



Fatigue behaviour of multiblock thermoplastic elastomers. 3. Stepwise increasing strain test of poly(aliphatic/aromatic-ester) copolymers

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Abstract

The fatigue behaviour of poly(aliphatic/aromatic-ester) (PED) multiblock copolymers has been evaluated using the hysteresis loop method. Stepwise increasing strain test (SIST) was performed at a frequency of 1 Hz. The strain levels were varied with increasing extension steps: 3, 5, 10, 15, 20, 25 and 30% of the initial strain, while minimum stress has been set at a constant value of 0.1 MPa. It has been found that soft PEDs show a very good stress relaxation due to the fact that they contain high amounts of the amorphous phase and their soft segments do not crystallize. PED copolymers, especially those containing low amounts of crystalline hard domains showed very good damping properties at small strain levels. It has also been found that PED's ability to store and dissipate energy is a function of the hard segment concentration. This method proved to be a useful tool for determining the changes in the material properties of PEDs and other thermoplastic elastomers during deformation.

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1. Introduction

Multiblock poly(aliphatic/aromatic-ester) (PED) copolymers belong to the interesting class of thermoplastic elastomers (TPE) [1] that exhibit rubber-like elasticity but are not covalently cross-linked. These copolymers are composed of poly(butylene terephthalate) (PBT) and dimer fatty acid (DFA) sequences [2,3]. The amorphous diacid is termed as the soft block and imparts an elastomeric characteristic to the polymer. The second block of such copolymer, being an aromatic terephthalic acid ester, is referred as the hard segment.

The hard thermoplastic blocks are incompatible with the soft elastomeric blocks and therefore, they are phase-separated on a microscopic scale. A microdomain lamellar morphology model has been already proposed for PED copolymers [4,5]. Transmission electron microscopy (TEM) indicated the formation of a lamellar morphology of crystalline PBT embedded in an amorphous matrix. It has

been found that thickness (in a range of 20 nm) and perfection of the crystalline lamellae were more pronounced for samples containing higher amounts of the hard domains.

PED copolymers are biocompatible and show no adverse biological effects after long term in vivo experiments [6,7]. Their thermal and static mechanical properties were described in [2,8] and according to those results they matched the mechanical requirements for use as temporary flexor tendon prosthesis. Recently evaluated fatigue properties with the application of a stepwise increasing load procedure indicated their good load-carrying properties, especially in the case of polymers containing a high amount of hard phase [9]. Furthermore, the long time cyclic loading via 'dynamic creep' measurements indicates a very good dimensional stability over 100,000 cycles [10].

In the case of natural tendons, they are known to exhibit time-dependent viscoelastic behaviour, which is independent of frequency in applied physiological range (1 to 1.37 Hz) but sensitive to the magnitude of strain [11–13]. Therefore, when the material experiences both load and displacement (strain) limits, it is important to perform stress- and strain-controlled testing [14]. This paper focuses on strain-controlled testing for which the stepwise

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Table 1

Static tensile properties and melting temperatures 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#	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 Bøethius apparatus #-sample in shape of a rope (6 mm diameter).

^a Hardness Shore D.

^b Hardness Shore A.

increasing strain test (SIST) presented here is a useful testing method.

In this work, we investigated the structural changes of the material as a function of the cyclic fatigue straining by hysteresis method. This method allows the digitalization of the hysteresis loop and, aside from the stress and strain related parameters, the stored energy, lost energy, damping and dynamic creep behaviour can all be determined [15–18]. The aim of the present work is to determine the effect of hard/soft segments concentration in PED copolymers on the changes of the strain-related material properties.

The testing protocol has also been used for the investigation of commercially available poly(ester-ether)s and medical grade poly(ether-urethane) thermoplastic elastomers currently used as biomedical polymers. Fatigue properties of studied TPEs, including PED copolymers have been compared to a chemically cross-linked silicone elastomer currently used in medicine.

2. Experimental

2.1. Material

The synthesis method of PED copolymers, involving transesterification and polycondensation from the melt, was described in previous publications [2,8]. Commercially available thermoplastic elastomers with a Shore D hardness of 55 were also included in the testing protocol: poly(ester-ether) thermoplastic elastomers of Arnitel 550, Arnitel UM 551 (DSM, The Netherlands) and Elitel (Elana SA, Poland) and medical grade poly(ether-urethane)s Pellethane 2363-55 DE (DOW Chemicals, USA). Soft PED copolymers were compared to poly(ether-urethane) having a known hardness of 80 Shore A (Pellethane 2363-80 AE). Additionally, chemically crosslinked medical grade Silastic® (Dow Corning, USA) silicone elastomer was used.

2.2. Sample preparation

Samples for fatigue testing were prepared by injection moulding using a pressure around 50 MPa. Die temperatures were approximately 25 °C higher than the melting point of the polymers while the mould was kept at room temperature. Samples were in the shape of dog-bones (samples S-2) with a thickness of 3 mm and a cross-section area of 12 mm².

2.3. Tensile testing

The quasi-static tensile datas were collected at room temperature with an Instron TM-M tensile tester equipped with a 500 N load cell employing a crosshead speed of 100 mm/min. The strain was measured using the clamp displacement (the starting clamp distance was 25 mm). The obtained results were averaged from 6 specimens (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 loops were used as described in our previous papers [9,10].

The SIST has been used to evaluate the strain dependent material changes. In this procedure, the dynamic strain increases after a certain number of cycles, while the minimum stress remains constant. In other words, the amplitude of the strain was stepwise increased and held constant within each step for a definite number of cycles. The test was performed at a frequency of 1 Hz and, for the investigation of the dynamic modulus changes, at 4 Hz (a physiological frequency range has been selected). The strain levels were varied by increasing strain steps: 3, 5, 10, 15, 20, 25 and 30% of the initial length of a sample while minimum

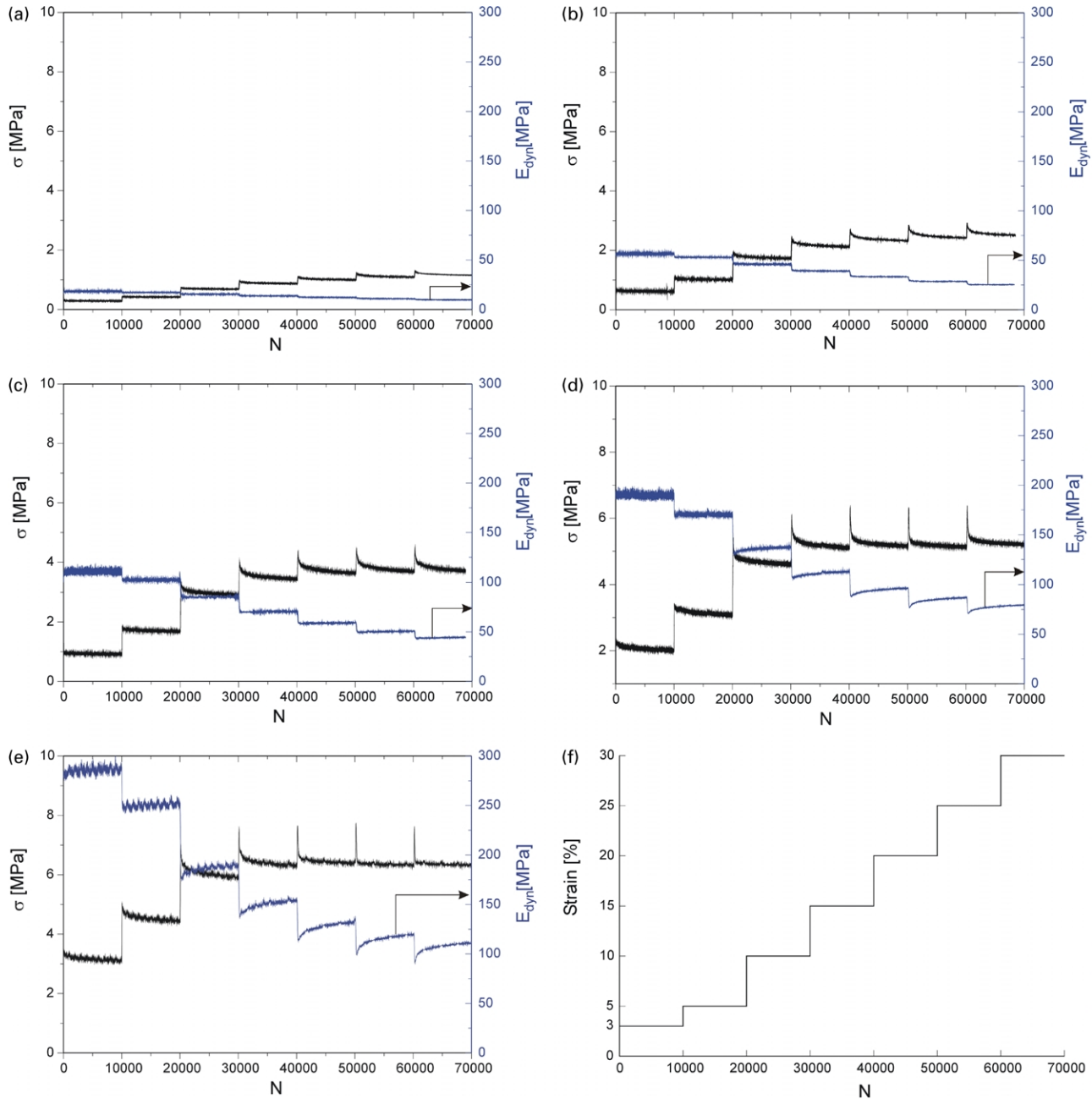


Fig. 1. Patterns of change in the stress and dynamic modulus (E_{dyn}) for PED copolymers as a function of the number of cycles and increasing strain levels: (a) M2674, (b) M4060, (c) M5050, (d) M6040, (e) M7030, (f) strain pattern as a function of the number of cycles; $f = 1 \text{ Hz}$, $T = 24 \text{ }^\circ\text{C}$.

stress has been set at a constant value of 0.1 MPa to prevent the specimen from buckling in the unloading phase. 10,000 cycles were imposed for every step and intervals of 100 cycles were implemented between every step to allow the controller to reach next higher strain level. The temperature of the sample was monitored with a thermo couple and no effect of hysteretic heating was observed.

2.5. Scanning electron microscopy (SEM)

Scanning electron micrographs (SEM) of the fracture

surfaces of polymers after fatigue experiments were acquired with a JEOL-JSM-IC848 microscope. All samples were fractured in liquid nitrogen, vacuum dried and coated with 60 Å of gold prior to scanning.

2.6. Small angle X-ray scattering (SAXS)

SAXS measurements were performed with a Bruker AXS Nanostar equipped with crossed Goebel-mirrors and a 2D Hi-star detector. The generator (sealed Cu-tube) was operated at 40 kV and 40 mA.

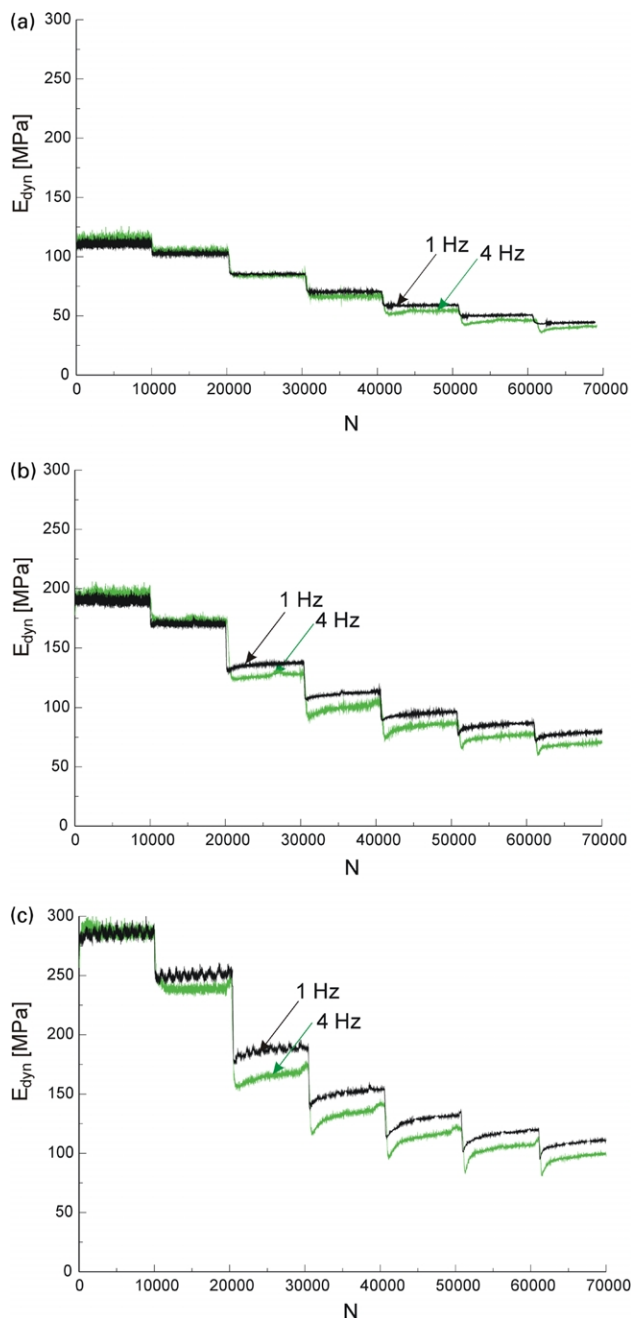


Fig. 2. Influence of the testing frequency (1 and 4 Hz) on dynamic modulus changes of selected PED samples as a function of the number of cycles: (a) M4060, (b) M5050, (c) M7030; $T = 24\text{ }^{\circ}\text{C}$.

3. Results and discussion

The formulations of PED copolymers, mechanical properties and melting temperatures of PEDs and reference materials are given in Table 1. The tensile strength and melting temperature of PED copolymers increase, as expected, with increasing hard segment content, while elongation at break decreases. Poly(ester-ether)s and poly(ether-urethanes) of comparable hardness show significant differences in the stress at break values (from 21 to

48 MPa) and in the melting temperatures ranging from 195 to 207 $^{\circ}\text{C}$.

Fig. 1(a)–(e) demonstrate the results of the SIST of PED samples (samples M2674–M7030) subjected to straining at predefined values from 3 to 30% as indicated in strain pattern regime in Fig. 1(f). The applied stepwise increasing straining allows for identification of the deformation level above the structural changes that occur in the polymer. It was found for all PEDs that the initial stress induced by the applied deformation is higher for polymers containing a higher amount of crystalline hard domains (especially samples M6040 and M7030). Typical relaxation effects are observed for all steps when samples are exposed to the increasing strain. Softer PEDs (M2674 and M4060) show very strong stress relaxation due to the fact that they contain a higher amount of the amorphous phase. This caused that the polymer chains are able to form an entropically more favoured compact random coil configuration. In consequence, a large amount of the elongation can be recovered instantaneously. The improved dynamic stress relaxation, and thus improved fatigue behaviour of softer polymers could also be explained by the fact that soft segments do not crystallize (crystallization of soft segments in segmented polyurethanes has been identified in [19] as an important factor dramatically reducing fatigue resistance).

Fig. 1(a)–(e) shows also the dynamic modulus changes during SIST for PED copolymers. In general, a decrease in dynamic modulus as a function of the applied strain level is observed within each increasing step of deformation.

The characteristic decrease of the dynamic modulus can be explained by typical strain softening behaviour due to stress relaxation. The strain softening phenomenon is caused by disruption of the crystalline structure upon straining as observed in segmented poly(ether-ester-amides) [20,21]. Two opposing processes were observed in these polymers: disruption of the interconnecting crystalline structure and orientation of the crystalline lamellae in the straining direction. In the case of PED copolymers, a strain

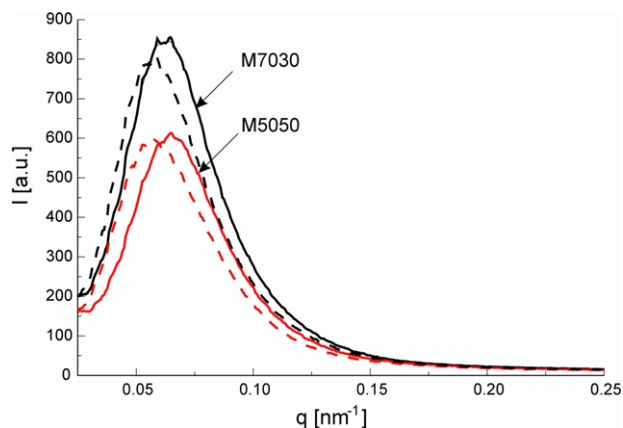


Fig. 3. SAXS profiles of PED copolymers with different hard segments content (50 and 70 wt.%) after stepwise increasing strain test (70,000 cycles). Dotted line—pre-oriented samples; solid line—samples after fatigue. $f = 1\text{ Hz}$, $T = 24\text{ }^{\circ}\text{C}$.

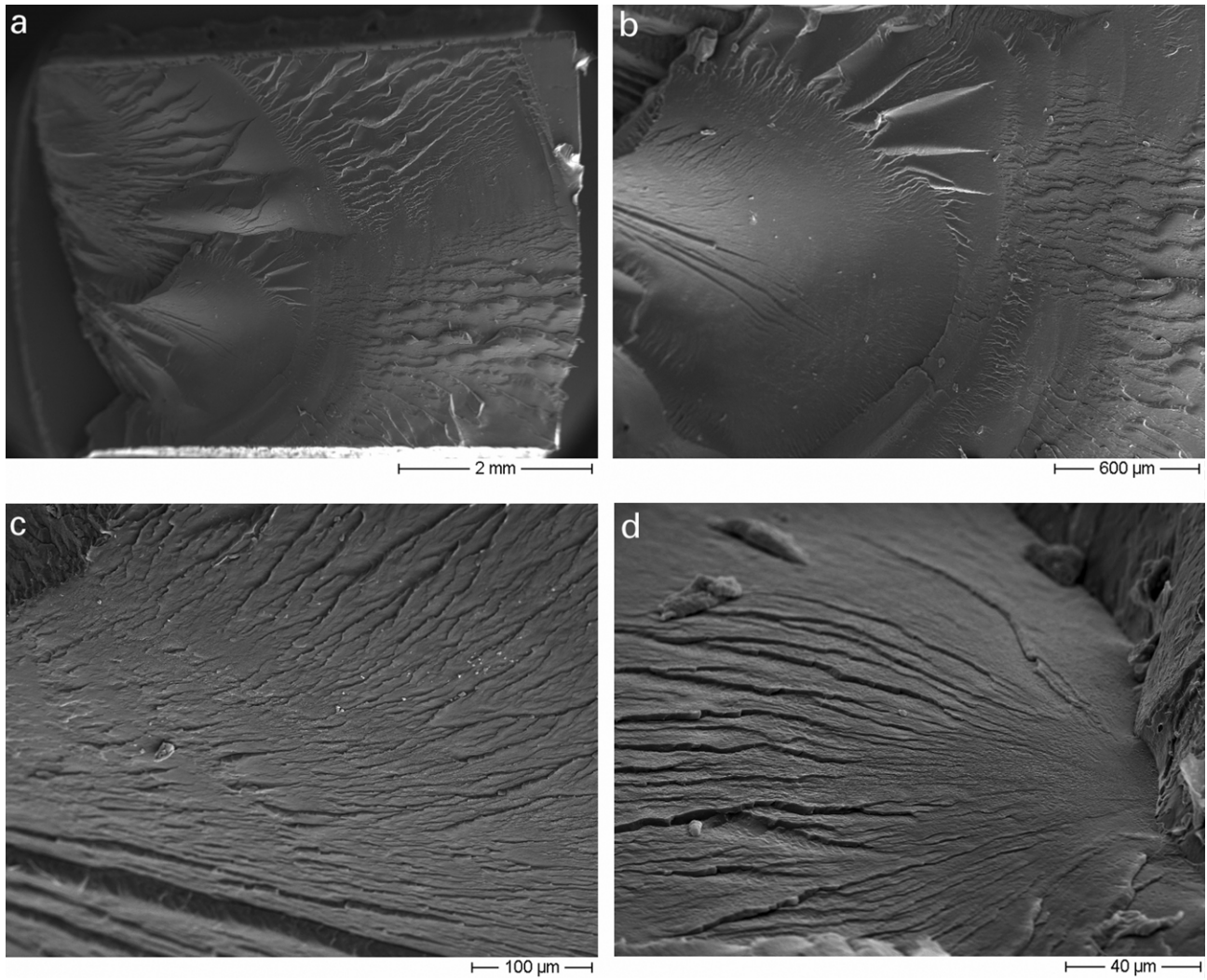


Fig. 4. Fracture surface (in LN₂) of the PED sample containing 70 wt.% of PBT. $f = 1$ Hz, $T = 24$ °C.

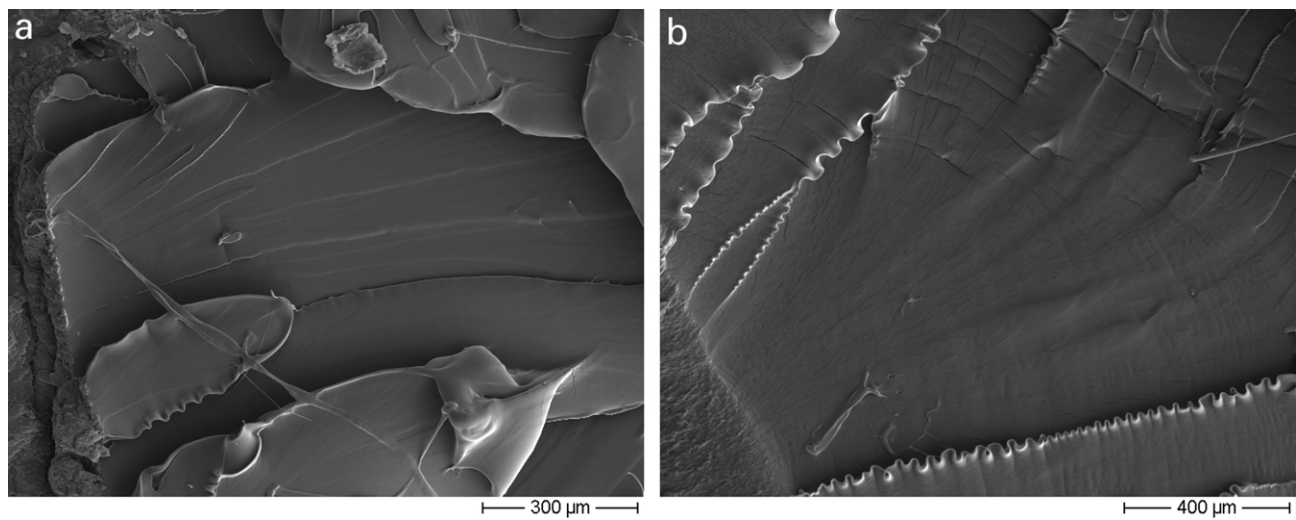


Fig. 5. Fracture surface of the fatigued PED copolymer containing 26 wt.% of PBT. $f = 1$ Hz, $T = 24$ °C.

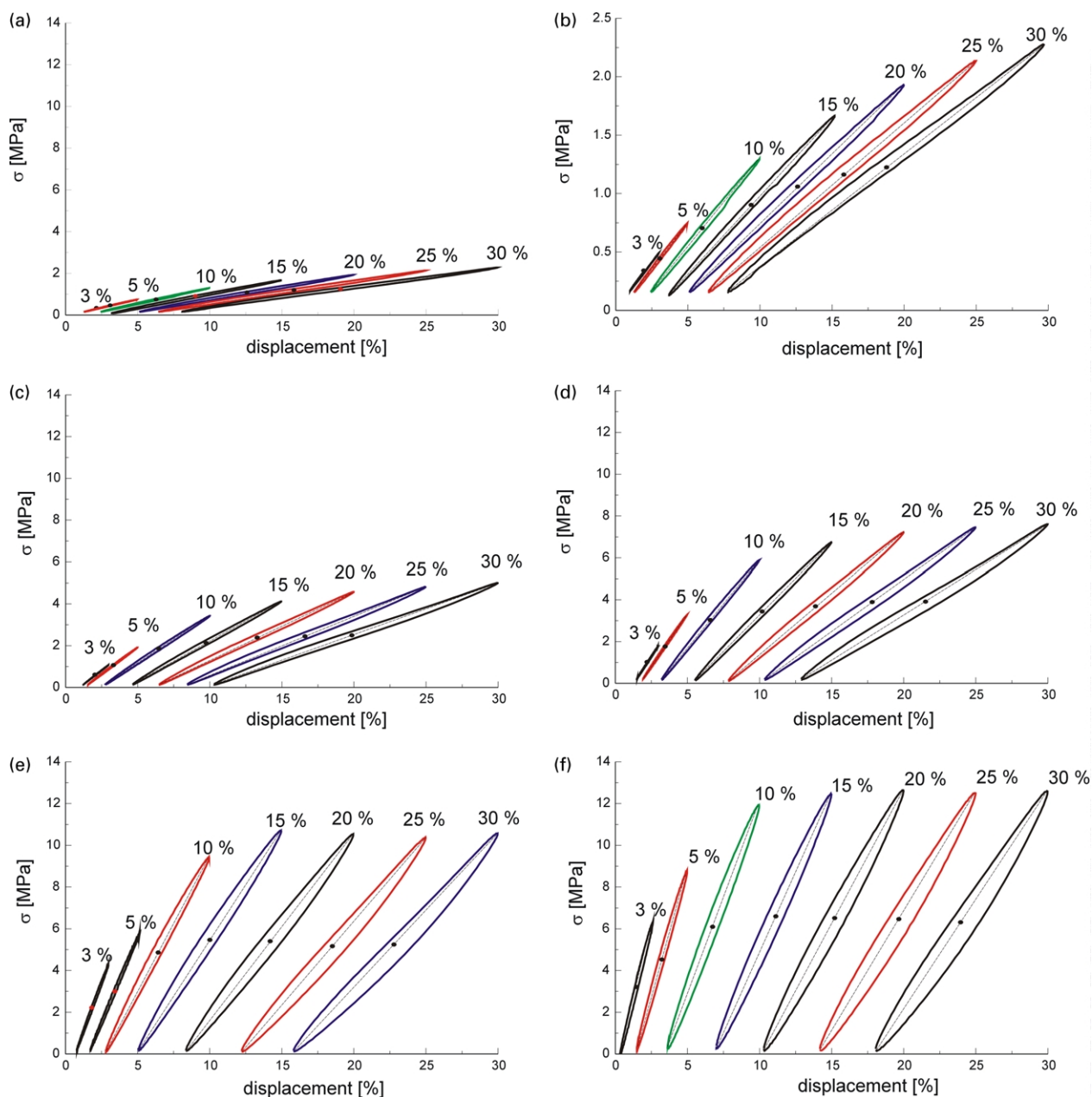


Fig. 6. Hysteresis loops corresponding to stepwise increasing strain levels (numbers given above the loops) for PED copolymers containing: (a) and (b) 26 wt.%, (c) 40 wt.%, (d) 50 wt.%, (e) 60 wt.% and (f) 70 wt.% of the hard segments of PBT. $f = 1 \text{ Hz}$, $T = 24 \text{ }^\circ\text{C}$.

softening behaviour can be explained by stress relaxation and orientation of the crystallites, as will be discussed.

Another interesting behaviour has been observed for PED copolymers. On each strain level a slight increase in the modulus as a function of the number of cycles can be observed especially for copolymers with higher hard segment concentration.

An increase of modulus within a single strain level can be explained by strain hardening. During this process, the oriented lamellae are broken up, and the amorphous phase starts to orient [21]. The strain hardening (increase of the modulus) is more pronounced at a higher frequency (Fig. 2) and for polymers with higher hard segment contents (60 and

70 wt.%). The increase of crystallinity favours the strain hardening due to the orientation of crystals and the pull-out of tie molecules from crystallites. As a consequence, a plastic, irreversible deformation within the test section of the samples takes place.

This is especially significant if the external strain is applied at higher, stepwise increasing deformation levels (above 10% for softer polymers containing up to 40 wt.% of hard segments, and above 5% for polymers containing more than 50 wt.% of hard segments). A possible mechanism responsible for the observed changes can be disentanglement and slipping of the polymer chains as a consequence of the pull-out of tie molecules from the

neighbouring microfibrils as also observed for poly(ether-ester)s [22]. For PED copolymers, this effect is much more pronounced at larger deformation levels and increased concentrations of the crystalline phase.

Comparison of SAXS profiles (Fig. 3) performed for two pre-oriented samples (containing 50 and 70 wt.% of hard segments, respectively) confirm that the intensity of the scattering maximum as a function of the magnitude of the scattering vector, q , which is given by the equation: $q = (4\pi/\lambda)\sin(\nu)$ with ν and λ being the scattering angle and the wavelength of X-rays ($\lambda = 1.54$), respectively is higher for polymer containing a higher concentration of hard segments (Fig. 3, sample M7030, dotted line). The peak height in Fig. 3 suggests that the quality of the microphase separation and the hard segment length is higher (more ordered) for PED containing 70 wt.% of PBT compared to a sample containing 50 wt.% of hard segments. This difference is due to a higher concentration of the amorphous phase in sample M5050. In this case, the hard segments are not easily forming an ordered structure. The comparison of scattering profiles for pre-oriented samples (dotted line) and for fatigued sample, i.e. 30% of deformation and 70,000 cycles (solid line) indicates that the peak maxima after fatigue are shifted towards higher values of the scattering angle. Their height is much more influenced by the applied strain, as in the case of a sample containing a higher amount of hard domains (M7030). Based on the structural model developed by Fakirov et al. [22] for poly(ether-ester)s, a similar model describing structural changes in PEDs during fatigue testing can be proposed. The highly oriented copolymers consist of microfibrils connected by a large number of tie molecules (the amount of tie molecules is much larger than in the case of the homopolymer). The higher extent of relaxation (higher contribution of the microfibrils free of interfibrillar contacts) results in the shrinkage of the microfibrils and subsequently decreases the long spacing indicating plastic deformation.

In an ideal elastomer, no stress relaxation occurs as there is no plastic deformation. Rapid increase of the stress in semi-crystalline polymers induces appearance of a plastic deformation expressed as necking of the sample. The scanning electron micrographs taken at the fracture surface in the necking zone (sample fractured in liquid nitrogen) visualise the plastic deformation as being a consequence of subsequent straining (polymer containing 70 wt.% of hard segments, Fig. 4).

In contrast, the softest material containing a high amount of amorphous phase (only 26 wt.% of PBT, Fig. 5) shows a smooth fracture surface that indicates ductile deformation behaviour. Higher magnification reveals formation of striation bands and the appearance of voiding in the zones where shrinkage is not possible.

The relaxation processes can be monitored by the characteristic shift of the hysteresis loop along the strain axes as shown in Fig. 6. Comparison of the hysteresis loops for PED copolymers containing different hard/soft segment

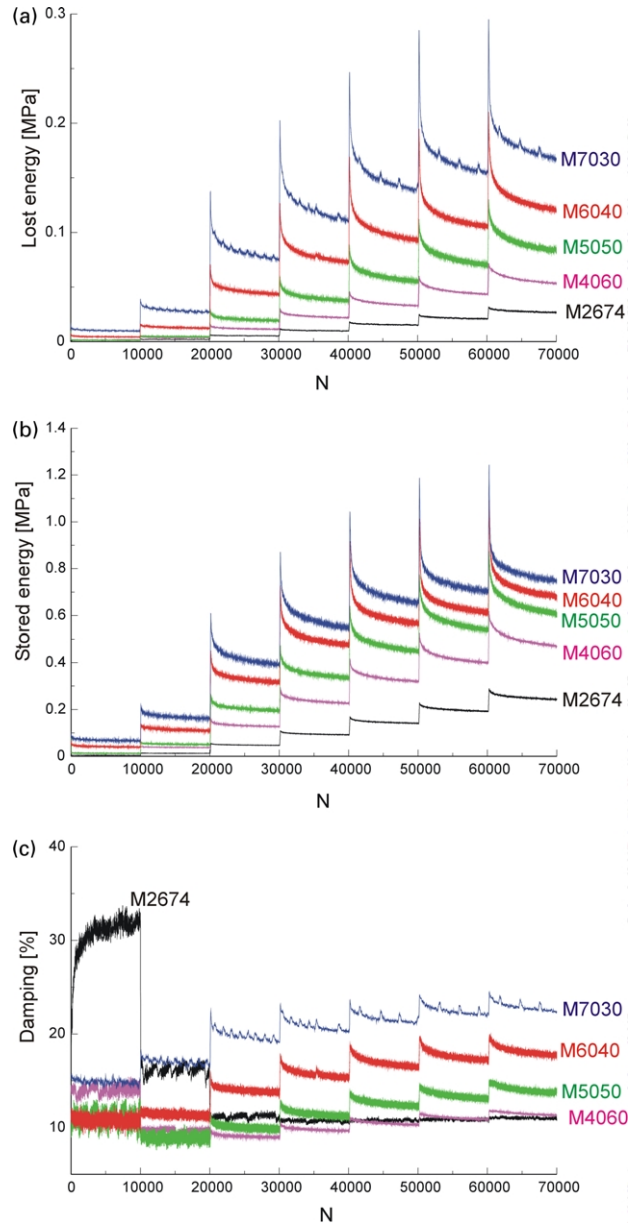


Fig. 7. The lost energy (a), the stored energy (b), and damping (c) of PED copolymers: $f = 1$ Hz, $T = 24$ °C.

concentrations clearly demonstrate differences in the damping behaviour for flexible and rigid materials: rigid polymers show a larger area of the hysteresis loop (Fig. 6(e) and (f)) compared to very soft materials (Fig. 6(a)–(d)). The height of the hysteresis loop and the position of its mid-point are also very clear indications for the appearance of plastic deformation as a function of the hard segments concentration: for polymers containing up to 50 wt.% of hard segments (Fig. 6(a)–(d)), the height of the hysteresis loop and its mid-point remain steady-static after 20% of deformation, while for the harder materials, i.e. M6040 and M7030 (Fig. 6(e)–(f)), this steady-static height of the hysteresis loop and the mid-point remain constant after 10% of deformation.

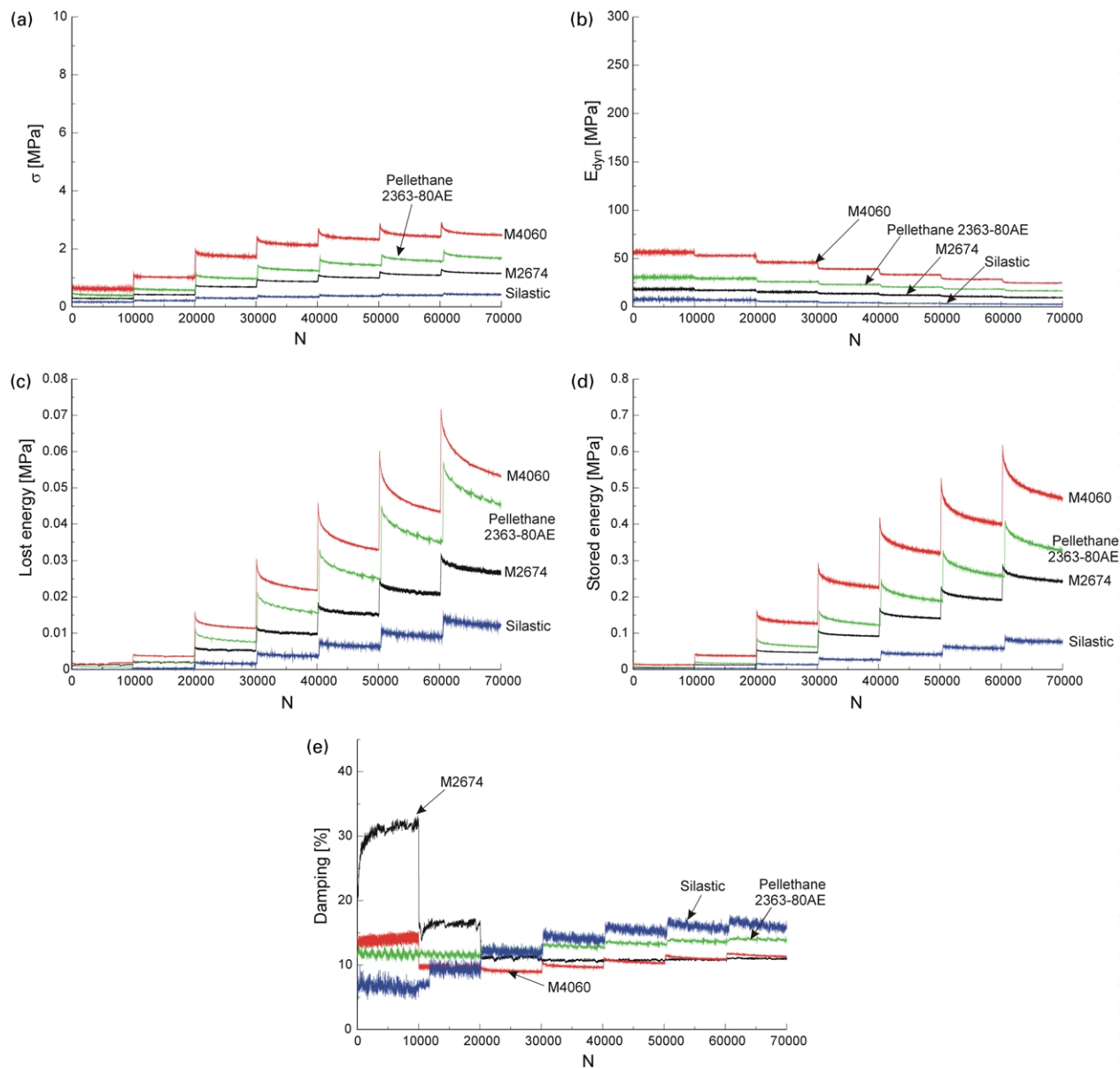


Fig. 8. The stress (a), the dynamic modulus (b), the lost energy (c), the stored energy (d), and damping (e) for soft PED copolymers and reference materials as a function of the number of cycles and increasing strain levels: $f = 1$ Hz, $T = 24$ °C.

The hysteresis measurements also allows the monitoring of the changes of other important parameters, such as lost energy, stored energy and changes in the materials damping behaviour as a function of the number of cycles. Fig. 7 illustrates these changes for PED copolymers. As shown, the lost energy and stored energy are changing along with variations in the hard/soft segment ratios: the parameters are increasing with increasing hard segment concentration as a function of the number of cycles and the applied strain level (Fig. 7(a) and (b)). In contrary, the softest polymer shows the highest damping for small (3–5%) straining (Fig. 7(c)). This behaviour can indicate, that at such compositions (only 26 wt.% of the hard segments, degree of the polycondensation equals 1) the material flows due to a lack of strong segmental interactions stabilizing

the nanostructure at the molecular level. Therefore, a highly homogenous rather than a microphase separated structure with rubber-like elasticity, is expected for this polymer.

Comparison of different soft elastomers (thermoplastic elastomers and chemically cross-linked Silicone rubber) reveal different relaxation behaviours and their ability to store and dissipate energy, as shown in Fig. 8. Silastic elastomer, which is chemically cross-linked and therefore thermally and mechanically stable below the degradation temperature, shows the smallest changes in the level of stress, dynamic modulus, lost work and stored work within stepwise increasing strain regime (Fig. 8(a)–(d)). The material damping increases stepwise from around 7–15% (Fig. 8(e)).

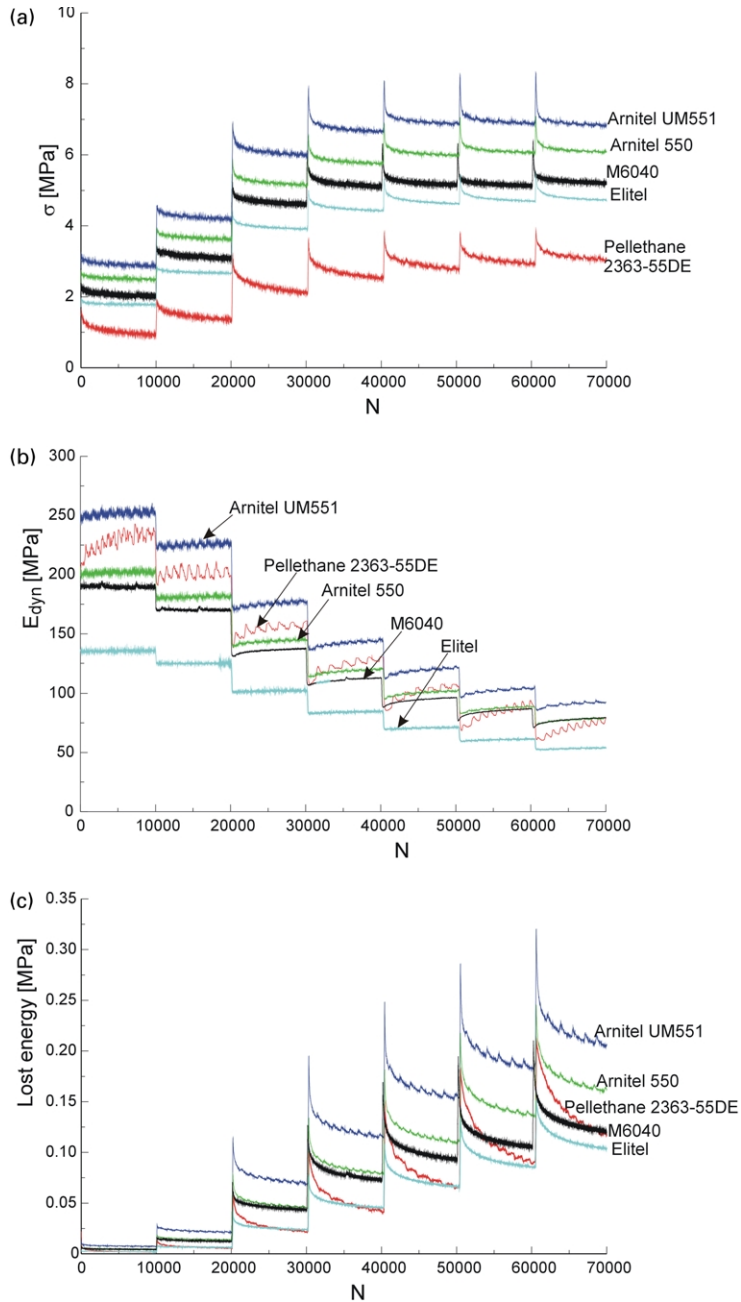


Fig. 9. The stress (a), the dynamic modulus (b), the lost energy (c), the stored energy (d), and damping (e) for PED copolymers and reference materials characterized by a hardness of 55, Shore D, as a function of the number of cycles and increasing strain levels: $f = 1$ Hz, $T = 24$ °C.

Multiblock copolymers with semicrystalline hard segments such as PEDs and poly(ether-urethane) (PU) are more sensitive to cyclic repeated straining since their physical cross-linking points are relatively unstable against mechanical and thermal impact. Thus, their domain structure may undergo various types of restructuring processes, such as extension of the interdomain distance, tilting and orienting of the anisotropic domains, and breakup and reformation of the phase-separated structure. It can be seen from Fig. 7(a)–(d), that poly(ether-urethane) can be ranked between samples M2674 and M4060 regarding the changes of stress,

dynamic modulus and energy related parameters. This is also valid for the damping behaviour (Fig. 7(e)) but only at small strain levels (3–5%). At higher strain levels, PU shows higher damping than PED copolymers but lower than Silastic elastomer.

The magnitude of structural changes is larger when the concentration of physical cross-links (hard domains) increases. Therefore, multiblock copolymers characterised by higher hardness (Fig. 9) indicate much stronger structural changes occurring during the deformation process, as expressed by a significant drop of the stress level within

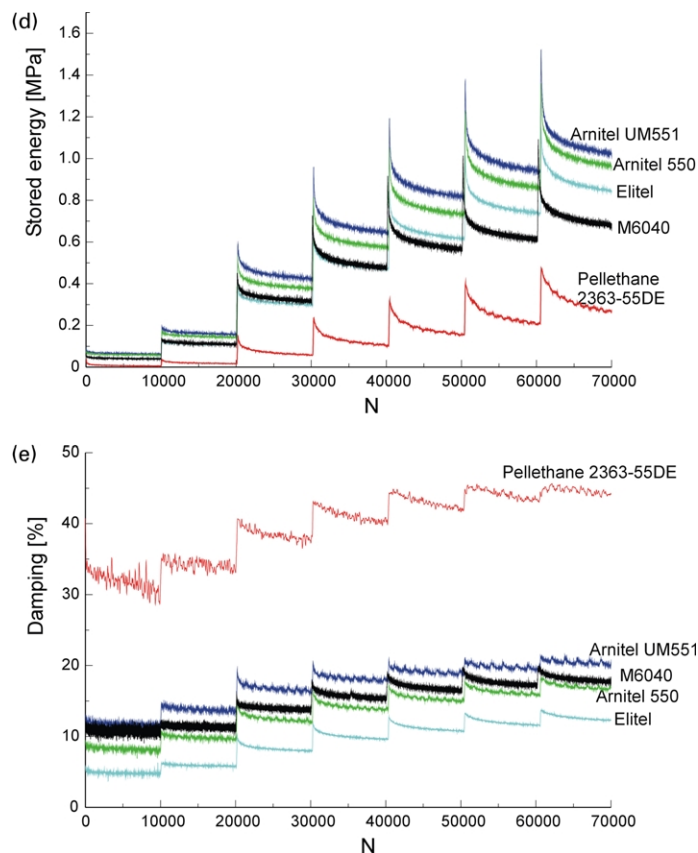


Fig. 9 (continued)

each single strain level (Fig. 9(a)). The lowest stress were found for the PU materials, while the PED sample (M6040) ranged in between the values for poly(ester-ether) copolymers. The ester-type copolymers with crystalline hard domains show larger deformations compared to the urethane copolymer, because the PU crystalline hard segments are additionally stabilised by hydrogen bonds, contributing to higher cohesiveness of the hard domains [23].

Changes of the dynamic modulus (Fig. 9(b)) indicate an appearance of strain hardening, as already discussed, for PED copolymers. The lowest values of the stored energy, found for the PU copolymer, (Fig. 9(d)) contributes to the highest damping within all strain levels (Fig. 9(e)). PED copolymer (M6040) shows higher damping than Arnitel 550 and Elitel poly(ester-ether)s.

4. Conclusions

The hysteresis measuring method has been found as a useful tool for the evaluation of fatigue properties of thermoplastic poly(aliphatic/aromatic-ester) (PED) multi-block elastomers. Their strain-related properties during stepwise increasing strain testing have been especially investigated. The stepwise increasing strain method (SIST)

is well suitable to identify the deformation level at which structural changes occur in the polymer. It has been found that soft PEDs show a very good stress relaxation due to the fact that they contain a high amount of amorphous phase and their soft segments do not crystallize. Polymers of higher crystallinity showed a very pronounced relaxation that resulted in the plastic, irreversible deformation of samples. A mechanism of pull-out of tie molecules from the neighbouring microfibrils has been used for explaining these changes. PED copolymers, especially those containing low amounts of crystalline hard domains showed very good damping properties (up to 30%) at small strain level (3%). In general, the damping has also been found that PED's ability to store and dissipate energy is a function of a hard segments concentration. The SIST method has been found as useful to determine the changes in material properties during the deformation of PEDs as well as other thermo-plastic elastomers.

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