term endoluminal (vascular) device applications and more stable than stents made of medical-grade polyurethanes (PUs) [4]. Our own investigation of SIBS with 30 wt% PS verified good biocompatibility and twice the fatigue life measured for medical-grade silicone using the hysteresis method adopted for soft biomaterials under stress-controlled conditions [12]. Under Single Load Testing (SLT, 1.25 MPa) SIBS30 displayed less than half the dynamic creep compared to silicone, both in air and *in vitro* (37 °C, in simulated body fluid).

As a continuation of this work, in this paper we present the results of strain-controlled fatigue testing of SIBS, since both creep and stress relaxation are important properties of biological tissues, related to their viscoelastic behavior. Strain-controlled fatigue testing, or in other words, dynamic stress relaxation testing of SIBS was performed in air and under simulated physiological conditions, and compared to polyurethane and polyester biomaterials.

2. Materials and methods

2.1. Materials

Commercially test marketed SIBS (TS30, low MW type with 30 wt% PS hard blocks, specific gravity = 0.95 g/cm [3], JIS-A hardness = 56, tensile stress = 10.8 MPa with 440% elongation) was

* Corresponding author. Tel.: +1 330 972 6203; fax: +1 330 972 5290.
E-mail address: jpuskas@uakron.edu (J.E. Puskas).

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Table 1
Tensile and hardness data.

Sample code	σ_r[a] (MPa)	ε[b] (%)	E_{mod}[c] (MPa)	Shore A
TS30	5.6 ± 0.8	220 ± 10	12.0 ± 1.7	56
PED26	5.0 ± 0.2	500 ± 60	14.0 ± 0.7	80
PU	21.0 ± 3.1	630 ± 50	20.0 ± 6.1	80

[a] σ_r = stress at break (ultimate tensile strength, UTS) at 100 mm/min.
[b] ε = elongation at break.
[c] E_{mod} = Young's modulus.

obtained by courtesy of Kuraray America, Inc., New York, USA, a subsidiary of Kuraray Co., Ltd., Osaka, Japan. Its molecular weight (MW) and molecular weight distribution were measured to be $M_n = 60{,}000$ g/mol and $M_w/M_n = 1.56$ [13]. Poly(aliphatic/aromatic-ester) multiblock copolymer (PED26) containing 26 wt% poly(butylene terephthalate) (PBT) hard blocks and 74 wt% dimmer fatty acid (DFA) soft blocks was synthesized by transesterification and polycondensation in the melt as reported earlier [14]. A medical grade polyurethane based on 4,4′-(diphenylmethane)-diisocyanate and poly(tetramethylene oxide) (Pellethane-80AE, PU) was obtained from Dow Chemicals, USA. Table 1 summarizes the tensile and hardness values reported for these polymers [12,15,16].

Simulated body fluid (SBF) was prepared by adding reagent grade chemicals to 8.8 L of distilled water to obtain ion concentrations (Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^-, HPO_4^{2-} and SO_4^{2-}) found in the human body: NaCl (55.4 g), $NaHCO_3$ (21.47 g), $MgCl_2 \cdot 6H_2O$ (1.79 g), Na_2SO_4 (0.0044 g), $NaNH_4HPO_4$ (1.43 g), KCl (3.29 g), $CaCl_2$ (1.29 g). All chemicals were obtained from Aldrich, Germany. The SBF was buffered with tris-hydroxymethyl aminomethane to a pH of 7.4 to mimic physiological conditions [17–19]. pH was measured by Hanna Instruments HI 8314 membrane pH meter.

2.2. Dynamic fatigue (stress relaxation) testing

Samples (S2 dumbbells, 3 mm thick, 12 mm^2 cross sectional area) for fatigue testing were prepared by injection molding using a pressure of ~50 MPa. Die temperatures were approximately 25 °C higher than the melting point of the polymers (TS30 = 100 °C, PED26 = 152 °C, PU = 195 °C), while the mold was kept at room temperature. 2–5 specimens were used in each test. An Instron 8400/8800 machine was used in conjunction with the DynMat custom software package (BASF). A 100 N Kraftaufnehmer KAF-S load cell was bolted to the cross-head in order to measure instantaneous forces on the polymer as a function of time. Strain was measured as the displacement of the moving head from the clamp. Testing in SBF was carried out in the temperature controlled environmental chamber, charged with SBF to the minimum level required to totally immerse the samples.

Long-term strain-controlled tests for evaluation of dynamic relaxation were conducted for 100,000 cycles in air using 10% maximum strain at 1 Hz. The minimum stress was controlled at 0.2 MPa to avoid buckling. Subsequently, 36,000 cycle tests were carried out: the first 12,000 cycles (3 h and 20 min) were conducted

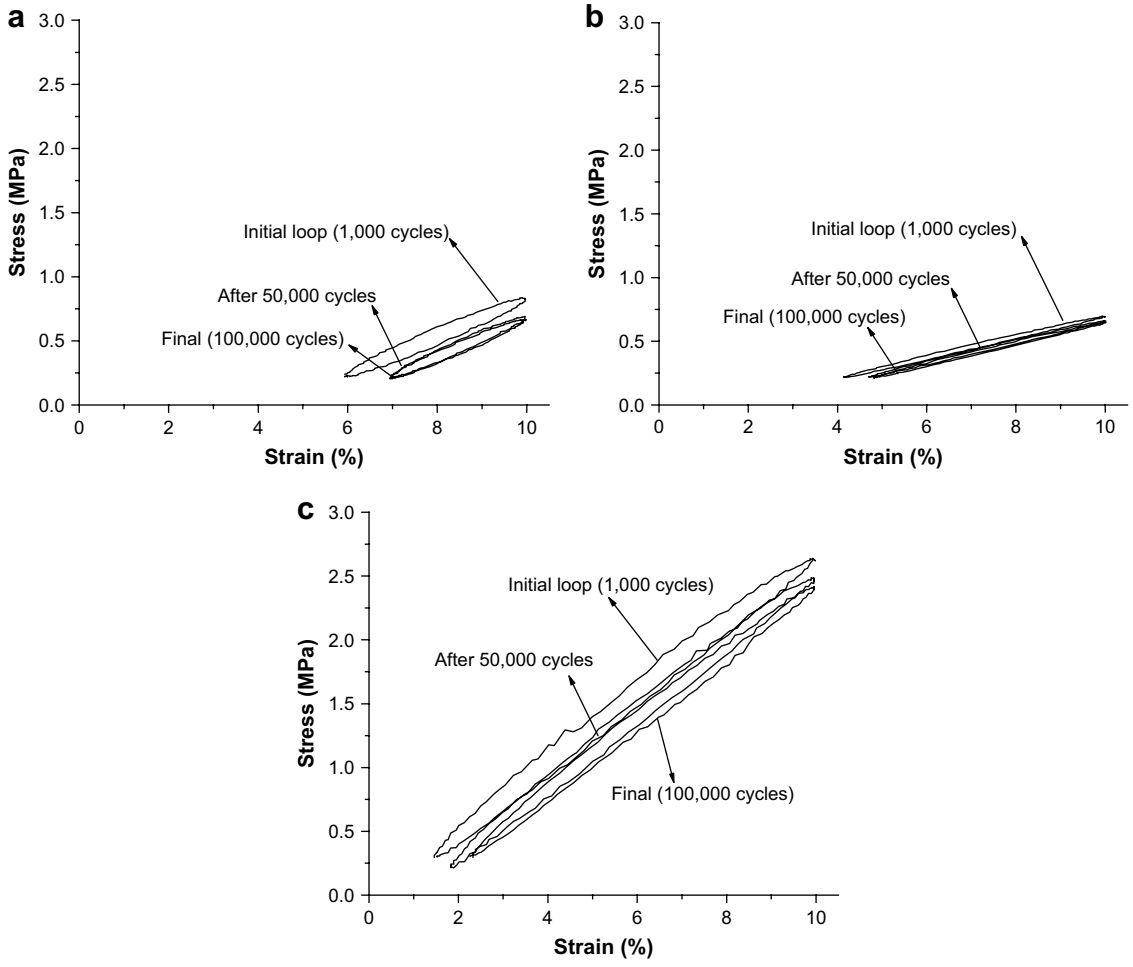

Fig. 1. Hysteresis loops of (a) TS30, (b) PED26 and (c) PU. 10% strain in air at 24 °C.

Table 2
Strain-controlled fatigue testing (100,000 cycles in air at 24 °C). 10% strain, 1 Hz.

Material	Initial stress (MPa)	Steady state (MPa)	Stress change (%)	E_{dyn} (MPa)	Damping (%)	Loss energy (J/m^3)	Stored energy (J/m^3)	Stiffness (MPa)
TS30	0.58	0.44	24.1	15	29	0.0022	0.0076	14
PED26	0.49	0.43	12.2	9.5	11	0.0013	0.0118	8
PU	1.52	1.36	10.5	29	12	0.0102	0.0822	27

in air at 24 °C in order to provide a baseline; the second 12,000 cycles were conducted in SBF at 24 °C, and the third period of 12,000 cycles was conducted in SBF at 37 °C to mimic physiological conditions.

3. Results and discussion

3.1. Dynamic stress relaxation in air at room temperature

SIBS block copolymers resembling silicone elastomer exhibit optimum tensile strength and elongation properties at around 30 wt% hard phase content [7,8,20]. The composition of TS30 is similar to PED26 in terms of hard segment content, but the latter has semicrystalline hard phases [15] and consequently is harder than SIBS30 (Shore A 80 vs. 56). More detailed comparative testing was performed with PED26 and TS30, including a PU with the same Shore A hardness as PED26. Fig. 1 displays hysteresis loops at 1000, 50,000 and 100,000 cycles, and Table 2 summarizes representative data obtained from the loops.

Testing very soft materials possess special challenges. In these measurements the minimum stress was controlled at 0.2 MPa to avoid buckling, so the minimum strain values were different for these materials (see Fig. 1). Nevertheless we can get some insight from the comparison of stress, dynamic modulus, loss and stored energy evolution during long-term testing (100,000 cycles), shown in Fig. 2.

TS30 showed the highest value of relieved stress under constant strain (highest dynamic relaxation at 24.1%, Table 2). PED26 and PU had similar relative change (12.2% and 10.5%). This can be explained by the differences in polymer structure and phase morphology, represented in Fig. 3. TS30 is an amorphous styrenic triblock copolymer with a long PIB elastomer midblock, with the PS sequences forming discrete 30–40 nm-size phases in the continuous PIB matrix [7]. In contrast, PU and PED26 are semicrystalline segmented copolymers with much shorter soft blocks and hydrogen bonding. This also reflects differences in the lost and stored energy and damping values – TS30 had the largest damping, due to its PIB soft segment; PIB-based rubbers and TPEs are known for their high damping properties [7]. In spite of its softness, the dynamic modulus (E_{dyn}) and stiffness of TS30 were found to be in between PED26 and PU (Table 2 and Fig. 2). E_{dyn} remained constant in all three cases (Fig. 2b), indicating good fatigue properties under the test conditions.

3.2. *Stress relaxation* in vitro

The effects of temperature and SBF on the fatigue properties (dynamic stress relaxation) of the TPEs were investigated at 10%

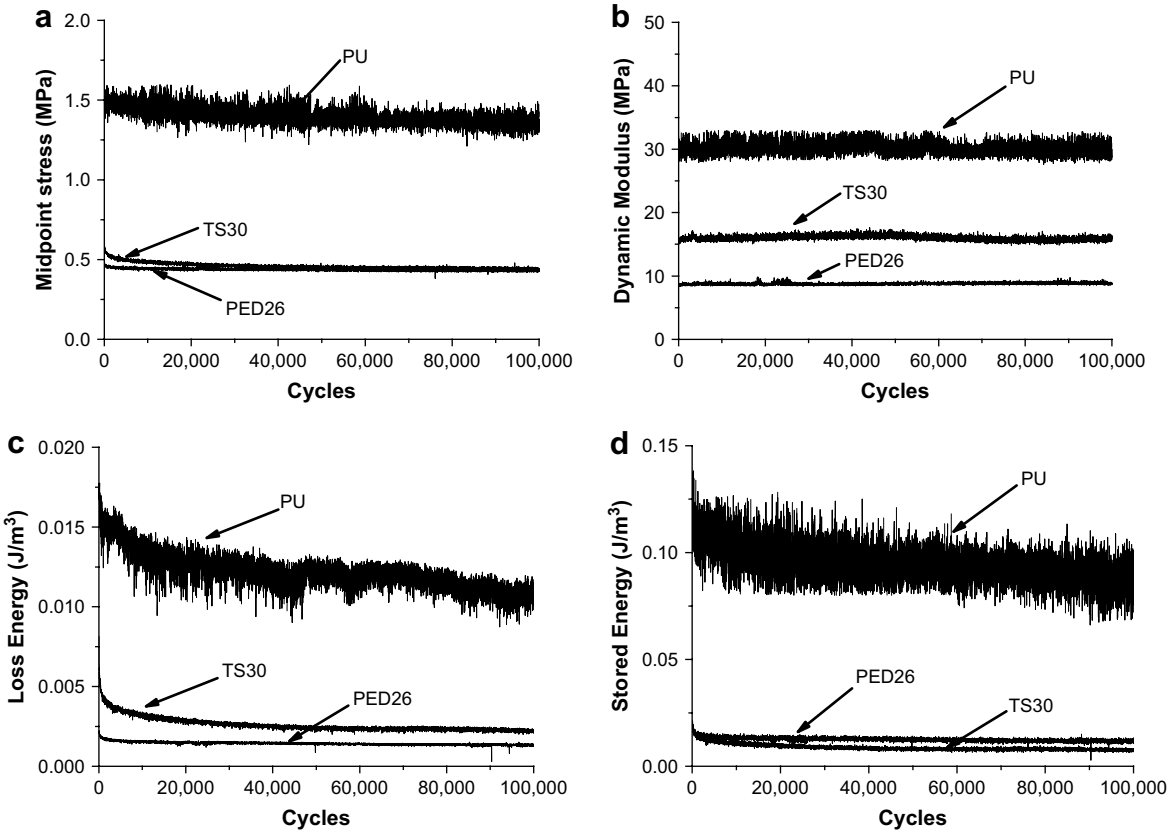

Fig. 2. Evolution of (a) midpoint stress, (b) dynamic modulus, (c) loss energy and (d) stored energy in TS30, PED26 and PU at 10% strain in air at 24 °C.

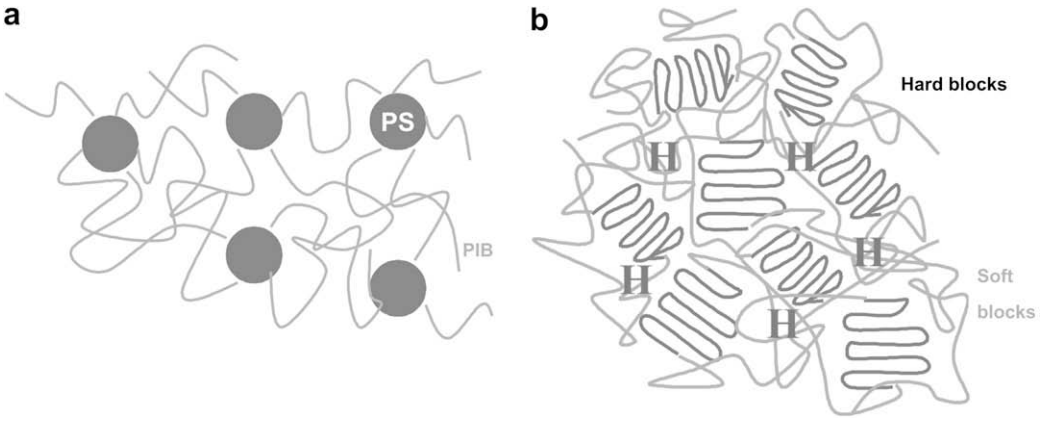

Fig. 3. Comparison of the structure and phase morphology of (a) TS30 and (b) PED26 and PU.

strain under three different conditions: (i) in air at 24 °C (0–12,000 cycles), (ii) in SBF at 24 °C (12,000–24,000 cycles) and (iii) in SBF at 37 °C (24,000–36,000 cycles). Similarly to that in Fig. 1, TS30 had larger hysteresis loops than PED26. In all cases the loop sizes decreased somewhat, while their shape did not change. This indicates that very little or no structural change or permanent damage occurred.

Fig. 4a shows changes of relieved stress under constant dynamic strain. The midpoint of stress values obtained from the hysteresis loops in air at 24 °C for TS30 and PED26 were found to be much lower than those of PU. Upon the addition of SBF, a change in stress was observed for PU, while stresses in PED26 and TS30 remained nearly constant. Upon heating the SBF to 37 °C, each polymer experienced a drop in midpoint stress values, with the largest change observed in PU. The dynamic moduli and the stored and lost energy derived from the hysteresis loops are presented in Fig. 4b, c and d, respectively. Fig. 4b shows that PED26 has lower E_{dyn} than TS30, despite their similar initial stresses (Table 2) and soft phase

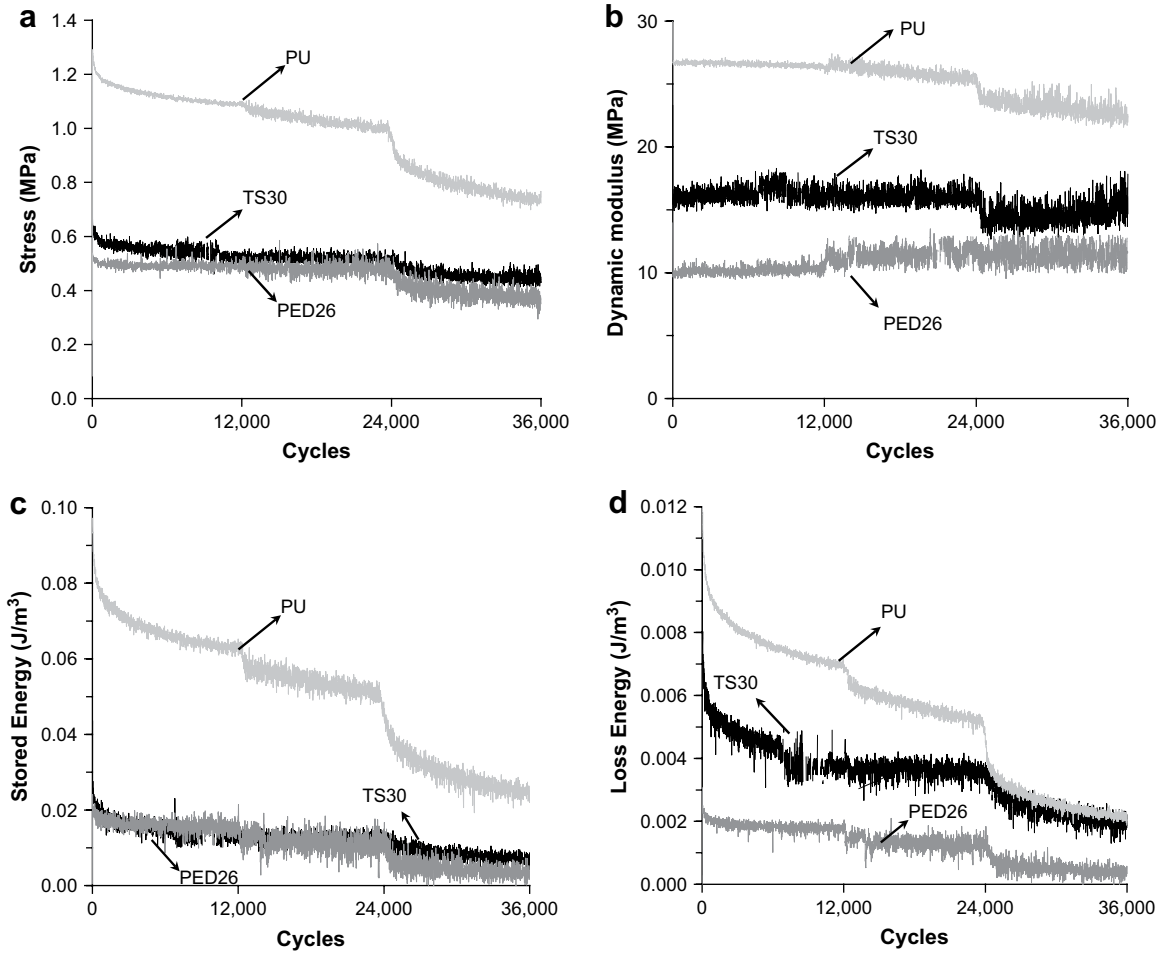

Fig. 4. Stress (a), dynamic modulus (b), stored (c) and loss energy (d) evolution in TS30, PED26 and PU at a strain of 10% in air at 24 °C (0–12,000 cycles), in SBF at 24 °C (12,000–24,000 cycles) and in SBF at 37 °C (24,000–36,000 cycles).

content. In terms of the stored energy, PU is the stiffest whereas TS30 and PED26 have very comparable values. In terms of damping, PED26 and PU behave similarly, whereas TS30 has the highest damping (Table 2). TS30 and PED26 were relatively insensitive to SBF and temperature changes, while PU experienced the largest changes in physical properties and proved to be the most sensitive to elevated temperature (37 °C). It should be mentioned that, because of the relative softness of the materials (especially TS30) the stress values were close to the measurement limits of the instrument, resulting in small signal to noise ratios. However, comparison of the effect of SBF and temperature on the materials investigated was possible under the conditions used. Both of PED26 and TS30 performed relatively better than PU under simulated physiological conditions, which experienced the largest changes in dynamic properties.

4. Conclusions

The dynamic stress relaxation properties of a linear SIBS copolymer with 30 wt% PS (TS30), an emerging soft biomaterial when compared with those of a polyester having 26 wt% hard segments (PED26) and a commercial PU. Testing was carried out in air and in SBF at 24 °C and 37 °C, using the hysteresis method that is being developed for the testing of very soft materials such as TS30. During long-term testing (100,000 cycles) the TS30 showed the highest dynamic relaxation. The TS30 and the PED26 were relatively insensitive to SBF and temperature changes, while the PU experienced the largest changes in physical properties and proved to be the most sensitive to elevated temperature (37 °C). The findings in this work are significant for the fatigue testing of soft biomaterials and long-term implant applications.

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References

[1] Martinie HM. US Patent 3,683,421; 1972.
[2] Koch R, Freudiger S, Fluckiger H. US Patent 5,192,322; 1993.
[3] Dumitriu S, editor. Polymeric biomaterials. 2nd ed. New York: Marcel Dekker; 2002.
[4] Pinchuk L, Wilson GJ, Barry JJ, Schoephoerster RT, Parel JM, Kennedy JP. Biomaterials 2008;29:448–60.
[5] Publication PO30025 U.S. Food and Drug Administration. Taxus Express2™ Paclitaxel-eluting coronary stent system (monorail and over the wire). Washington, DC: U.S. Government Printing Office; 2004.
[6] Ratner BD, Hoffman AS, Schoen FJ, Lemons JE, editors. Biomaterials science: an introduction to materials in science. 2nd ed. Amsterdam: Elsevier Press; 2004.
[7] Holden G, Kricheldorf HR, Quirk R, editors. Thermoplastic elastomers. 3rd ed. Munich: Hanser Publishers; 2004.
[8] Kennedy JP, Puskas JE, Kaszas G, Hager W. US Patent 4,946,897; 1990.
[9] Kaszas G, Puskas JE, Hager W, Kennedy JP. J Polym Sci Part A Polym Chem 1991;29(3):427–35.
[10] Puskas JE, Paulo C, Anthony P. US Patent 6,747,098; 2004.
[11] Puskas JE, Chen Y. Biomacromolecules 2004;5(4):1141–54.
[12] El Fray M, Prowans P, Puskas JE, Altstädt V. Biomacromolecules 2006;7(3): 844–50.
[13] Puskas JE, Antony P, El Fray M, Altstädt V. Eur Polym J 2003;39(10):2041–9.
[14] El Fray M, Altstädt V. Macromol Symp 2003;199:125–33.
[15] El Fray M, Altstädt V. Polymer 2004;45(1):263–73.
[16] El Fray M, Altstädt V. Polymer 2003;44(16):4635–42.
[17] Renke-Gluszko M, El Fray M. Biomaterials 2004;25(21):5191–8.
[18] Cahoon JR, Holte RN. J Biomed Mater Res 1981;15(2):137–45.
[19] Cho SB, Miyaji F, Kokubo T, Nakamura T. J Mater Sci Mater Med 1998; 9(5):279–84.
[20] TS Polymer (Data Sheet). Kurary Co. Ltd., Tsukuba Research Lab; 1997.