MECHANICAL HYSTERESIS LOOP METHOD FOR CREEP ASSESSMENT OF ELASTOMERIC NANOCOMPOSITES

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Keywords: fatigue of elastomers, dynamic creep, thermoplastic elastomers, nanocomposites

Abstract

The mechanical hysteresis loop measurement method was successfully applied to evaluate the fatigue properties of elastomeric nanocomposites. New multiblock polyester-matrix nanocomposites were prepared by the in situ polycondensation. Materials, differing in nanometric SiO_2 concentration (up to 0.3wt%), exhibit different "dynamic creep" behaviour which can be correlated with the nanoparticles content.

1 Introduction

Many loads are cyclic in nature, therefore the characterization of deformation and fracture properties of materials (natural or synthetic) is of great interest. Specifically, polymers and tissue (tendon, heart, joints) experienced to loading patterns, show time-dependent viscoelastic properties in term of changes in stiffness, hysteresis loop or creep behavior [1]. To evaluate fatigue of soft materials, the mechanical hysteresis loop method is very useful, since it provides information about structural changes of the material [2,3]. Silicone rubber or so called Swanson finger joint is the most popular material for hand plastic surgery (in metacarpophalangeal join reconstruction in rheumatic arthritis patients), since it demonstrates good biocompatibility and flexibility, however, poor mechanical properties under repeating cyclic loading which brings patients to complications, including implant rupture [4]. Therefore, there is a need for implants with enhanced mechanical (fatigue) properties. New poly(aliphatic/aromatic-ester)s (PED) of segmented (multiblock) structure belong to the group of thermoplastic elastomers and are composed of semicrystalline poly(butylene terephthalate) (PBT) (hard segments) and dimer of fatty acid, namely hydrogenated dilinoleic acid (DLA) (soft segments) [5,6]. The resulting nanostructured morphology contributes to different mechanical properties, locating these new PED materials between commercially available thermoplastic poly(urethane-ether) and poly(ester-ether) elastomers. Their long-term mechanical properties (fatigue) are superior compared to medical grade polyurethanes or silicone rubber [7] what makes them as very interesting materials for soft tissue reconstruction. PED copolymers have been evaluated as candidate materials for preparation of temporary tendon prosthesis [6]. PEDs are synthesized without thermal, and often irritant thermal stabilizers due to excellent oxygen and thermal stability. This feature is especially important if material is used for biomedical applications. PED copolymers are biocompatible *in vitro* and *in vivo* [8,9], and when specially modified with active molecules, they show antibacterial properties [6]. To enhance the mechanical properties of these materials, we prepared composites using fumed silica of variable concentration, but not exceeding 1wt%

[10]. The aim of this work was to evaluate the fatigue properties of these new elastomeric nanocomposites by using mechanical hysteresis loop method.

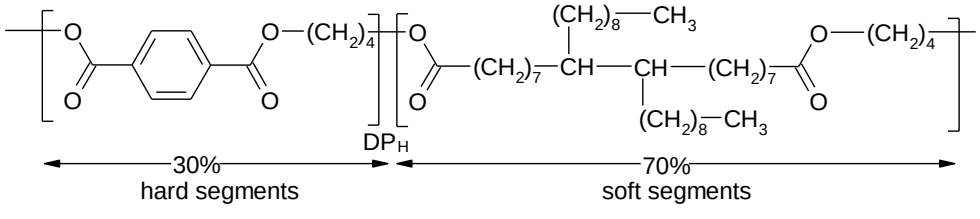
2 Materials and testing methods

The following chemicals were used for the synthesis of elastomeric nanocomposites: dimethyl terephthalate (DMT) which constituted the hard segments was purchased from Elana, Poland; 1,4-butanediol (BD) of analytical grade and the catalysts ($Ti(OBu)_4$) were purchased from Aldrich. Dimerized fatty acid (DLA) which constituted the soft segments and which is a molecule resulting from the covalent bonds formation between aliphatic chains of two units of linoleic acid (here called also a dilinileic acid) was generously supplied by the Uniqema Croda, The Netherlands. The nanofiller, Aerosil A130, hydrophilic (HF), 16 nm in size, was generously provided by Evonik.

Polymer/nanosilica composites were prepared *in-situ* during polycondensation. The synthesis route was the classic two-stage melt polycondensation. In the first stage, DMT and BG were introduced to a steel reactor and the transesterification reaction was run at 150-180 °C in the presence of a catalyst. Methanol was collected as a by-product and continuously removed from the reactor *via* a reflux condenser. After the conversion reached 95%, which was estimated based on the amount of released methanol, nano-silica was added as a dispersion in DLA (during polycondensation). The dispersion of nanofiller in co-monomer was prepared prior to adding it to the reactor. To obtain good dispersion and to disintegrate the agglomerates, high shearing forces (IKA ULTRA-TURRAX T-25, 12 000 rpm for 5 minutes) were applied. The dispersion was added followed by the titanate (IV) catalyst. The pressure was then decreased step-wise in order to eliminate the BG excess. After that the temperature was raised and the polycondensation stage was run at 250-255 °C and at 0.2-0.4 hPa pressure. The reaction end-point was estimated upon the power consumption of the stirrer motor when the product of highest melt viscosity was obtained. After reaction, the temperature was decreased to 190-200 °C and the polymer bulk was evacuated from the reactor through a nozzle to a Teflon plate. Then the polymer melt was cooled down to room temperature in air, dried for 3 days and cut into small pellets.

The hard segments content was 30 wt. % by feed in all materials – resulting in soft, transparent and elastomeric polymers, only the nanofiller amount varied as 0.1, 0.2 and 0.3 wt. %, respectively. The segmental composition and the nanofiller amount were selected upon previous experience with TiO_2–based polymer matrix nanocomposites [11,12].

The chemical structure of the polymer matrix is presented in *Fig.1*. The neat material and the nanocomposites were transparent.



DP_H - degree of polycondensation of hard segments = 1.23 (30 wt%)

Figure 1 Chemical structure of the neat PBT/DLA copolymer

Mechanical testing. The quasi-static tensile data for compression moulded samples were collected at room temperature with an Instron 3366 tensile tester equipped with a 500 N load cell, at a crosshead speed of 100 mm/min. The strain was measured using the clamp displacement according to DIN 53 455. The starting clamp distance was 25 mm. The results were averaged from 6 specimens with cross section of 0.5×4 mm.

Mechanical hysteresis loop method for fatigue testing. An electrodynamic test machine with a digital controller, Instron Electropuls E3000 and Bluehil software package was used to study nanocomposite properties. Testing machine was equipped with a 500-N load cell, and the strain was measured as the clamp displacement. For the hysteresis measurement method, the stepwise increasing load testing procedure (SILT) was used as a rapid test for the determination of the load dependent quantity changes [2]. In this procedure, the dynamic load increases after a certain number of cycles, while the load ratio remains constant. In other words, the amplitude of the load is stepwise increased and held constant within each step for a definite number of cycles. The specimens were subjected to a stress controlled sinusoidal oscillation. The frequency, f, was in a range of 1 - 4 Hz and no hysteretic heating was detected at the surface of the specimen. The SILT method was carried out in order to obtain load limits for a long time dynamic loading. The maximum stress was set at a value corresponding to one of ten prescribed stress levels in the range 5 – 50% of the ultimate tensile stress (UTS) at 5% increments. The stress was kept constant during a period of 1 000 cycles and set to the next higher level afterwords. An interval of 100 cycles has been implemented between every step to allow the controller to reach a higher loading level. The frequency of the cyclic loading was varied according to the stress levels such as:

- at stress levels of 5,10 and 15 % of the UTS the frequency was 4 Hz,
- at stress levels of 20, 25 and 30 % of the UTS the frequency was 3 Hz,
- at stress levels of 35 and 40 % of the UTS the frequency was 2 Hz,
- at stress levels of 45 and 50% of theUTS the frequency was 1 Hz. The digital controller was used to keep the load level constant at each stress level with an accuracy of 5 %.

The load ratio, R, was 0.1. This load ratio indicates that sinusoidal oscillations are cyclic repetitious in tension mode.

3 Results and discussion

The results from the quasi-static tensile measurements are given in Table 1. The σ_r values (UTS) in Table 1 are the baseline for the design of the testing protocol for the hysteresis measurements.

n°	**Hard/soft segments ratio (wt. %)**	**HF-SiO_2 (wt.%)**	**Young's modulus (MPa)**	**σ (UTS) (MPa)**	**ε (%)**
1.	30/70	0	13.0±1.85	6.59±0.25	869±99
2.	30/70	0.1	11.7±0.55	7.43±0.26	590±51
3.	30/70	0.2	11.0±0.81	6.96±0.16	883±53
4.	30/70	0.3	12.3±0.48	6.60±0.13	580±40

σ – (UTS) stress at break (ultimate tensile strength), ε – elongation at break

Table 1. Static tensile properties of nanocomposites

Figs. 2 a-d demonstrate the characteristic pattern of changes at the maximum strain of PBT/DLA samples with and without nanoparticles during *SILT*. For all samples the maximum strain exponentially increases with increasing load level. The comparison of the *SILT* results of samples, characterized by different concentration of nanoparticles at constant hard/soft segments ratio, indicate that sample containing 0.3wt% of SiO_2 reach the load limit at higher stresses and after a higher number of steps compared to polymer without nanofiller.

The characteristic change in the shape of the hysteresis loop is demonstrated in Figs. 3a,b. The area of the hysteresis loop increases with increasing load level for the neat copolymer (Fig. 3a) and for polymer containing nanometric silica (Fig. 3b), with differences being negligible for these materials.

Performed *SILT* test allowed to determine the absolute change of the stiffness within a single stress level, which drops up to 5 %.

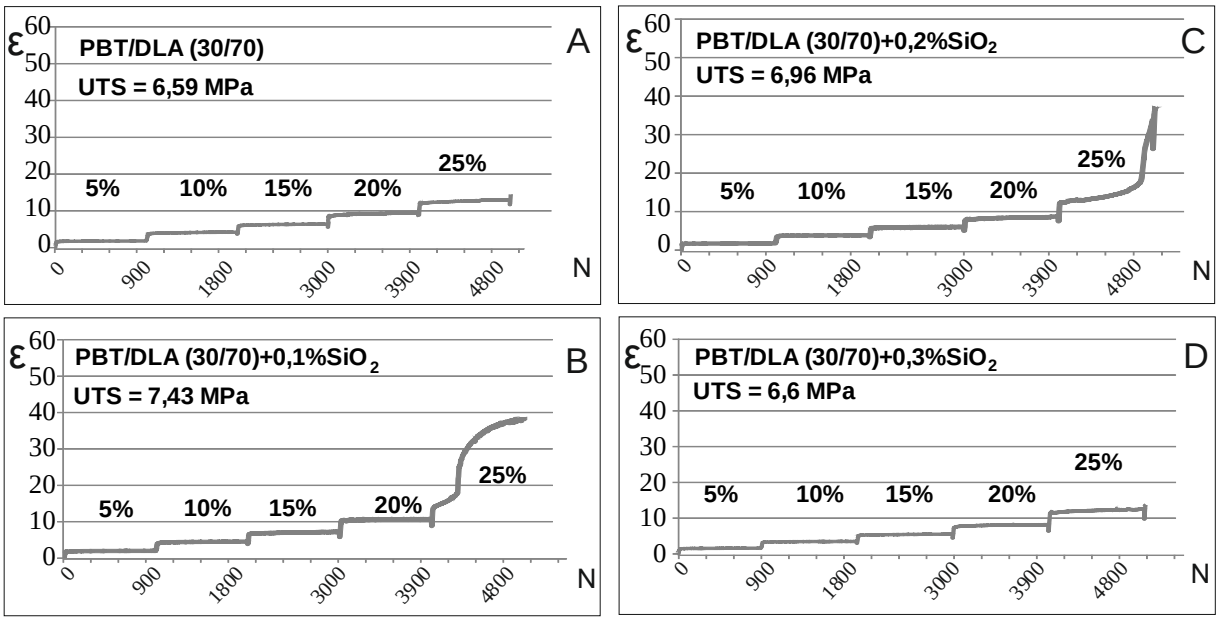


Figure 2 Patterns of change in the strain for the PBT/DLA copolymers containing a variable content of SiO_2 nanoparticles; a) the neat PBT/DLA, b) 0.1% SiO_2, c) 0.2% SiO_2, d) 0.3% SiO_2. The numbers on the curves refer to the percentage of the UTS. f = 4 Hz and 3 Hz. T = 24 °C.

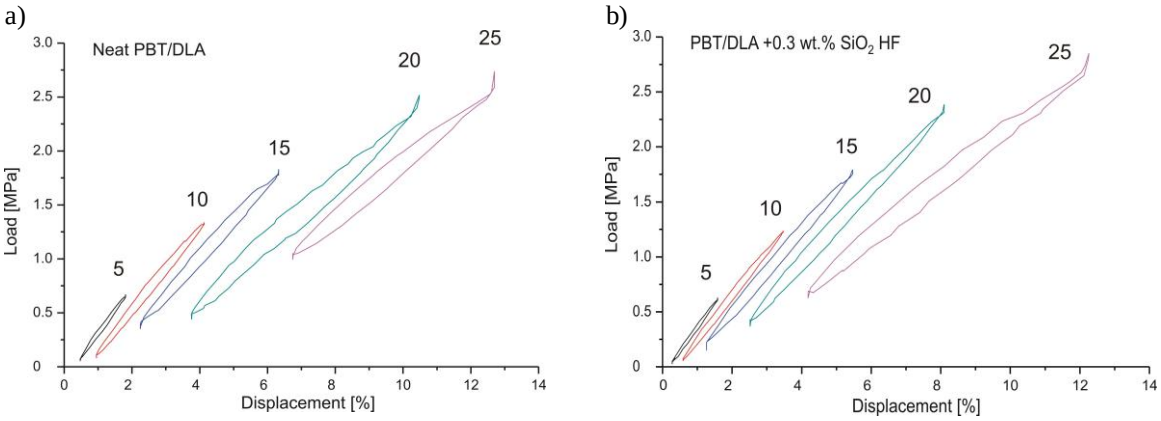


Figure 3 Representative hysteresis loops for each load level (the numbers on the loops refer to the percentage of the UTS); a) the neat PED copolymer; b) sample containing 0.3 wt% nanometric silica. T = 24 °C.

Then the load value, σ_L (Table 2) ascribed to this step level can be determined and further used for another experiment, such as long term dynamic loading (referred to as "dynamic creep") of polymers during a single load testing, as reported for multiblock copolymers in [7].

N°	**Hard/soft segments ratio (wt. %)**	**HF-SiO_2 (wt. %)**	**σ_L (MPa)**
1.	30/70	0	1.09
2.	30/70	0.1	0.74
3.	30/70	0.2	0.79
4.	30/70	0.3	1.32

Table 2. Load values, σ_L derived from SILT test corresponding to the dynamic modulus drop up to 5% within a single load level

4 Conclusion

For the first time, the fatigue properties of elastomeric nanocomposites were evaluated by the hysteresis measurement method. The strain and stiffness were successfully evaluated during a stepwise increasing load test. As expected, poly (aliphatic/aromatic-ester) copolymers containing different concentration of nanometric silica exhibit a different performance during the load-carrying cyclic testing. Based on the hysteresis measurement method it was possible to evaluate good load-carrying properties of polymers containing a high amount of the nanoparticles. Therefore, these materials can be considered as good candidates for applications where materials are subjected to oscillatory deformations (for example finer joints).

Acknowledgements

The authors would like to thank the National Research Centre (NCN) for the support of this research within research project N N507 47 1838.

References

[1] Argon A.S. *Topics in Fracture and Fatigue*. Springer Verlag, New York (1992).

[2] El Fray M., Altstädt V., Fatigue behaviour of multiblock thermoplastic elastomers. 1. Stepwise increasing load testing of poly(aliphatic/aromatic-ester) copolymers, *Polymer*, 44, pp. 4635-4642 (2003)

[3] El Fray M., *Nanostructured elastomeric biomaterials for soft tissue reconstruction*, Publishing House of the Warsaw University of Technology, Warszawa (2003).

[4] Dumitriu S., *Polymeric Biomaterials*, Marcel Dekker Inc., New York (2002).

[5] Prowans P., El Fray M., Slonecki J.: Biocompatibility studies of new multiblock poly(ester-ester)s composed of poly(butylene terephthalate) and dimerized fatty acid, *Biomaterials*, 23, pp. 2973-2978 (2002).

[6] El Fray M., Bartkowiak A., Prowans P., Slonecki J., „Physical and mechanical behaviour of electron-beam irradiated and ethylene oxide sterilized multiblock polyester", *J. Mater. Sci.- Mater. Med.*, 11 (11), pp. 757-762 (2000).

[7] El Fray M., Altstädt V., Fatigue behaviour of multiblock thermoplastic elastomers. 2. Dynamic creep of poly(aliphatic/aromatic-ester) copolymers, *Polymer*, 44, pp. 4643-4650 (2003).

[8] Renke-Gluszko M., El Fray M., The effect of simulated body fluid on mechanical properties of multiblock poly(aliphatic/aromatic-ester) copolymers, *Biomaterials*, 25, pp. 5191-5198 (2004).

[9] Prowans P., El Fray M., Jursa J., Study on degradation and systemic toxicity of multiblock poly(aliphatic/aromatic-ester) copolymers, *Polimery*, 50 (2), pp. 131-138 (2005).

[10] El Fray M., Rybko M., Piegat A., Silica-polyester nanocomposites prepared by polycondensation in situ: synthesis and mechanical properties, *Materials Science Forum*, 714, pp. 277-282 (2012).

[11] El Fray M., Boccaccini A.R., Novel hybrid PET/DFA-TiO_2 nanocomposites by *in-situ* polycondensation, *Materials Letters*, 59 (18), pp. 2300-2304 (2005).

[12] Piegat A., El Fray M., Jawad H., Chen Q., Boccaccini A. R., Inhibition of calcification of polymer-ceramic composites incorporating nanocrystalline TiO_2, *Advances in Applied Ceramics*, 107(5), pp. 287-292 (2008).