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Fatigue behaviour of multiblock thermoplastic elastomers. 2. Dynamic creep of poly(aliphatic/aromatic-ester) copolymers

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Abstract

The 'dynamic creep' behaviour of poly(aliphatic/aromatic-ester) (PED) multiblock copolymers has been evaluated by the hysteresis measurements method. The effect of the hard/soft segments concentration on the microphase separation in PED copolymers was determined by means of differential scanning calorimetry. The 'dynamic creep' of PED copolymers has been compared with poly(ether–ester) and segmented polyurethanes indicating on the good creep behaviour of PEDs compared to those materials. It was found that the hard segment content influences the creep behaviour of PED copolymers at ambient and elevated temperature indicating that stiffer materials are less susceptible to environmental conditions than polymers containing a high amount of the soft phase. PED copolymers compare very well with commercially available poly(ester–ethers) and show much lower creep compared to poly(ether–urethanes).

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

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1. Introduction

Multiblock poly(aliphatic/aromatic-ester) (PED) copolymers belong to a very interesting class of polymeric materials which are called thermoplastic elastomers (TPEs). Unlike segmented polyurethanes and poly(ester–ether)s, most of the PEDs are constructed of relatively short blocks randomly distributed along the polymer chain. Copolymerization of aliphatic and aromatic ester units gives, however, high molecular weight polymers with considerable mechanical strength and flexibility [1–3]. The terephthaloyl segment, very frequently used as aromatic ester unit, is responsible for such good mechanical properties while aliphatic ester segments impart material elastomeric properties with controlled degradability, if required [4,5]. Interesting monomer, successfully applied as an aliphatic building block, is dimer fatty acid (DFA) usually synthesised by dimerization of oleic, linoleic and linolenic acids [6–8]. Especially, PED multiblock copolymers (PED) composed of poly(butylene terephthalate) (PBT) and DFA are recently extensively studied for biomedical applications [9–11]. They show good biocompatibility with no adverse biological effects after long term in vivo experiments [11]. Their thermal and static mechanical properties described in Ref. [7] indicated that they match requirements regarding the mechanical properties to perform their function in applications such as temporary flexor tendon prosthesis. Recently, evaluated fatigue properties with applications of a stepwise increasing load procedure indicated their good load-carrying properties especially in the case of polymers containing a high amount of the hard phase [12].

The knowledge about creep properties of elastomers is of great importance when they are expected to remain structurally stable within long duration loadings. Normally creep is defined as the length change during a constant loading (Fig. 1) [13]. When a sinusoidal force pattern (dynamic loading) is applied in a creep test, the strain increase can be referred to as 'dynamic creep'. The amount of stresses applied for the evaluation of the dynamic creep behaviour of polymers can be determined from the stepwise increasing load tests (SILT) [12,14,15]. These values have to be in a range in which no damage of the material is expected. In the case of PED multiblock copolymers as described in our earlier publication [12], these values were ranging from 1.25 to 6 MPa, depending on the mechanical

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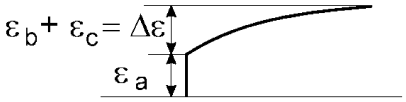

Fig. 1. Schematic representation of a creep curve. ε_a—the immediate elastic (instant) deformation—recoverable; ε_b—the delayed elastic deformation—recoverable; ε_c—the Newtonian flow—unrecoverable; $\Delta\varepsilon$—absolute creep.

characteristic of each polymer within hard segment range from 26 to 70 wt%.

In this study, the 'dynamic creep' was investigated by monitoring the position of the hysteresis loop. Especially, the change of the strain-related material properties as a function of the hard/soft segments concentration within PED copolymer series have been evaluated. Important parameters influencing the creep resistance are beside applied stresses and duration of the test, the testing temperature and environment. Therefore PED copolymers were investigated at elevated temperature and for future biomedical applications in the presence of a liquid environment of simulated physiological fluid (SPF).

The 'dynamic creep' has also been studied for commercially available poly(ester–ether) and medical grade poly(ether–urethane)s TPEs. Fatigue properties of TPEs, including PED copolymers have been compared to chemically cross-linked, silicone elastomer currently used in medicine, which is known to have an excellent creep resistance.

2. Experimental

2.1. Material

The synthesis methods of PED copolymers, involving transesterification and polycondensation from the melt are described in previous publications [7,16]. Commercially available TPEs of hardness Shore D of 55 were also used: poly(ester–ether) TPEs of Arnitel 550, Arnitel UM 551 (DSM, The Netherlands) and Elitel (Elana SA, Poland), and 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. Differential scanning calorimetry

Differential scanning calorimetry (DSC) scans were performed with a TA Instruments (DSC-2920) apparatus. The samples were dried in vacuum at 70 °C, and then kept in desiccator. The process was carried out in a triple cycle: first heating, then cooling, and second heating in the temperature ranges from −120 °C to the temperature which was 30 °C higher than the melting point of each copolymer. The rate of heating and cooling was 10 °C/min. The glass transition temperature (T_g) was determined from the temperature diagrams as the mid point of the inflection on the curve.

2.4. 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 200 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.

2.5. Dynamic creep from the hysteresis measurements

A servo-hydraulic test machine with a digital controller (Instron 8400/8800) and a software package for the evaluation of the hysteresis loop were used as described in our previous paper [12].

The *stepwise increasing load procedure* [12,14,15] has been used as a rapid testing method for the determination of load-dependent changes of elongation in the so called 'dynamic creep'. Briefly, in this procedure the dynamic load is increasing after a certain number of cycles while the load ratio remain constant. In other words, the amplitude of the load is stepwise increased and held constant within each step for a definite number of cycles.

In a *single load test* (*SLT*) the specimens were subjected to a stress controlled sinusoidal oscillation. The frequency f, was 1 Hz and no hysteretic heating was detected at the surface of the specimen. The maximum stress was set at a

Table 1
Load values, σ_L derived from SILT test used for evaluation of 'dynamic creep' behaviour

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

value pre-selected from the SILT (Table 1). The stress was kept constant during a period of 100,000 cycles when samples were tested in air at 24 °C and for 36,000 cycles for tests performed in an environmental chamber at variable temperature and environment conditions. The digital controller was used to keep the load level constant with an accuracy of 5%.

The load ratio, R, was 0.1. This load ratio indicates that sinusoidal oscillations were cyclic repeated in tension mode at minimum load ten times lower than maximum load. The temperature of the sample was monitored and no effect of hysteretic heating was observed.

2.6. Simulated physiological fluid

A SPF consists of ions, such as Na^+, K^+ Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^-, HPO_4^{2-}, and SO_4^{2-} with concentrations nearly equal to those of human body fluid. It was prepared by dissolving reagent-grade chemicals in distilled water and buffered at appropriate pH (7.4). Samples in a shape of S-2 dog-bones were fixed in the sample holder inside the environmental chamber filled with SPF and tested.

3. Results and discussion

3.1. Influence of the hard/soft segments ratio in PED copolymers on the structure

The effect of hard/soft segment content on thermal transitions is shown in Table 2. In the case of PED copolymers three transitions were detected upon heating. In a first heating ramp, a small endotherm appears in the temperature range of 53–55 °C (T_{g2}) which is also typical for poly(ester–ether) multiblock TPEs and segmented polyurethanes [17,18]. This endotherm is usually ascribed to the thermal history of polymers crystallized from the melt and as being the result of internal stresses in the polymer melt and break-up of short-range order induced by room temperature annealing; it also has been called the glass transition of the hard segments [17–19].

Heating polymers above the melting point (T_{m2}) of the hard domains causes the hard domain becomes fluid and then diassociate, and phase mixing of the hard and soft segments occurs. On cooling, the hard and the soft segments become incompatible again and the phase separates into microdomains (appearance of the crystallization exotherm, T_c, see Table 2). This process leads to the reformation of the physical cross-links in such a way, that during the second heating the small endotherm in the region of 53–55 °C disappears. The glass transition of soft segments (T_g) appears in the low-temperature region and shifts to higher temperatures with increasing hard segments content. It is worth to point out that the change of the heat capacity at T_g, ΔC_p decreases with increasing hard segments content. This result can be explained by considering a higher degree of crystallinity for samples containing a higher concentration of hard segments and a formation of a well-defined hard segment domains.

Table 2
Differential scanning calorimetry of PED copolymers

Sample	Soft segments		Hard segments				
	T_{g1} (°C)	ΔC_p (J/g/°C)	T_{g2} (°C)	T_{m2} (°C)	ΔH_{m2} (J/g)	T_{c2} (°C)	$W_{c,h}$ (%)
M2674	−41.7	0.331	53.3	117.2	10.6	24.3	7.3
M4060	−35.7	0.285	53.7	145.5	14.5	64.3	10.0
M5050	−33.0	0.249	55.7	170.8	16.8	122.3	11.6
M6040	−25.2	0.222	58.3	188.2	24.9	134.8	17.2
M7030	−18.2	0.224	56.6	198.8	36.2	157.3	25.0

T_{g1}—glass transition of the soft segments, ΔC_p—change of the heat capacity at glass transition; T_{g2}, T_{m2}, T_{c2}—glass transition, melting, and crystallization temperatures, respectively, of the hard segments; ΔH_{m2}—melting enthalpy of the hard segments; $W_{c,h}$—mass content of PBT crystallites in the polymer.

3.2. Structural changes in PED copolymers due to 'dynamic creep'

For a given polymer (Fig. 1), during creep a relatively large amount of motion takes place after instanteneous deformation (combining an elastic and plastic shear) in regions where many chain segments are still relaxed (so called primary or immediate elastic deformation region), and then a steady rate of creep is becoming established. This is due to the fact that most chains consist at that region of a uniformly strained material.

Fig. 2 shows dynamic creep curves of PEDs during constant loading (SLT) for each polymer with a frequency of 1 Hz for a period of 100,000 cycles in air at 24 °C. All polymers show an asymptotic curve (Fig. 2(a)). The immediate elastic deformation region (length change) for the softer polymers is significantly larger than it is for the stiffer materials (Fig. 2(a)). The absolute creep, $\Delta\varepsilon$ (defined as a sum of the recoverable delayed deformation and unrecoverable Newtonian flow, see Fig. 1) decreases with increasing hard segments concentration (increasing crystallinity) as demonstrated in Fig. 2(b).

The influence of the hard/soft segments concentration is also well demonstrated by the changes of the slope and the area of the hysteresis loop taken at the cycle number 50,000 for each PED copolymer as demonstrated in Fig. 3. Polymers containing low content of the soft segments, i.e. of low crystallinity show larger displacement than stiffer polymers. Aromatic ring-containing hard segments are very rigidly held together and have much greater inertia than methylene carbons lined up in an aliphatic chain of DFA of the soft segments, and in consequence show higher stiffness and lower displacement values of more rigid polymers (containing a higher amount of the hard segments).

The 'dynamic creep' depends not only on the mobility of

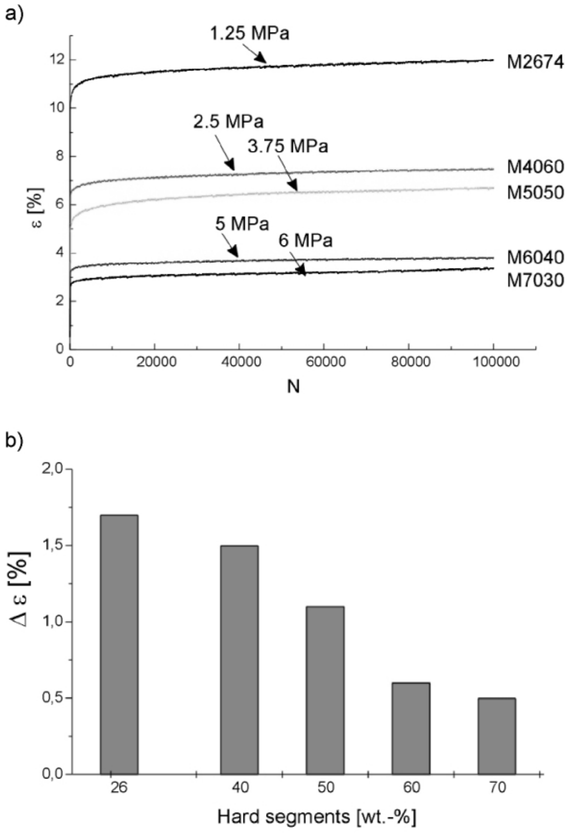

Fig. 2. (a) Dynamic creep (ε) curves of PED samples; loading patterns are indicated for each polymer, (b) absolute creep (Δε) values for PED copolymers. Test frequency: 1 Hz, number of cycles (N) : 100,000. $T = 24$ °C.

the chain segments and crystallinity, but also on the strength of secondary bonds [10]. This is clearly indicated by the comparison of different elastomers used in this study (Fig. 4). The cross-linked three-dimensional network of a silicone elastomer (Silastic) shows very high creep resistance. However, it shows the largest immediate elastic deformation (about 28%) at relatively low applied load (0.5 MPa). This can be an indication for a very low stability of chemical cross-links under instant loading (deformation).

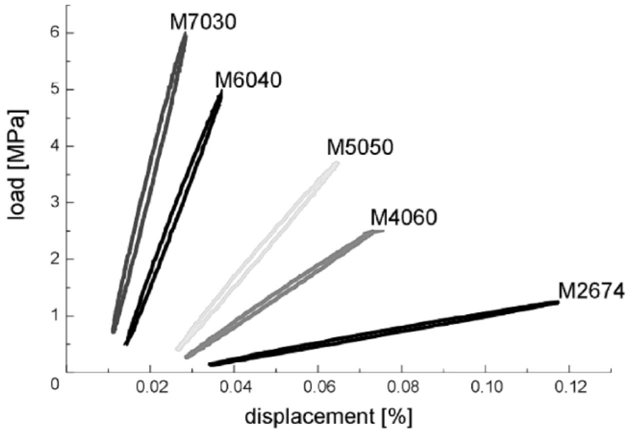

Fig. 3. Hysteresis loops of PED copolymers taken at cycle number 50,000.

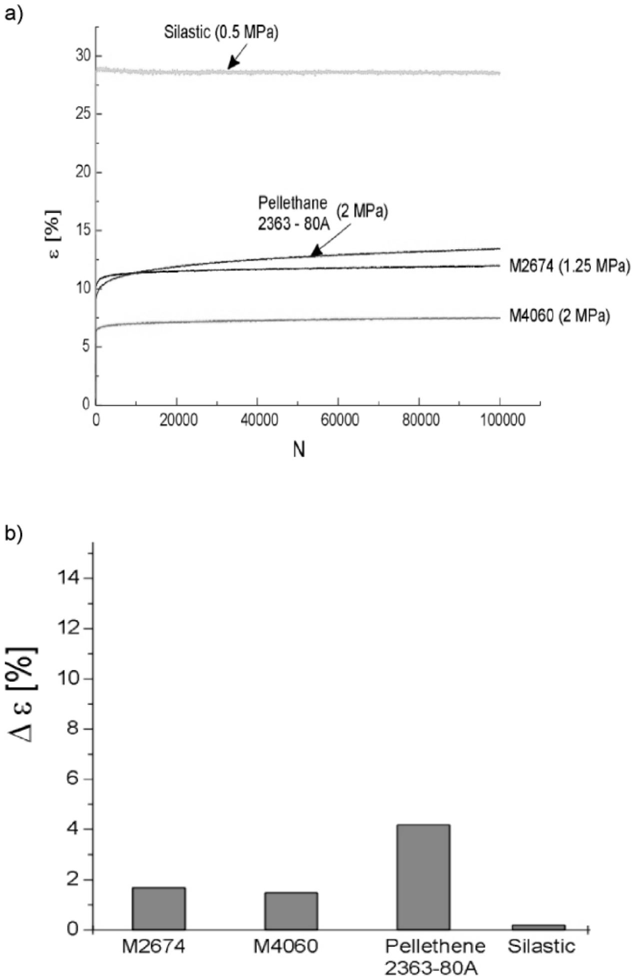

Fig. 4. (a) Dynamic creep (ε) curves of soft PED copolymers and other reference materials; loading patterns are indicated for each polymer; (b) absolute creep (Δε) values for these copolymers. Test frequency: 1 Hz, number of cycles (N) : 100,000. $T = 24$ °C.

Multiblock copolymers containing dimerized fatty acid in the soft segments and showing microphase separated structure have lower values of immediate elastic deformation than silicone elastomer. PED copolymer containing 40 wt% of the hard phase shows very low value of immediate elastic deformation and very low creep (about 1.8%) after 100,000 cycles. PED copolymers are more resistant to creep compared to polyurethane copolymers (polyurethanes usually show good resistance to creep due to the presence of strong hydrogen bonds stabilizing microstructure). Lower creep resistance of a polyurethane sample can be interpreted following Takahara's et.al [20,21] suggestions, that under the cyclic deformation the destruction of the hard segment domains and/or intermixing of the hard and soft segments can take place.

Fig. 5 presents the comparison of hysteresis loop patterns of soft polymers tested under constant load. The hysteresis loop of a Silastic elastomer, which shows very high creep resistance, exhibits very high displacement and a very low value of the force. The much broader hysteresis loop of a

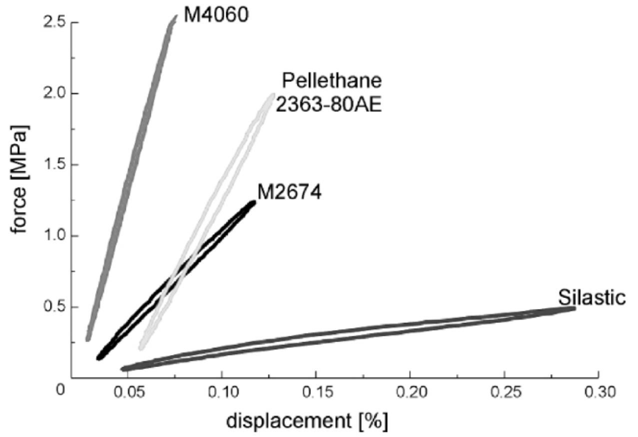

Fig. 5. Hysteresis loops of soft PED copolymers and reference materials taken at cycle number 50,000.

polyurethane copolymer compared to PED copolymers can indicate structural changes, and in consequence induces high energy dissipation and very large creeping, as it was already discussed.

When multiblock copolymers of the same hardness (ShD 55) are loaded with the same load amplitude (4 MPa) a different creep behaviour is observed as well for polyester-type multiblock copolymers, including PED containing 60 wt% of hard segments as for polyurethane samples (Fig. 6). Polyesters are very stable under applied load, which can indicate on a very high segmental stability (good phase separation). A noticeable creepage, observed for the polyurethane sample, can be explained by an appearance of a very low creep (apparent) modulus with phase mixing between hard and soft segments domains proceeded with increasing fatigue time (increasing number of the cycles). Low modulus has already been observed in static testing: polyester samples revealed Young's modulus of 140–160 MPa, while polyurethane samples of the same hardness showed Young's modulus of 68 MPa [12]. As can also be seen from Fig. 7 the hysteresis loop of a polyurethane copolymer shows a very large area which can testify about large energy dissipation.

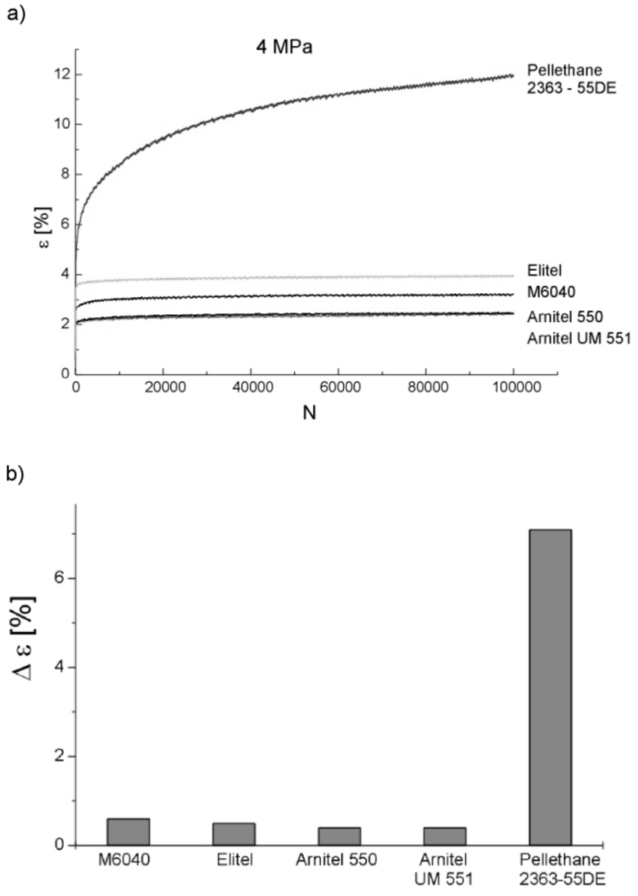

Fig. 6. (a) Dynamic creep (ε) curves of soft PED copolymers and other reference materials; loading patterns are indicated for each polymer; (b) absolute creep ($\Delta\varepsilon$) values for these polymers. Test frequency: 1 Hz, number of cycles (N) : 100,000. $T = 24$ °C.

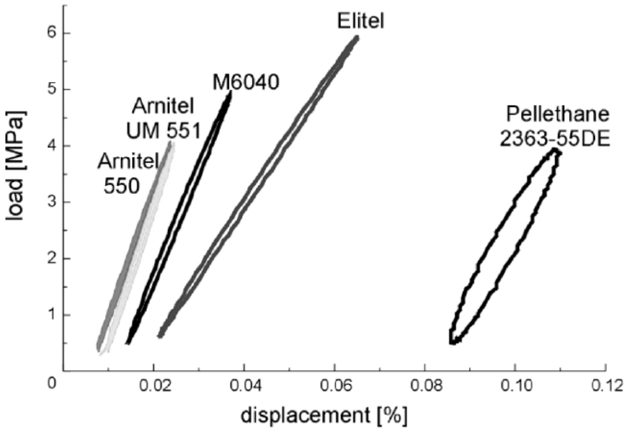

Fig. 7. Hysteresis loops of soft PED copolymers and reference materials taken at cycle number 50,000.

Important parameters influencing creep resistance are not only applied stresses and duration of the test but are equally important as the testing temperature and an environment. In

Fig. 8. Environmental chamber attached to servohydraulic testing machine.

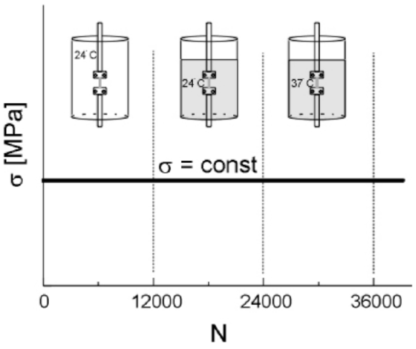

Fig. 9. Schematic representation of testing protocol for different temperature and environmental conditions. *N*—number of cycles.

order to study dynamic creep behaviour of PED copolymers at elevated temperature and in the presence of a liquid environment, a special environmental chamber has been designed (Fig. 8).

Constant temperature and environmental conditions were kept by immersing samples in simulated body fluid at 24 and 37 °C for a defined number of cycles. One would expect an additional effect of the hydrostatic forces from the liquid, therefore, samples were tested in different conditions: in air at 24 °C, in presence of SPF at 24 °C, and in presence of SPF at 37 °C. A schematic representation of the testing procedure is shown in Fig. 9.

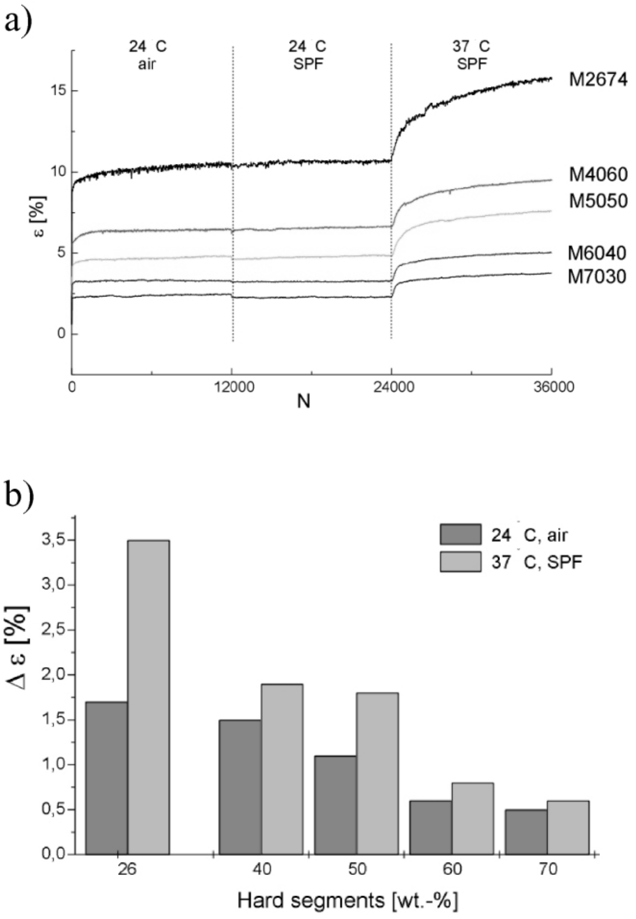

Fig. 10. (a) Dynamic creep (ε) curves of PED samples under different temperature and environmental conditions; (b) creep ($\Delta\varepsilon$) values for these copolymers at different environment and temperature. Test frequency: 1 Hz, number of cycles (*N*) : 36,000.

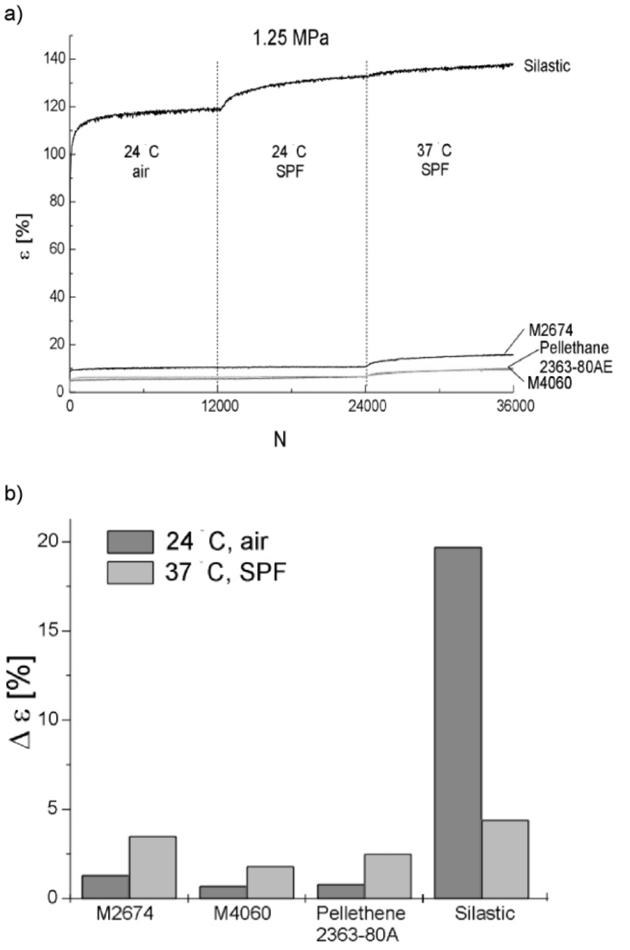

Fig. 11. (a) Dynamic creep (ε) curves of PED multiblock copolymer and other soft reference materials under different temperature and environmental conditions; (b) absolute creep ($\Delta\varepsilon$) values for these copolymers at different environment and temperature; constant loading of 1.25 MPa. Test frequency: 1 Hz, number of cycles (*N*) : 36,000.

PED copolymers tested at different temperature and environment conditions reveal, a significant influence of the elevated temperature (37 °C) on the creeping behaviour (Fig. 10). No significant influence, however, of the testing environment (air or liquid) at the same temperature (24 °C) has been observed.

Due to the special design of an environmental chamber, allowing to reach very high elongations, it was possible to test all soft reference materials with the same applied load of 1.25 MPa. Silastic elastomer, which is a chemically cross-linked elastomer, shows tremendous instant deformation up to 100% (Fig. 11). This material is also very sensitive to action of hydrostatic forces when the chamber is filled out with SPF and the temperature is maintained still at 24 °C. The absolute creep change is estimated at 12%. All tested materials, including reference poly(ether–urethane) are

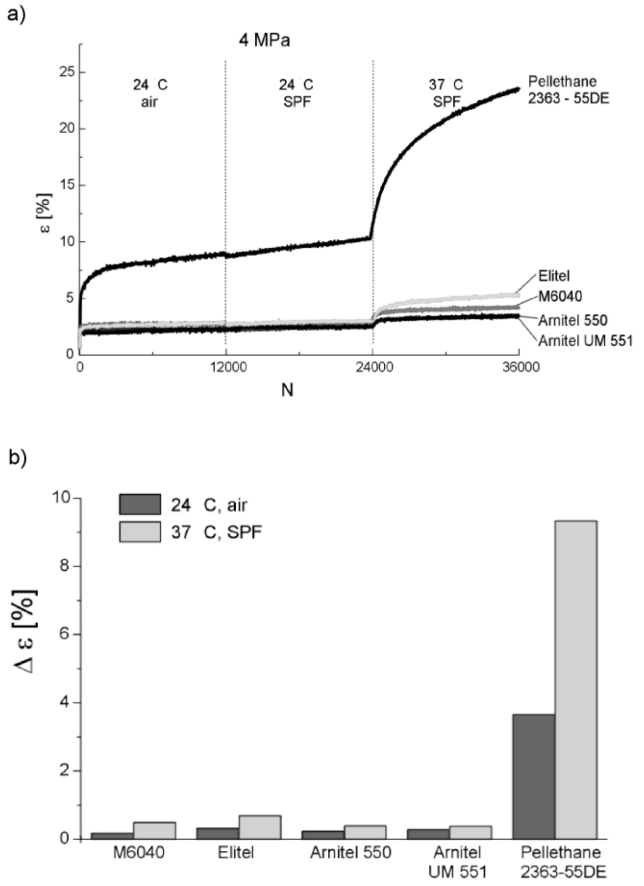

Fig. 12. (a) Dynamic creep (ε) curves of PED multiblock copolymer and reference materials of Shore hardness D of 55 under different temperature and environmental conditions; (b) absolute creep ($\Delta\varepsilon$) values for these copolymers at different environment and temperature; constant loading of 4 MPa. Test frequency: 1 Hz, number of cycles (N) : 36,000.

physically cross-linked TPE (except Silastic elastomer), show good creep resistance at elevated temperature and in the presence of a liquid environment. PEDs and polyurethane copolymer containing crystallizable physical cross-links shows much better resistance to creep (the best results were obtained for PED copolymer containing 40 wt% of the hard segments, see Fig. 11).

When multiblock TPE copolymers of the same hardness (Sh D 55) were subjected to cyclic loading in the presence of different temperature and environmental conditions, one can observe that polyester-type copolymers show much better resistance to creep than polyurethane Pelletane copolymer (Fig. 12(b)) when samples are tested at the same load of 4 MPa.

4. Conclusions

The hysteresis loop measurement method can successfully be applied to evaluate the fatigue properties of thermoplastic PED multiblock elastomers in terms of their creep behaviour. PED copolymers, differing in their composition (hard/soft segments concentration), exhibit different ‘dynamic creep’ behaviour which can be correlated with the hard segments content: the higher the hard segments content, the lower the absolute creep of copolymers. The hard segment content influences the behaviour at ambient and elevated temperatures indicating that stiffer materials are less susceptible to environmental conditions than polymers containing a high amount of the soft phase. PED copolymers compare very well with commercially available poly(ester–ethers) and show much better creep resistance compared to poly(ether–urethanes) when samples of similar hardness (Shore D 55) are compared. Soft PED copolymers show also good creep behaviour when tested at different temperatures and environmental conditions: the best creep resistance has been found for PED copolymer containing 40 wt% of the hard segments. The degree of crystallinity has been calculated as 10% and seems to be an optimum for good creep properties (the probability of structural changes within the crystals is higher at higher crystallinity). Evaluated properties can be very useful in the design of semi-crystalline polymers which are subjected to a long duration loading.

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