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Fatigue behaviour of multiblock thermoplastic elastomers. 1. Stepwise increasing load testing of poly(aliphatic/aromatic-ester) copolymers

M. El Fray*, V. Altstädt

Department of Polymer Engineering, University of Bayreuth, Universitaetsstr. 30, D-95447 Bayreuth, Germany

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Abstract

Fatigue properties of poly(aliphatic/aromatic-ester) (PED) multiblock copolymers were evaluated based on the hysteresis measurement method. This method allows the digitalization of the hysteresis loop and beside the determination of stress and strain-related parameters, stored energy, lost energy, damping and dynamic creep behaviour can be determined. The correlation between hard/soft segment concentration of PED copolymers, and fundamental parameters, which derived during the cyclic loading (using *stepwise increasing load testing*, *SILT*), has indicated a good load-carrying performance of polymers containing a high amount of the hard phase. PED copolymers compare very well with commercially available poly(ester–ethers) and show a much better performance than poly(ester–urethanes) when samples are loaded at the same fatigue stress level relative to their ultimate tensile strength. Softer PEDs and poly(ether–urethane) copolymer show much higher values of dynamic modulus than chemically cross-linked silicone elastomer. Therefore, these multiblock copolymers can be considered as good candidates for applications where materials are subjected to oscillatory deformations (for example passive flexor tendon reconstruction).

Keywords: Poly(butylene terephthalate); Dimer fatty acid; Hysteresis measurements

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1. Introduction

The characterisation of deformation and fracture properties of materials is of great interest, particularly if they are subjected to cyclic loads (fatigue). Many loads are cyclic in nature like in the case of tendons which experience loading patterns in vivo and show time-dependent viscoelastic properties in terms of change in stiffness, hysteresis loop or creep behaviour [1].

When a polymer system is subjected to an applied stress, a great variety of chemical and rheological events may occur in a given polymer. The net effect of the several competing processes depends on many factors, including temperature, environment, and basic molecular properties of the polymer [2].

In a conventional fatigue test, the specimen is subjected to cyclic loading and the number of cycles to failure is monitored [2,3]. The results are then presented as S–N curves, i.e. stress versus number of cycles to failure.

Another testing approach is the hysteresis method which additionally gives information about structural changes of the material. Different properties can be determined simultaneously—stress, strain amplitude, stiffnesses and stored and lost energies, material damping and the cyclic creep behaviour [4–7]. A wide range of different polymeric systems like polymer blends, block and graft copolymers, and also composites have already been investigated for the evaluation of fatigue properties [8,9]. Especially, thermoplastic multiblock elastomers (TPE) are a very interesting class of polymeric materials but their fatigue properties are not widely studied via this new hysteresis measurement method [9].

TPEs are composed from different blocks of macromolecule segments which are alternated along the main chain. They are connected through thermally labile connections (often referred to physical cross-links). These junctions can be glassy or crystalline; they might be ionic associations or groups connected by hydrogen bonds. These groups have features of physical cross-links and they are called as the

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* Corresponding author. Address: Technical University of Szczecin, Polymer Institute, Pulaskiego 10, 70322 Szczecin, Poland.

E-mail address: mirfray@ps.pl (M. El Fray).

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'hard segments'. In contrast to chemically cross-linked materials, the physical cross-links are reversible and can be disrupted at elevated temperatures or in solvents, which give the material its good processability. Increasing concentration of hard segments contribute to an increase of the Young's modulus and the yield stress. Other segments which are characterized by 'small' elastic modulus, low glass transition temperature and low bond cohesion energy are called the 'soft segments' and contribute to the improvement of both the flexibility and extensibility of TPEs [10,11].

Segmented copolymers such as poly(ether–ester)s (PEE) or segmented polyurethanes (PEU) possess a high tensile strain comparable to chemically cross-linked rubbers ranging from 500 to 800%, while their tensile stress is higher than that of chemically cross-linked rubbers, i.e. 20–50 MPa for PEE or PEU and 10–30 MPa for cross-linked rubbers [12–15]. By varying the hard/soft segments composition and concentration, and additionally using thermal and mechanical conditioning, the multiblock copolymers are made to change their physical, chemical and mechanical properties, as well as the morphology. They behave as classical thermoplastics of high stiffness or as polymeric materials of high elasticity, and change their physical properties from crystalline to amorphous polymers.

Aliphatic, most frequently amorphous oligoethers, i.e. poly(tetramethylene oxide) are used as building blocks for soft segments. However, polymers containing aliphatic units, derived from a long chain dicarboxylic aliphatic acid and polyester hard segments, are also known [16–20]. These multiblock poly(aliphatic/aromatic-ester) (PED) copolymers are composed of dimer fatty acid (DFA) and poly(butylene therephthalate) (PBT). DFA imparts to the materials excellent oxidation resistance and the processing flexibility. PED copolymers show good biocompatibility with no adverse biological effects after long term in vivo experiments [21]. Their thermal and static mechanical properties were already described [17] and match requirements to perform their function in the planned application as temporary flexor tendon prosthesis.

To select appropriate material for the development of artificial tendons as temporary devices until the neosheath generation, important criteria in term of biofunctionality of such prosthesis are not only tissue compatibility and appropriate static mechanical properties (strength and flexibility) but also fatigue behaviour during the dynamic loading. Silicone rubber or so called Hunter prosthesis (silicone-Dacron prosthesis) is the most popular material which meets these criteria associated with biocompatibility and flexibility, however, their fatigue properties, according to the authors knowledge, have never been studied before.

Therefore, in this study, fatigue properties have been investigated for new PED multiblock copolymers and for silicone, a medical grade elastomer (Silastic®). Hysteresis measurements were successfully applied in the study of fatigue properties of these soft materials. This method is very useful because it gives information about the structural changes of the material as a function of the cyclic fatigue loading conditions.

Since investigations on the fatigue properties of multiblock thermoplastic elastomers are still rare in literature, different commercially available TPEs have been included in the testing protocol to give readers an overview on a broader spectrum of elastomeric materials, which are currently used in medical applications. These include thermoplastic elastomers of poly(ester–ether) type and medical grade poly(ether–urethane)s.

2. Experimental

2.1. Material

The synthesis method of PED copolymers, involving transesterification and polycondensation from the melt has been described in previous publications [17,18]. Commercially available thermoplastic elastomers of Shore D hardness 55 were also included: poly(ester–ether) thermoplastic elastomers of Arnitel 550, Arnitel UM 551 (DSM, The Netherlands) and Elitel (Elana SA, Poland) as well as medical grade poly(ether–urethane)s Pellethane 55 DE (DOW Chemicals, USA). Soft PED copolymers were compared to poly(ether–urethane) of hardness Shore A of 80 (Pellethane 2363-80 AE). Additionally, chemically cross-linked medical grade Silastic® (Dow Corning, USA) silicone elastomer has also been used.

2.2. Sample preparation

Samples for tensile and fatigue testing were prepared by injection moulding at a pressure of around 50 MPa. The die temperatures were approximately 3–5 °C higher than the melting point of the polymers, while the mould temperature was kept at room temperature. Samples were in a shape of dog-bones (samples S-2) with a thickness of 3mm and 12 mm^2 in the cross-section area.

2.3. Tensile testing

The quasi-static tensile data were collected at room temperature with an Instron TM-M tensile tester, equipped with a 500 N load cell, at a cross-head speed of 100 mm/min. The strain was measured as the clamp displacement (the starting clamp distance was 25 mm). The obtained results were averaged from 6 specimens (the test was performed according to DIN 53 455 standard).

2.4. Fatigue testing

A servo-hydraulic test machine with a digital controller (Instron 8400/8800) and a software package for the evaluation of the hysteresis loop [22] was used to study the PED copolymers and other TPEs, including silicone elastomers as a reference material. A servo-hydraulic test machine was equipped with a 200 N load cell and 10 kN cylinder. The strain was measured as the clamp displacement. A possible phase shift between stress and strain signal was minimized below 20 μs by the experimental set-up.

The experimental setup used for performing hysteresis measurements is shown schematically in Fig. 1. It is designed in a way that a possible phase shift between stress and strain signal is minimized. The available software package makes it possible that the hysteresis loop of any polymer material, which is measured continuously, is digitized and a mid-curve is calculated in the hysteresis loop. The mid-curve is intersecting the hysteresis loop for equal strain. By this it is possible, also in the case of non-linear viscoelastic material behaviour, to determine strain-, stiffness- and energy-related material properties. In addition, very small changes in material damping can be detected by this method and used as a damage criterion for the understanding of the material behaviour.

For the hysteresis measurement method, the stepwise increasing load testing procedure (SILT) is helpful as a rapid test for the determination of the load-dependent quantity changes [4,6,7]. 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 afterwards. 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 the UTS 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%.

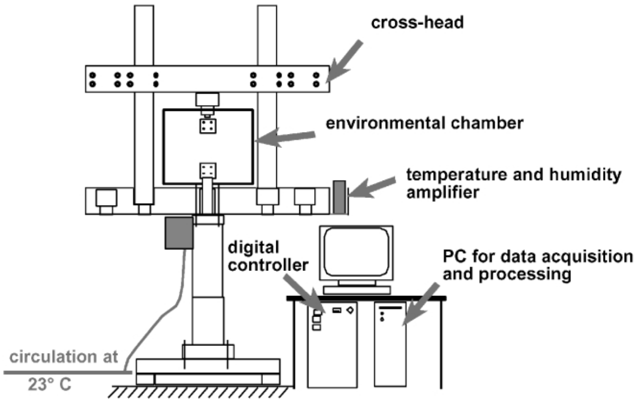

Fig. 1. Experimental set-up for hysteresis measurements.

The load ratio, R, was 0.1. This load ratio indicates that sinusoidal oscillations are cyclic repetitious in tension mode. The temperature of the sample was monitored with a thermo couple and no effect of hysteretic heating was observed.

3. Results and discussion

The formulations of the studied polymers and the results from the quasi-static tensile measurements are given in Table 1 and Fig. 2. The σ_r values (UTS) in Table 1 are the baseline for the design of the testing protocol for the hysteresis measurements.

Fig. 3(a)–(e) demonstrate the characteristic pattern of changes at the maximum stress and strain, and the dynamic modulus of PED samples during SILT. For all PED samples the dynamic modulus exponentially decreases with increasing load level. If the absolute change of the stiffness within a single stress level drops up to 5%, then the load value, σ_L (Table 2) ascribed to this step level can be used for another experiment, such as long term dynamic loading (referred to as 'dynamic creep') of polymers during a single load testing, as reported in Ref. [23].

The comparison of the SILT results of samples, characterized by different hard/soft segments ratio, and in consequence in their physical properties as from flexible, soft material (M2674, Fig. 3(a) to rigid polymer (M7030, Fig. 3(e)), indicate that rigid samples reach the load limit at higher stresses but after a lower number of steps compared to softer polymers (semi-rigid samples show characteristic necking during subsequent cyclic loading which is an evidence of plastic deformation).

The influence of the hard segments content on fatigue properties evaluated, by hysteresis measurements, is also well demonstrated by the change in the shape of the hysteresis loop (Fig. 4(a)–(e)). With higher hard segments content (higher crystallinity), a lower displacement and a larger area of the hysteresis loop were observed. The area of the hysteresis loop increases with increasing load level for each polymer. It has been found that displacement of the hysteresis loop depends on the test frequency as demonstrated in Fig. 4(e)), representing a copolymer tested at

Table 1
Static tensile properties and melting temperature of PED copolymers and reference copolymers. Sample geometry (S-2) according to ASTM D 1897-77. Cross-head speed of 100 mm/min

Sample code	PBT (wt%)	DFA (wt%)	E_{mod} (MPa)	σ_Y (MPa)	σ_r (UTS) (MPa)	ε_r (%)	T_m (°C)
M2674 (19[a])	26	74	14 ± 0.7	–	5 ± 0.2	502 ± 59	152
M4060 (37[a])	40	60	42 ± 0.4	6 ± 0.2	11 ± 1.5	570 ± 40	183
M5050 (47[a])	50	50	78 ± 2.3	9 ± 0.2	21 ± 0.7	540 ± 45	196
M6040 (55[a])	60	40	145 ± 3.6	13 ± 0.3	23 ± 1.4	400 ± 42	200
M7030 (60[a])	70	30	216 ± 7.0	17 ± 0.8	26 ± 1.7	330 ± 59	220
Arnitel UM551	55[a]		180 ± 6.3	14 ± 0.2	24 ± 1.3	400 ± 45	195
Arnitel 550	55[a]		165 ± 4.9	11 ± 0.4	21 ± 1.5	350 ± 43	207
Elitel	55[a]		108 ± 2.6	19 ± 0.3	30 ± 1.3	750 ± 40	205
Pellethane 2363-55DE	55[a]		68 ± 19.2	–	48 ± 5.9	430 ± 48	200
Pellethane 2363-80AE	80[b]		20 ± 6.1	–	21 ± 3.0	630 ± 50	195
Silastic[c]	80[b]		3 ± 0.4	0.5 ± 0.2	6 ± 1.5	750 ± 10	–

σ_r—stress at break; σ_Y—yield stress; ε_r—elongation at break; E_{mod}—Young's modulus; T_m—melting point determined on a Böethius apparatus.

[a] Hardness shore D.

[b] Hardness shore A.

[c] Sample in shape of a rope (6 mm diameter).

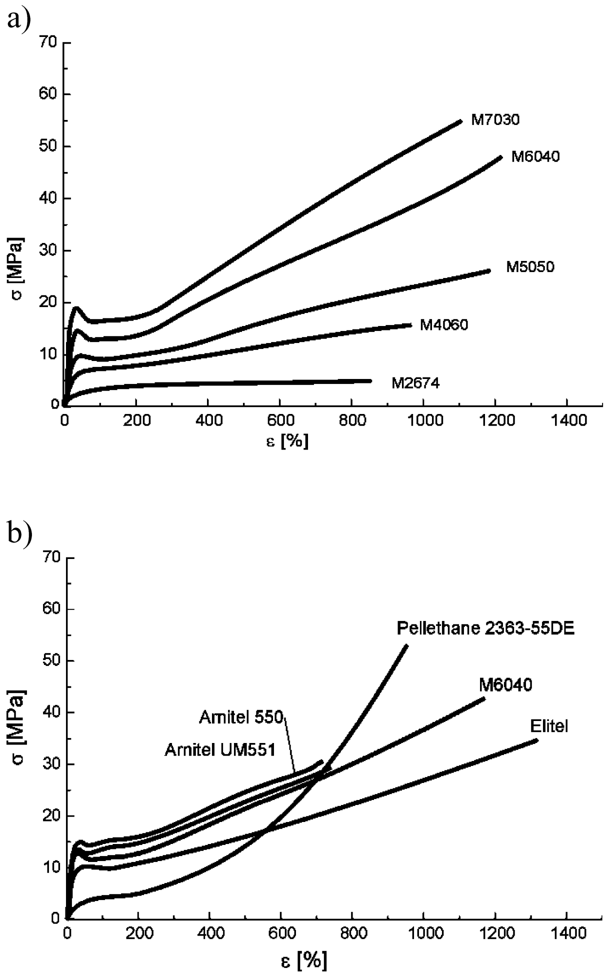

Fig. 2. Stress–strain curves of PED copolymers (a) and reference materials (b). Measurements performed on thin polymer films (0.5 mm), cross-head speed of 100 mm/min.

1 Hz. It shows much lower values of displacement compared with the same material tested at 4 Hz (Fig. 4(d)).

The stepwise increasing load test has also been performed for the reference multiblock poly(ether/ester–ester)s and poly(ether–urethane)s. Changes of the dynamic modulus for copolymers, having similar hardness (Shore D 55) are presented in Fig. 5.

It can be seen that PED copolymer reveals very similar characteristics to Arnitel type PEEs. The chemical modification by the cross-linking agent [24] of PEE type Elitel might be an explanation for lower values of the dynamic modulus. The highest modulus is demonstrated by the PEU multiblock copolymer (Pellethane), however, it drops very fast with the number of cycles and the increasing load level.

A similar comparison has been made among the soft PED copolymers (samples M2476 and M4060), PEU and chemically cross-linked silicone elastomer (Silastic) (Fig. 6).

As shown in Fig. 6, a significant difference in the dynamic modulus patterns has been found between soft materials, subjected to stepwise increasing load conditions,

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

Sample code	σ_L (MPa)
M2674	1.25
M4060	2.0–2.5
M5050	3.75–4.0
M6040	5.0
M7030	6.0
Arnitel UM551	4.0
Arnitel 550	4.0
Elitel	4.0
Pellethane 2363-55DE	4.0
Pellethane 2363-80AE	2.0
Silastic	0.5

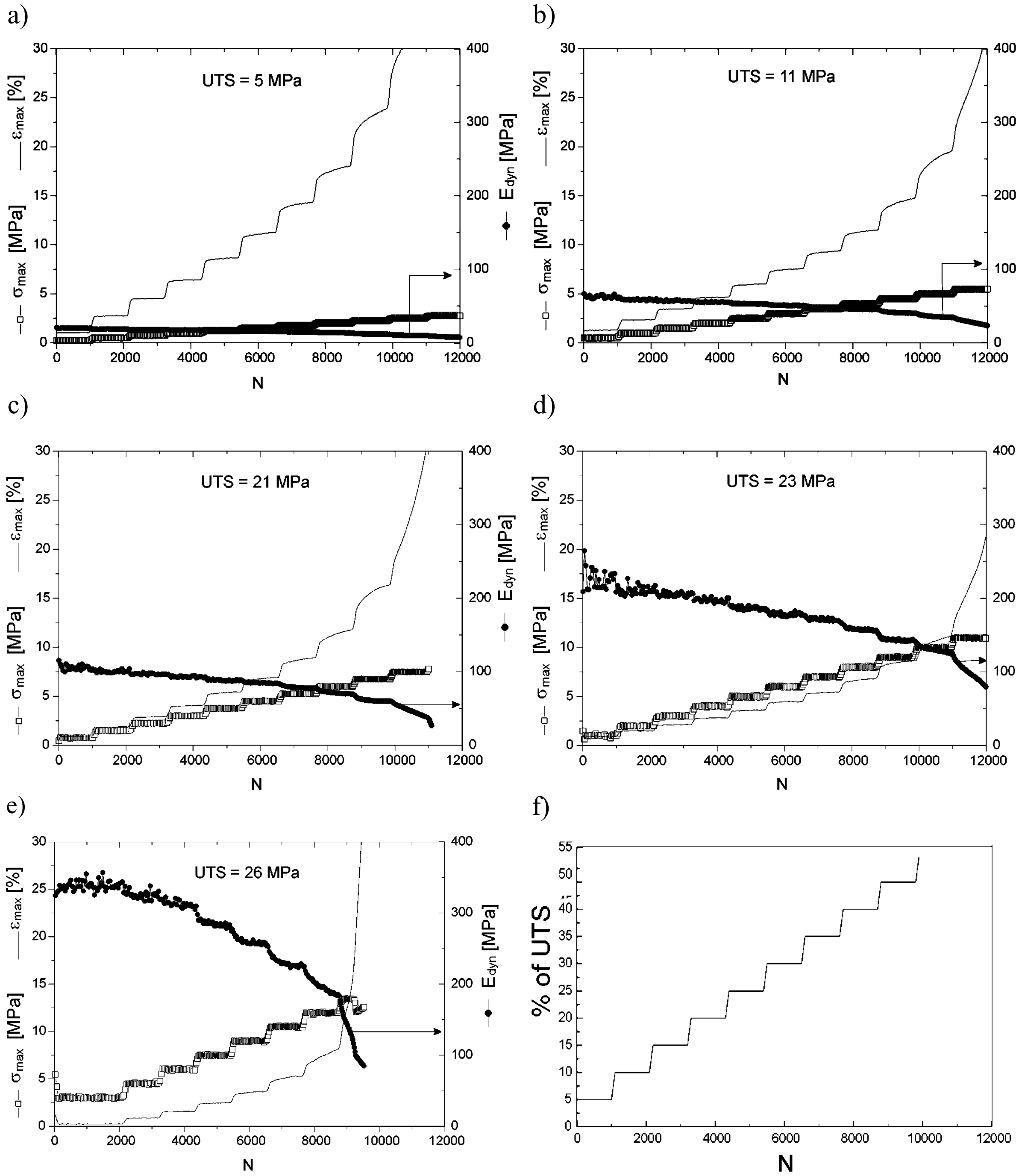

Fig. 3. Patterns of change in the stress, strain and dynamic modulus for the PED copolymers containing a variable content of hard/soft segments: (a) M2674, (b) M4060, (c) M5050, (d) M6040, (e) M7030, (f) loading pattern as a percentage of UTS increasing in a 5% increments. $f = 4$ Hz. $T = 24$ °C.

especially for the silicone elastomer. The ultimate tensile strength (UTS) for considered samples: M2674, M4060, Pellethane 2363-80AE, and Silastic is in a range of 5, 11, 21, and 6 MPa, respectively. In spite of similar UTS values of M2674 and Silastic samples, the last one shows a significantly different pattern of E_{dyn} changes. This can be explained by the fact, that in the absence of chemical cross-links, the structure of PEDs is stabilized by physical cross-links (crystalline ester domains). The silicone elastomer, which is chemically cross-linked shows an extremely low dynamic modulus and can withstand the subsequent oscillatory loading up to only 15% of its UTS while the thermoplastic elastomer sample can be loaded up to 40% of its UTS. Such poor mechanical properties in terms of dynamic modulus, lost during subsequent loading, are an important argument against the use of silicone elastomer for load-bearing applications. It is known that silicone elastomers have been used as flexible joints in the hand

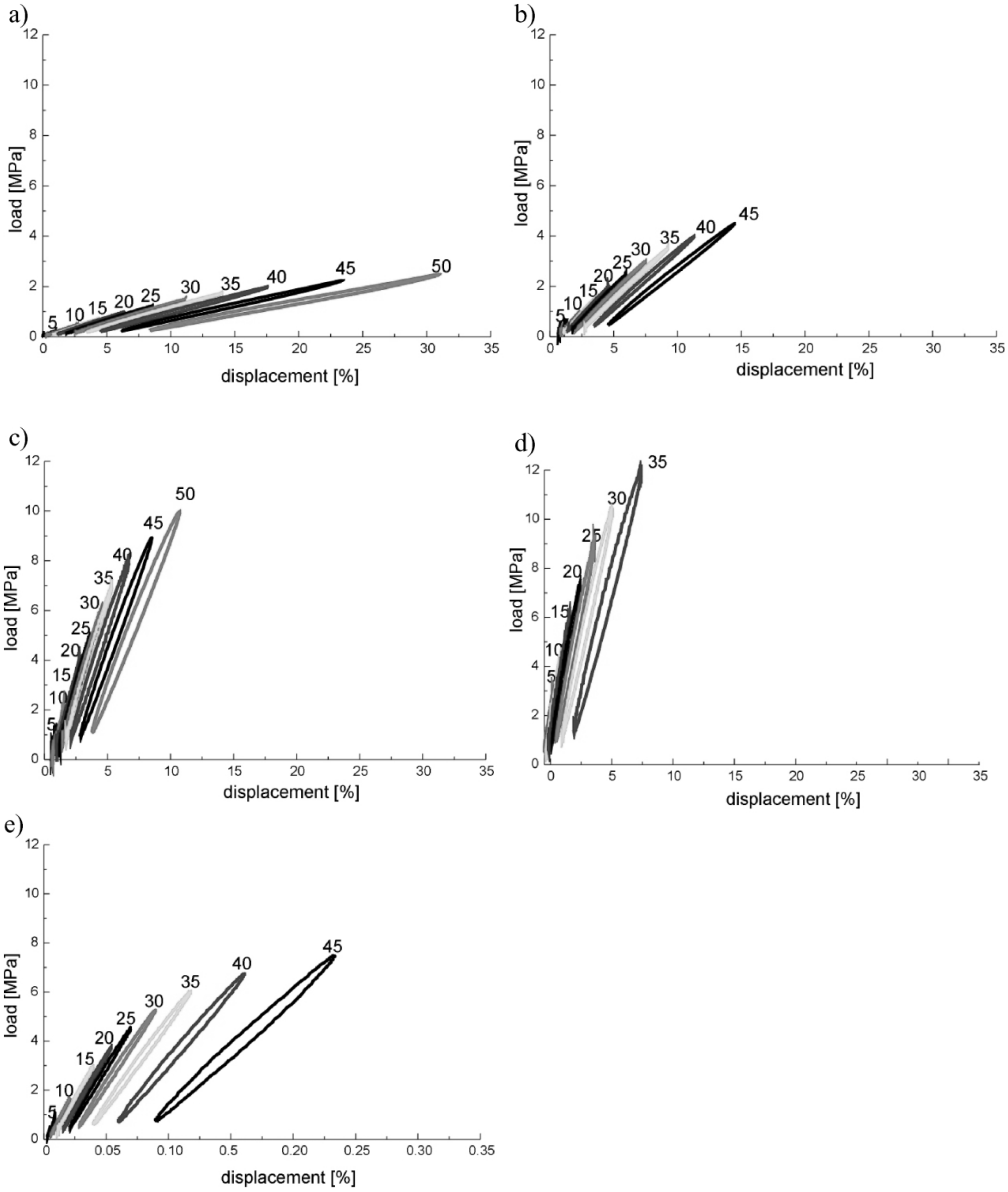

Fig. 4. Representative hysteresis loops for each load level (the numbers on the loops refer to the percentage of the UTS); (a)–(d) PED copolymers containing 26, 40, 60 and 70 wt% of hard segments, testing frequency of 4 Hz; (e) sample containing 60 wt% of hard segments tested at 1 Hz. $T = 24$ °C.

arthoplasty for many years [25,26] and it is susceptible to fracture. This susceptibility is usually explained by a fairly low resistance to the tearing of silicone elastomers [27]. In terms of the dynamic modulus changes as shown in Fig. 6 it may be concluded, that such extremely low values of E_{dyn} during the oscillatory deformations can also be considered as an important factor influencing the failure of silicone implants for load-bearing applications. In conclusion, thermoplastic flexible elastomers, especially PED multiblock copolymers can be considered as good candidates for applications where materials are subjected to oscillatory deformations.

In Fig. 6, the multiblock PEU shows much higher dynamic modulus values, but its modulus drop starts much

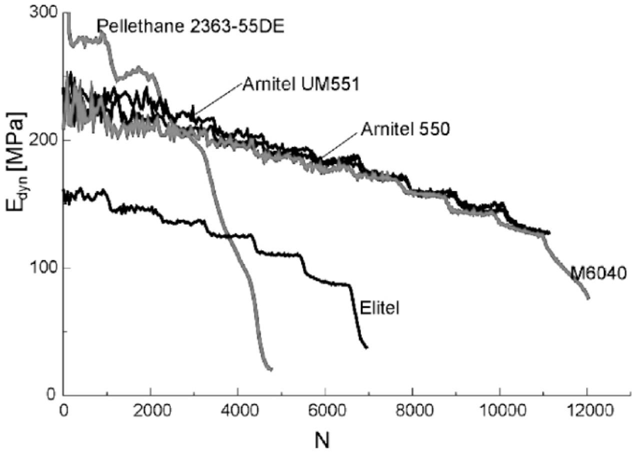

Fig. 5. Representative patterns of change in the dynamic modulus for the PED and reference multiblock copolymers characterized by Shore D hardness 55. Different stress levels of the UTS in a 5% increments. $T = 24$ ° C.

faster than its softer counterpart (M2674 sample). Pellethane thermoplastic PEU also belongs to the group of thermoplastic elastomers, its structure is additionally stabilised by hydrogen bonds between adjacent macrochains. Therefore, the dynamic modulus change is more similar to the PED sample which contains more crystalline domains, i.e. 40 wt% of hard domains (sample M4060).

4. Conclusions

For the first time, the fatigue properties of thermoplastic PED multiblock elastomers were evaluated by the hysteresis measurement method. The stress-, strain-, stiffness- and energy-related parameters were successfully evaluated during a stepwise increasing load test. This procedure, gives additional information about design allowances for long time dynamic fatigue loading of thermoplastic elastomers. As expected, poly(aliphatic/aromatic-ester) copolymers with different composition (hard/soft segments concentration) 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 hard phase. These polymers compare very well with commercially available poly(ester–ethers) and show a much better performance than poly(ester–urethanes) when samples are loaded at the same percentage of the UTS. Softer PEDs and poly(ether–urethane) copolymers show much higher values of the dynamic modulus than chemically cross-linked silicone elastomer. Therefore, thermoplastic elastomers, especially PED multiblock copolymers can be considered as good candidates for applications where materials are subjected to oscillatory deformations (for example passive flexor tendon reconstruction).

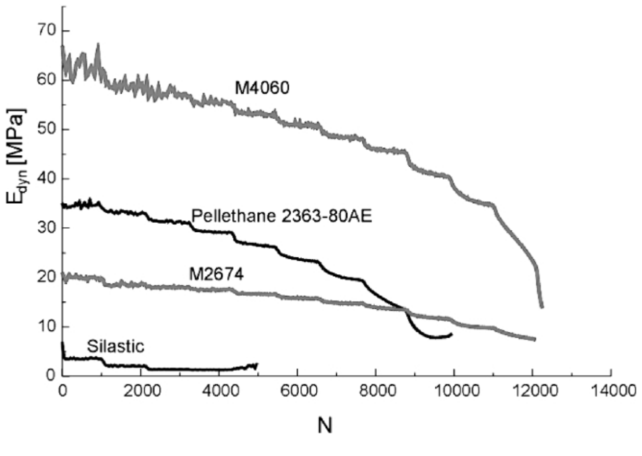

Fig. 6. Representative patterns of change in the dynamic modulus for very soft PEDs and reference multiblock copolymer. Additionally, chemically cross-linked silicone elastomer (Silastic) is compared. Different stress levels of the UTS in a 5% increments. $T = 24$ °C.

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References

[1] Kausch HH. Polymer properties and applications. In: Kausch HH, editor. Polymer fracture, vol. 2. New York: Springer; 1978.
[2] Argon AS. Topics in fracture and fatigue. New York: Springer; 1992.
[3] Owen MJ, Composite materials, vol. 5. New York: Academic Press; 1974.
[4] Altstädt V. Hysteresismessungen zur Charakterisierung der mechanisch-dynamischen Eigenschaften von R-SMC. PhD Dissertation, University Kassel; 1987.
[5] Renz R, Altstädt V, Ehrenstein GW. J Reinf Plast Compos 1988;7: 413–34.
[6] Orth F, Hoffmann L, Zilch-Bremer H, Ehrenstein GW. Compos Struct 1993;24:265–72.
[7] Raue F, Ehrenstein GW. Macromol Symp 1999;148:229–40.
[8] Ward IM. An introduction to the mechanical properties of solid polymers. Chichester: Wiley; 1993.
[9] Zysk T. Zum statischen und dynamischen Werkstoffverhalten von Thermoplastischen Elastomeren, PhD Dissertation, University Erlangen; 1993.
[10] Walker R, Rader CP, editors. Handbook of thermoplastic elastomers. New York: van Nostrand Reinhold; 1988.
[11] Cella RJ. J Polym Sci, Polym Symp 1973;42:727–39.
[12] Niesten MCEJ, Gaymans RJ. Polymer 2001;42:6199–207.
[13] Holden G, Legge NR, Quirk R, Schroeder HE, editors. Thermoplastic elastomers. Munich: Hanser Publishers; 1996.
[14] Legge NR, Holden G, Schroeder HE, editors. Thermoplastic elastomers. Munich: Carl Hanser; 1987.

[15] Auad ML, Frontini PM, Borrajo J, Aranguren MI. Polymer 2001;42: 3723–30.

[16] El Fray M, Slonecki J. Polish Patent PL. 308 185; 2000.

[17] El Fray M, Slonecki J. Angew Makromol Chem 1996;234:103–9.

[18] El Fray M, Slonecki J. Kautsch Gummi Kunstst 1996;10:691–7.

[19] El Fray M, Slonecki J. Macromol Chem Phys, Macromol Symp 1997; 122:335–42.

[20] El Fray M, Slonecki J. J Macromol Sci—Phys 1998;B37(2): 143–54.

[21] Prowans P, El Fray M, Slonecki J. Biomaterials 2002;23:2973–8.

[22] Drumm R. DynMat Hysteresis Measurements Software, BASF AG, Ludwigshafen.

[23] El Fray M, Altstädt V. Polymer. 2003;44 (15).

[24] Fakirov S, editor. Handbook of thermoplastic polyesters. Weinheim: Wiley-VCH Verlag; 2002.

[25] Blair WF, Shurr DG, Buckwalter JA. J Bone Joint Surg 1984;66A: 365–70.

[26] Vahvanen V, Viljakka T. J Hand Surg 1986;11A:333–9.

[27] Bieber EJ, Weiland AJ, Volenc-Dowling S. J Bone Joint Surg 1986; 68A:206–9.