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Polyurethanes having shape memory effects

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Segmented polyurethanes (PUs) were prepared from polycaprolactone diols (PCLs), 4,4′-diphenylmethane diisocyanate, and 1,4-butanediol, and tested for shape memory effects. Effects of soft segment molecular weight ($M_n = 2000$, 4000 and 8000), soft segment content (50–90%), and maximum strain ($\varepsilon_m = 100$, 200, and 600%) on the cyclic tensile properties as well as the dynamic mechanical, and mechanical properties below (25°C) and above (65°C) the shape recovery temperatures were studied. With increasing soft segment contents: i) glassy state modulus increased and rubbery state modulus decreased; ii) hardness increased at room temperature, and decreased at 65°C; iii) recovery strain decreased with PCL 2000, and increased with PCL 8000 based PUs. On the other hand, the increase in soft segment length resulted in: i) increased rubbery state modulus as well as glass state modulus; ii) increased hardness at room and high temperatures; iii) increased recovery strain at high soft segment content. Tensile yielding became clear with increasing soft segment length and content. Strain upon cooling and unloading (ε_u) and residual strain (ε_p) increased, and recovery strain (ε_r) decreased with cycling. Among these, residual strain was most sensitive to the cycling. Most of the cycling effects were confined during the first one or two cycles. These results were interpreted in terms of soft segment-hard segment phase separation and soft segment crystallization. Copyright © 1996 Elsevier Science Ltd.

(Keywords: shape memory polyurethane; dynamic mechanical properties)

INTRODUCTION

Shape memory polymers are fairly recently developed functional polymers which find applications in broad range of temperature sensing elements. These polymers basically consist of two phases, fixed points or frozen phase and reversible phase. Accordingly, excellent shape memory effects have often been observed with trans-polyisoprene (TPI)[1], styrene–butadiene copolymer (SB)[2] and segmented polyurethanes (PUs)[3]. In these materials, the crystalline soft domains (crystalline phase of TPI, crystalline polybutadiene segments and crystalline soft segment domains) form the reversible phase, with their crystalline melting temperature being the shape recovery temperature (T_s), and hard domains (crosslinks in TPI, styrene blocks in SB, and hard segments of PU) become the fixed points or frozen phases. Fixed points remain hard during the second shaping process which normally is done at a temperature higher than the shape recovery temperature. Reversible phase is subject to softening and hardening upon heating above T_s and cooling below T_s, respectively.

Basic principles of shape memory effects and their application procedure can be best described with their modulus (E)–temperature (T) behaviour, where a linear polymer with its crystalline melting temperature (T_m) of soft segment being T_s is assumed (*Figure 1*). Here T_h is the softening–hardening transition temperature of fixed phase, where T_l and T_u are the typical loading and unloading temperatures, respectively. During the primary processing, such as injection moulding, the materials are heated above T_h, where the previous memories are completely erased. During cooling in the mould, fixed phases emerge as the temperature decreases below T_h, and the formation is completed at T_s. Upon further cooling below T_s, soft segments crystallize and the materials are frozen to their glassy state. The shape of this moulded specimen is the original shape of the shape memory experiment.

The secondary shapings, such as extension, compression, and transfer moulding can be performed either at $T > T_s$, or $T < T_s$. When the sample is deformed at $T < T_s$, shape is simultaneously fixed upon completing the deformation. This method can be used to prepare braille boards for the blind. For example a letter erroneously raised on the board can be erased upon heating, and raised correctly at low temperature. On the other hand, when the sample is deformed at high temperature ($T_s < T < T_h$), the deformed shape is fixed upon subsequent cooling under constant strain. In both types of shaping, the original shape is recovered at high temperature. The driving force of shape recovery is the elastic strain generated during the deformation. Deformation at high temperature is much easier due to the lower

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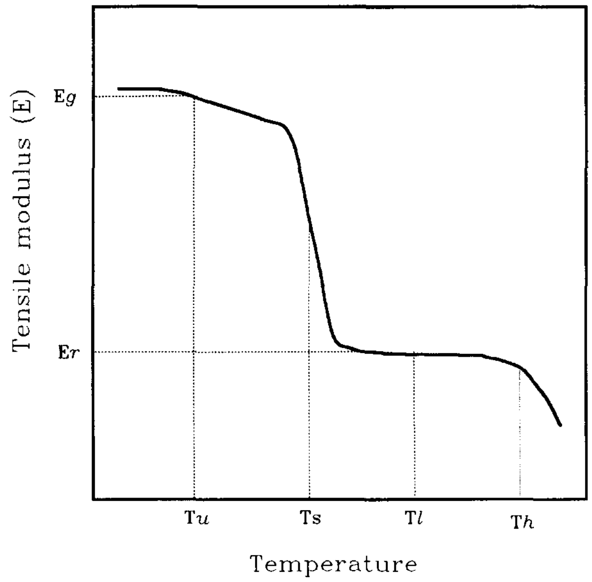


Figure 1 Typical modulus–temperature curve of shape memory polymer

rubbery modulus of the polymer, and makes the orientation of polymers more feasible. However, many of the orientations will be relaxed before their structures are frozen during the subsequent cooling cycle. On the other hand, deformation at low temperature is more difficult due to the higher glassy state modulus of the polymer, but the chain orientation will remain at a higher degree due to the slow relaxation of the orientations. A high glassy state modulus (E_g) will provide the materials with high shape fixity during simultaneous cooling and unloading, whereas the high rubbery modulus (E_r) with high elastic recovery at high temperature. In addition a sharp transition from glassy state to rubbery state makes the material sensitive to temperature variation. A high elasticity ratio (E_g/E_r), preferably a difference of two orders of magnitude, allows easy shaping at $T > T_s$ and great resistance to deformation at $T < T_s$. One or two of these requirements can be satisfied easily with many of the existing polymeric materials. However, to satisfy all of these properties systematic designs should be carried out to relate the structural varieties with the properties.

The stress–strain–temperature behaviour of the materials is of basic importance with regard to the shape fixing and shape memory effect evaluations. In addition, the shape memory polymer element is often subjected to cyclic deformation, such as in an actuator, and hence the cyclic characteristics are also of practical importance in evaluating the durability of the shape memory element[4].

Regarding shape memory materials, shape memory alloys and bimetal have been known for sometimes. As compared with these metallic compounds, shape memory polymers have low density, high shape recoverability, easy processability, and low cost. Segmented polyurethanes are basically block copolymers of soft segments and hard segments (*Figure 2*). Soft segments are polyols of typical molecular weight 1000–2000, whereas hard segments are built from diisocyanates and extenders. Depending on the types and compositions of soft and hard segments and preparation procedures the structure–property relationships of PUs are extremely diverse and easily controlled, and hence the shape recovery temperature can be set at any temperature between −30°C and 70°C, allowing a broad range of applications. They can be moulded using conventional processing techniques including extrusion, injection and blow moulding, which allow versatility of shaping.

We report the synthesis and structure–property–temperature relationships of shape memory polyurethanes, prepared from polycaprolactone diols (PCLs), 4,4′-diphenylmethane diisocyanate (MDI), and 1,4-butanediol (BD). The effects of molecular weight of polyol (2000, 4000, and 8000) and soft segment content (55–90%) have been studied in terms of stress–strain behaviour at below and above T_s, and cyclic tensile behaviour up to five cycles with varying maximum strains. The relationships between dynamic mechanic properties and shape memory effect have also been discussed intensively in this paper.

EXPERIMENTAL

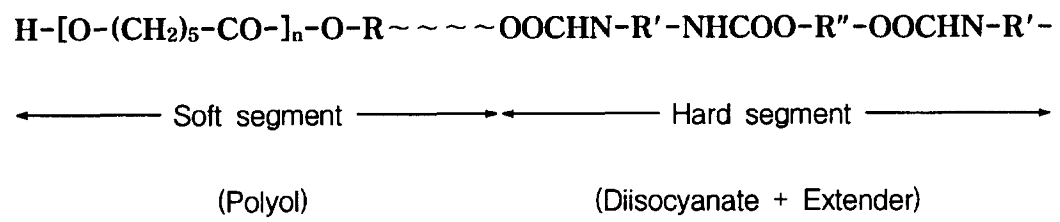
Materials and preparations of polyurethanes

Table 1 shows the basic formulations of the present experiments. PCL (Daicel) having molecular weight (M_n) 2000, 4000 and 8000 (hereafter called PCL 2000 etc.) were dried and degassed at 80–100°C under 1–2 mmHg for 5 h before use. Extra pure grades of MDI and BD were used with PCL to prepare segmented polyurethanes. PCL of molecular weight 8000 was not commercially available, and was prepared from condensation reactions between PCL 4000 and adipic acid. The reactions were carried out in dimethyl formamide (DMF) at 198°C. The progress of reaction was monitored by measuring the acid value of the reaction mixtures[5]. When the acid value approached 5.2, the reaction was stopped. Molecular weight determined from gel permeation chromatography (g.p.c.) was approximately 7950, and this will be referred to PCL 8000.

A 500 ml round-bottom, four-necked separable flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and condenser with drying tube was used as reactor to prepare the polyurethanes. Dried PCL and a molar excess of MDI were charged to the dried flask. The urethane forming reaction was carried out at 60°C for about 1.5 h, followed by chain extension with BD for

Table 1 Basic formulations of the experiments

Run	M_n of PCL	Moles of polyol	Moles of BD	Moles of MDI	Soft segment (%)
2–55	2000	1	3.9	4.9	55
2–70	2000	1	1.65	2.65	70
2–80	2000	1	0.7	1.7	80
2–90	2000	1	0	1	90
4–50	4000	1	10	11	50
4–60	4000	1	6	7	60
4–70	4000	1	4	5	70
4–75	4000	1	3	4	75
4–80	4000	1	2	3	70
4–85	4000	1	1	2	85
4–90	4000	1	0.3	1.3	90
8–55	8000	1	18	19	55
8–70	8000	1	9	10	70
8–80	8000	1	5	6	80
8–90	8000	1	2	3	90



$H\text{-}[O\text{-}(CH_2)_5\text{-}CO\text{-}]_n\text{-}O\text{-}R\sim\sim\sim\sim OOCHN\text{-}R'\text{-}NHCOO\text{-}R''\text{-}OOCHN\text{-}R'\text{-}$

Figure 2 Segmented polyurethanes

the same period of time. The progress of reactions in preparing the NCO-terminated prepolymers and chain extension step was monitored by measuring the isocyanate value. A standard di-*n*-butylamine back titration method was employed[6].

Film casting and tests

Films were prepared by solvent casting on a glass plate. After standing at 60°C for 3 h, films were further dried at 70°C under 2–4 mmHg for the next 4 days. Microtensile specimens (25 mm (length) × 5 mm (width) × 1 mm (thickness)) were prepared according to ASTM D-1822. Tensile and cyclic loading tests were done using a tensile tester (Tinius Olsen Series 1000), attached with a constant temperature heating chamber. Specimens were heated using a bundle of heating lamps, and cooled by spraying the compressed air. Loading and unloading together with heating and cooling were automatically controlled by a personal computer which was interfaced with the tensile tester. *Figure 3* defines a thermomechanical cycling test with loading at high temperature (T_l). Samples were elongated to a constant strain (ε_m) at a constant elongation rate ($\dot{\varepsilon}$). While maintaining the strain at ε_m, samples were cooled to low temperature (T_u) and unloaded. Upon removing the constraint at T_u a substantial recovery of strain, ε_u occurs. The samples were subsequently heated to T_l in 5 min, and stayed at that temperature for the next 10 min, allowing recovery of strain, ε_r. This completes one thermomechanical cycle leaving a residual strain, ε_p. The area below the loading curve corresponds to the total strain energy per unit volume, whereas the one below the unloading curve to recovery strain energy. Consequently the area enveloped by the loading and unloading curves is the dissipated strain energy.

The significance of various strains should be mentioned regarding the shape memory effect. The strain maintained after unloading, and the residual strain of each cycle can be used to define the shape fixity and recovery as follows.

$$\%\text{ shape fixity} = \frac{\varepsilon_u}{\varepsilon_m} \times 100$$

$$\%\text{ shape recovery} = \frac{\varepsilon_r}{\varepsilon_m} \times 100$$

where $\varepsilon_r = \varepsilon_m - \varepsilon_p$. The strain recovered upon unloading the samples, i.e. $\varepsilon_m - \varepsilon_u$, depends on the glassy state modulus of the materials. The higher the glassy state modulus, the smaller the recovered strain resulting in a great shape fixity.

Dynamic mechanical properties of the solution cast films were determined using a Rheovibron (Orientec, DDV-01FP) at 11 Hz, 3°C min^{-1}. Phase morphologies of the segmented PU were studied from X-ray scattering (Rigaku, D-max 2400). Hardnesses (Shore A and D) at room temperature and high temperature were determined to relate the soft segment crystallization with soft segment length, soft segment content, and soft segment–hard segment phase separations. The effect of molecular weight on the thermal properties of PCL was measured using a differential scanning calorimetry (d.s.c., Du Pont 2100). D.s.c. measurements were also performed to determine the crystallinity of soft segments as functions of soft segment length and content. Heat of crystallization (ΔH_c) in cooling was used to characterize the crystallizability of samples. The ΔH_c of 100% PCL, 136 J g^{-1}, evaluated from the melting depression of PCL by ethylbenzonate[7] was used to calculate the %crystallinity of the samples.

RESULTS AND DISCUSSION

Thermal properties and X-ray profiles

Table 2 shows the basic thermal properties variation with the molecular weight of PCL. The T_m of PCL 2000 is about 44°C, and it is increased to about 50°C for PCL 4000. The crystallization temperature (T_c) is also increased by about 5°C as the M_n of PCL is doubled. No further increase is observed beyond PCL 4000. On the contrary, ΔH_c and ΔH_f (heat of fusion) decrease monotonically with increasing molecular weight.

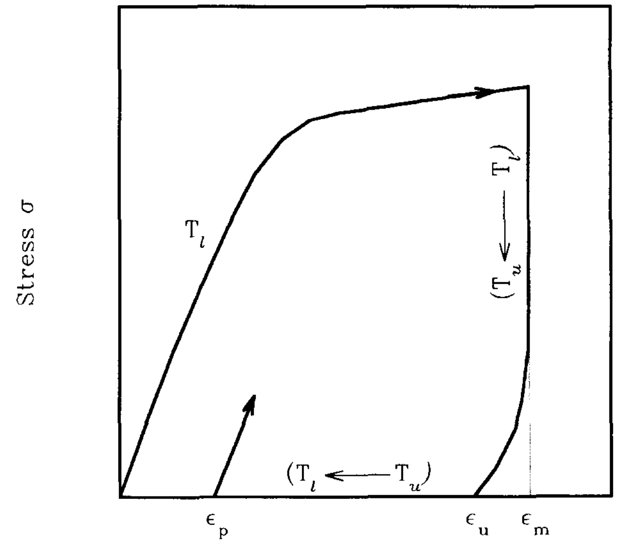


Figure 3 Cyclic tensile test with loading at high temperature ($T > T_s$)

Table 2 Thermal properties of PCL Diols

M_n	T_m(°C)	T_c(°C)	ΔH_f(J g^{-1})	ΔH_f(J g^{-1})
2000	44.3	25.3	83.4	76.0
4000	49.5	30.3	75.0	73.0
8000	50.0	29.5	65.2	63.0

Figure 4 shows typical X-ray diffraction profiles of PUs prepared from PCL 2000 and PCL 4000. The diffraction profile is a mere broad shoulder for PCL 2000 based PU. This implies that soft segment–hard segment phase mixings can disturb the soft segment crystallization, since PCL 2000 shows a melting enthotherm. On the contrary, PUs from PCL 4000 show well-defined peaks which magnify their intensity with increasing soft segment content. This suggests that soft segment–hard segment phase separation increases with increasing soft segment content as well as with the soft segment length of the PUs.

Figure 5 shows the crystallinities of the PUs as functions of soft segment length and content, determined from the d.s.c. measurements. It is clearly seen that the molecular weight of PCL is the main factor to determine the crystallizability of PUs. No crystallinity is observed with PCL 2000, a result consistent with the X-ray profiles. Crystallinity increases with increasing soft segment length and content due primarily to the increased soft segment–hard segment phase separation. For PUs of the same soft segment length, crystallinity of PCL segments decreases with increasing hard segment content.

Dynamic mechanical properties

Figures 6a and *6b* show the tensile storage modulus (E') and tan δ of PUs prepared from different M_ns of PCL at a fixed soft segment content (70%). A large difference in modulus below and above the transition temperature and a sharp glass–rubber transition are the most substantial properties to render the materials shape memory function, and these are seen from the Figure. The glass state modulus is due to elastic energy of crystalline domains and glass state amorphous domains, whereas the rubbery state modulus is due to the entropy elasticity owing to the two-phase structure of the material[8]. With a large elastic modulus ratio (E_g/E_r), high temperature deformation becomes easy while keeping the resistance to low temperature deformation great. Both glass modulus and rubbery modulus, and the transition temperature increase with increasing soft segment length. This is primarily due to the greater soft segment–hard segment phase separation and soft segment crystallization, evidenced from the X-ray diffraction profile (*Figure 4*) and d.s.c. measurements (*Figure 5*). As the soft segment crystallinity increases with increasing soft segment length, the glass transition of soft segment (based on the inflection point at about −45°C) becomes unclear. With phase separated structure, hard segments simulate physical crosslinks and effectively reinforce the soft segments in the rubbery state[9]. A larger glass modulus is desired in the sense that it gives larger shape fixity upon cooling and unloading during the cyclic deformation. When a larger strain must be obtained with a small stress at high temperature, a lower rubbery modulus such as the one from PCL 2000 based PU is a proper choice.

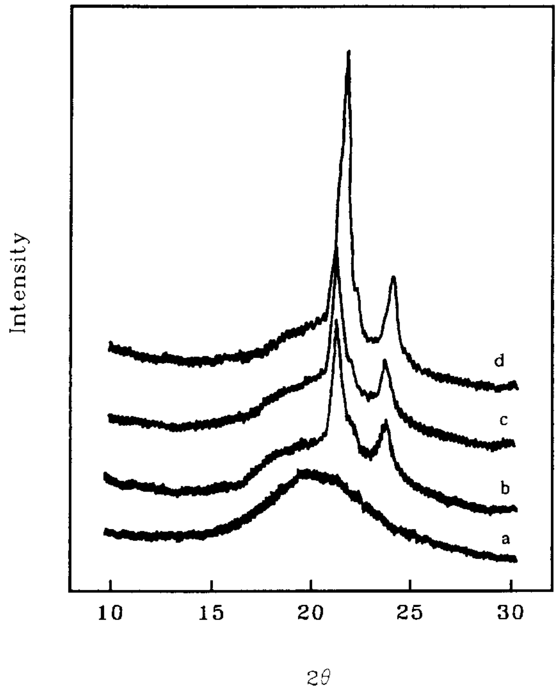


Figure 4 X-ray diffraction profiles of PCL 2000 and PCL 4000 based PUs: (a) PCL 2000–75%; (b) PCL 4000–60%; (c) PCL 4000–75%; (d) PCL 4000–85% (% = soft segment content)

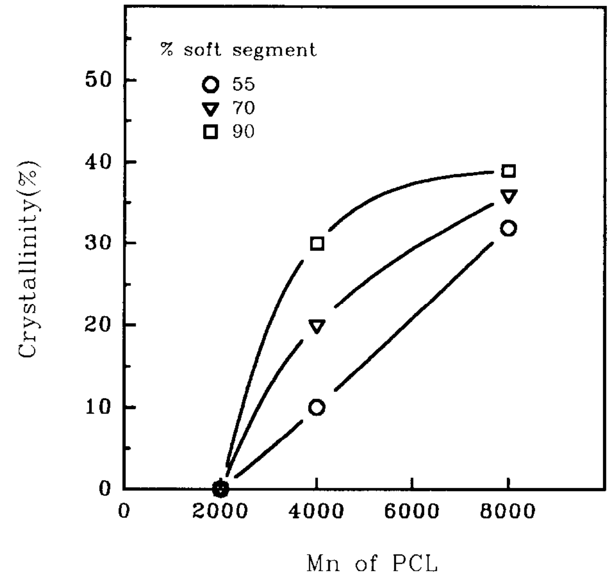


Figure 5 Crystallinities of the PUs vs. soft segment length and content

The magnitude and sharpness of the tan δ peak below the T_m of the soft segment, corresponding to the glass transition of the soft segment, decreases with increasing soft segment length. Since the tan δ corresponds to the strain energy dissipated by viscous friction, a larger tan δ implies that the material is more likely viscous than elastic. Elasticity of polymer increases with the increase of crystallinity. Therefore, PUs from PCL 2000 and PCL 4000 give greater damping as compared with PCL 8000 based PU. These low temperature damping characteristics largely depend on the extent of soft segment–hard segment phase separation and soft segment crystal-

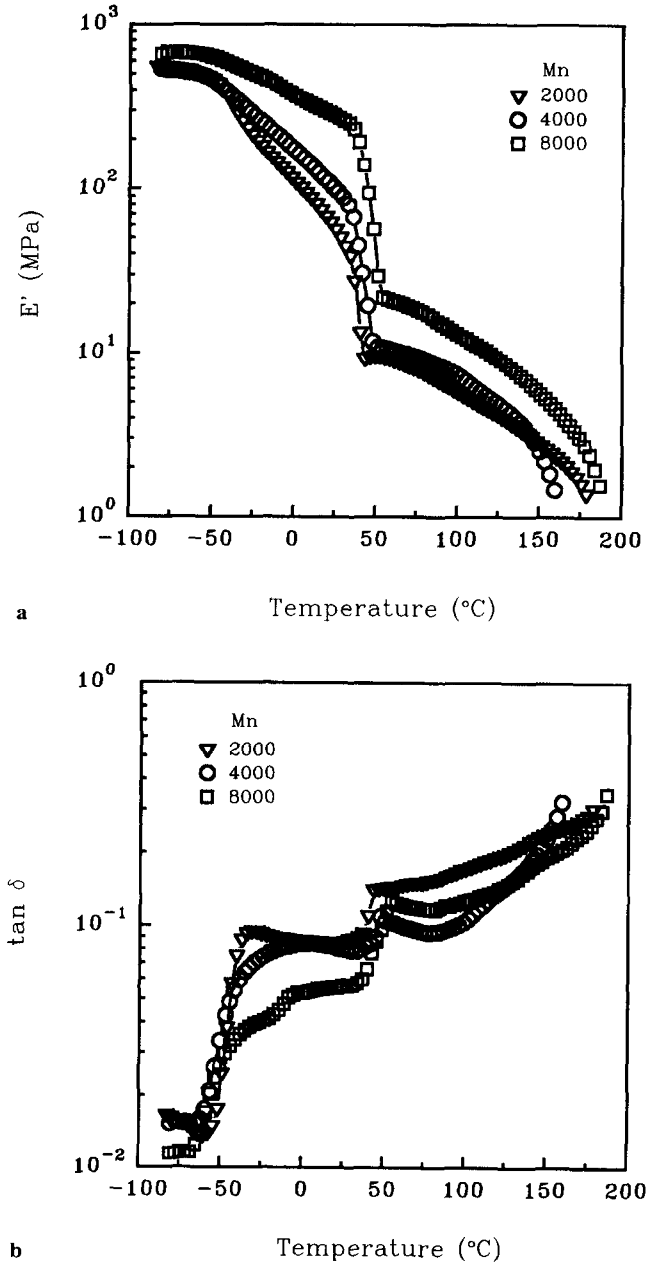


Figure 6 Effect of polyol molecular weight on the dynamic mechanical properties of PUs (soft segment content = 70%): (a) tensile storage modulus; (b) tan δ

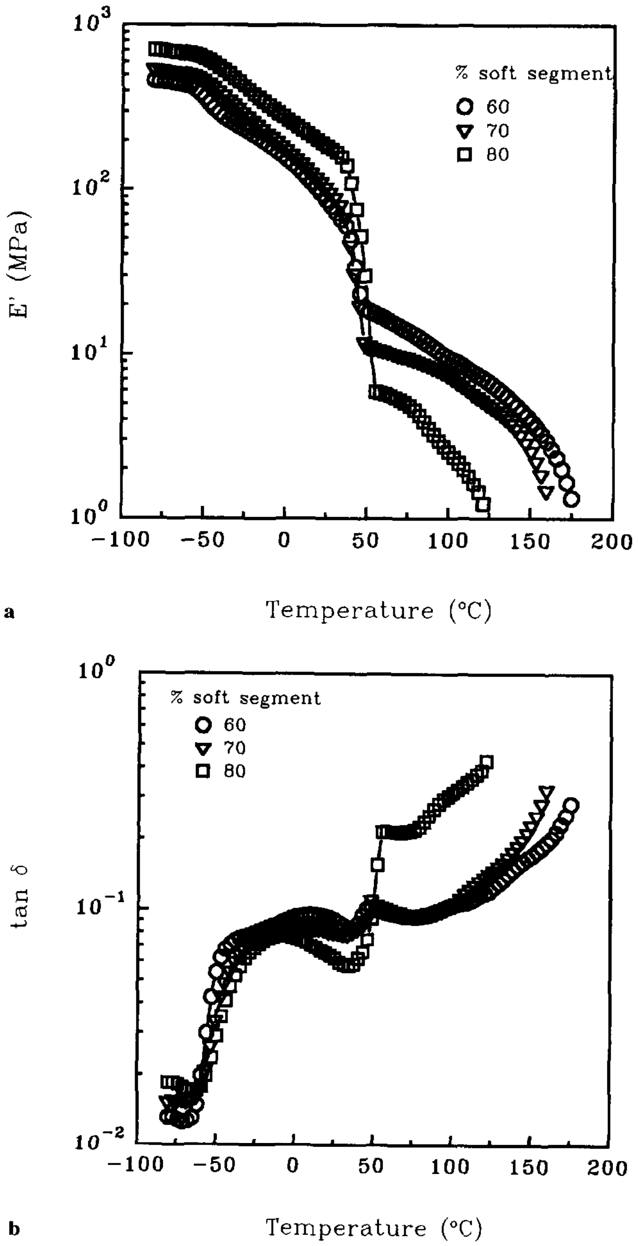


Figure 7 Effect of soft segment content on the dynamic mechanical properties of PUs (M_n of polyol = 4000): (a) tensile storage modulus; (b) tan δ

lization. The low temperature damping decreases with phase separation and soft segment crystallization. As the temperature increases above the T_m of soft segment, damping abruptly increases especially with PCL 8000 based PU due to the melting of soft segments.

The effect of soft segment content on the dynamic mechanical properties was studied with PCL 4000 based PUs and the results are shown in *Figures 7a* and *7b*. It is seen that higher soft segment content gives a higher glassy state modulus and a lower rubbery state modulus, resulting in a larger elastic modulus ratio. The difference is approximately two orders of magnitude for PU with 80% soft segment. However, as the soft segment content increases the rubbery region extends shorter due to the insufficient reinforcing effects of hard segments. In linear polymers, the rubbery plateau extends longer with increasing molecular weight, since the plateau region is the reversible process of entanglements and disentanglements, and larger molecules provide more entanglements. The insufficient numbers of hard segment domains should provide smaller number of physical crosslinks which act similar to entanglement points. The low temperature tan δ peak for PU with 80% soft segment is the lowest in magnitude and makes a well defined peak, indicative of the highest soft segment crystallinity and soft segment–hard segment phase separation[10]. However the tan δ of this particular PU is the highest as the temperature increases over the T_m due to the melting of the soft segments, which is a predominant component of this particular PU.

Hardness

Figures 8a–8c show the hardness of solution-cast PU films as a function of soft segment length and content.

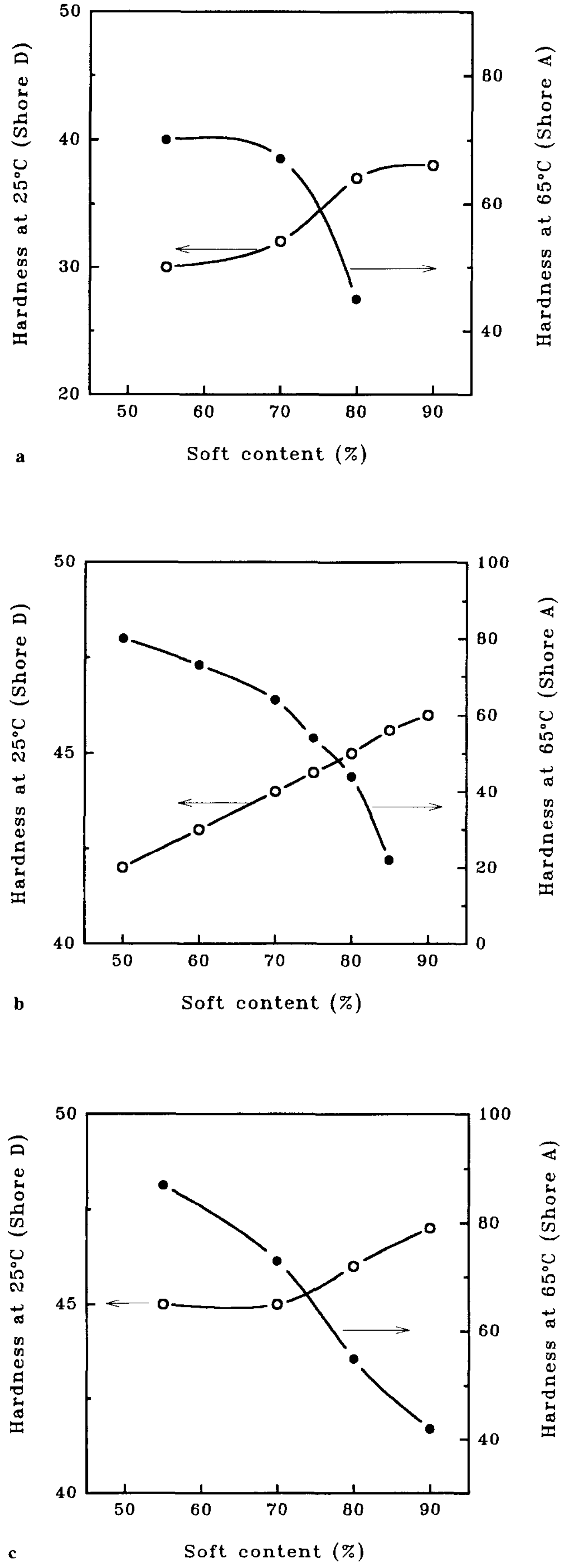


Figure 8 Hardness–composition relationships of the various PUs; (a) PCL 2000 based PUs; (b) PCL 4000 based PUs; (c) PCL 8000 based PUs

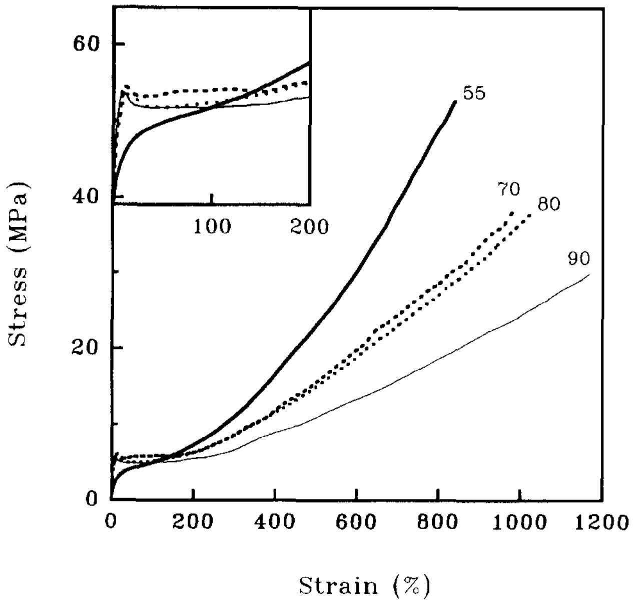


Figure 9 Stress–strain curves of PCL 2000 based PUs at 25°C (number designates soft segment content (%))

The room temperature hardness generally increases with increasing soft segment length and content. On the contrary, hardness at high temperatures (65°C) decreases with soft segment content and increases with the soft segment length. If the soft segments are noncrystallizable and phase mixed with hard segments, the increase in soft segment content should result in a decreased hardness owing to the decreased glass transition temperature of the PU. The increase of room temperature hardness with soft segment content is mainly due to the increased soft segment crystallinity for PCL 4000 and PCL 8000 based PUs. However, the corresponding increase for PCL 2000 based PUs is probably due to the increased extent of phase separation since the soft segments of PCL 2000

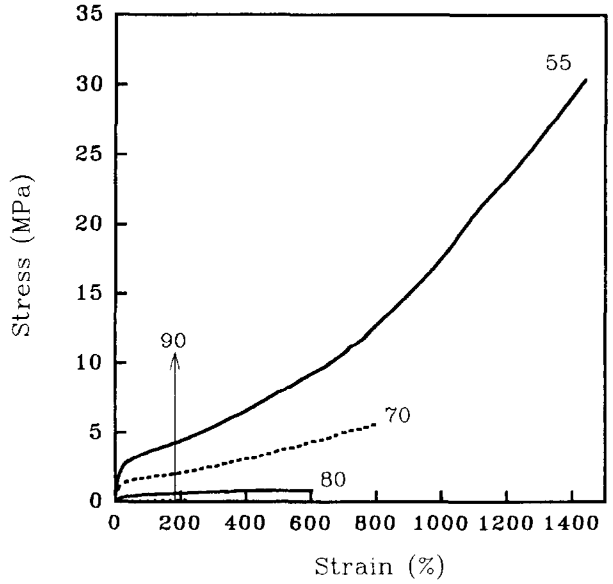


Figure 10 Stress–strain curves of PCL 2000 based PUs at 65°C

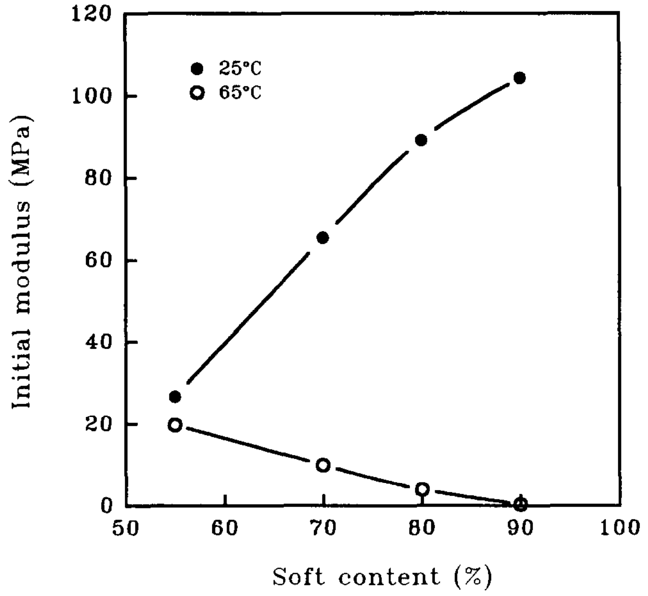


Figure 11 Initial moduli of PCL 2000 based PUs at 25 and 65°C

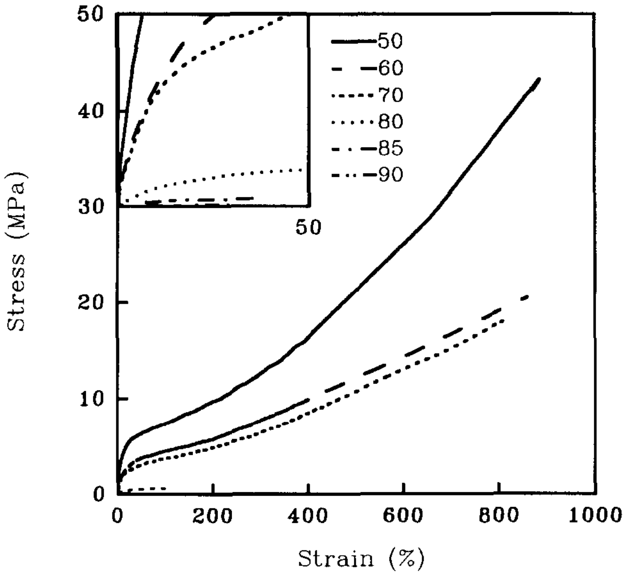


Figure 13 Stress–strain curves of PCL 4000 based PUs at 65°C

based PUs are not crystallizable (*Figures 4* and *5*). In addition, when the soft segment content is the same, larger soft segment length enhances the phase separation since the formation of isolated soft domains is more feasible with longer soft segments[11].

Hardness decrease with soft segment content at 65°C is due to the melting of more soft segments. However, the increase of high temperature hardness with soft segment length is presumably due to the greater phase separation. With increasing extent of phase separation, hard segments can effectively act as reinforcing fillers for the soft segments.

Tensile properties

Figure 9 shows the room temperature stress–strain behaviour of PCL 2000 based PUs of various soft segment contents. Tensile strength (ultimate) decreases and elongation at break increases with the increase in soft segment content. A larger elongation at break is often a sign of the greater extent of phase separation in segmented PUs[12,13]. Notably PUs containing 70% or more soft segments show upper yield points and necking with mild strain hardening. On the contrary PU of low soft segment does not show upper yield (only certain lower yield region is seen), but does show strong strain hardening. The difference is due to the soft segment–hard segment phase separation which is favoured with increasing soft segment content. With microphase separations, a yield is generally obtained similar to that with semicrystalline polymers. Since necking is a phenomenon of cross section contraction leading to a heterogeneous deformation of the specimen, polymer chains are likely to align along the extension direction during necking. Such orientation, together with those

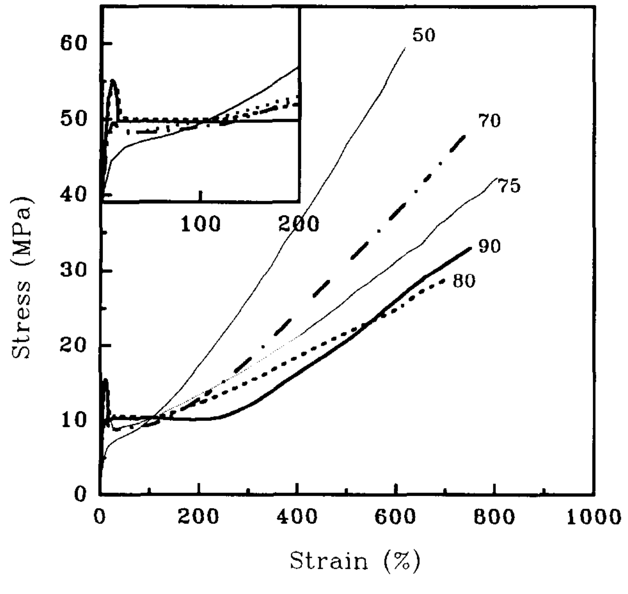


Figure 12 Stress–strain curves of PCL 4000 based PUs at 25°C

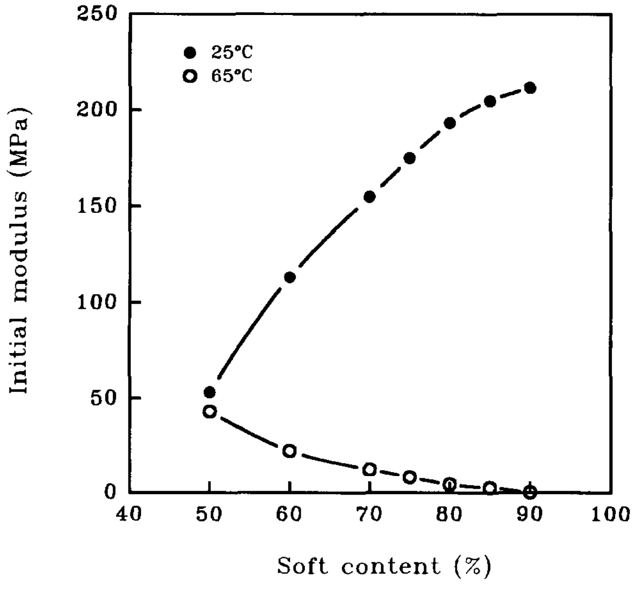


Figure 14 Initial moduli of PCL 4000 based PUs at 25 and 65°C

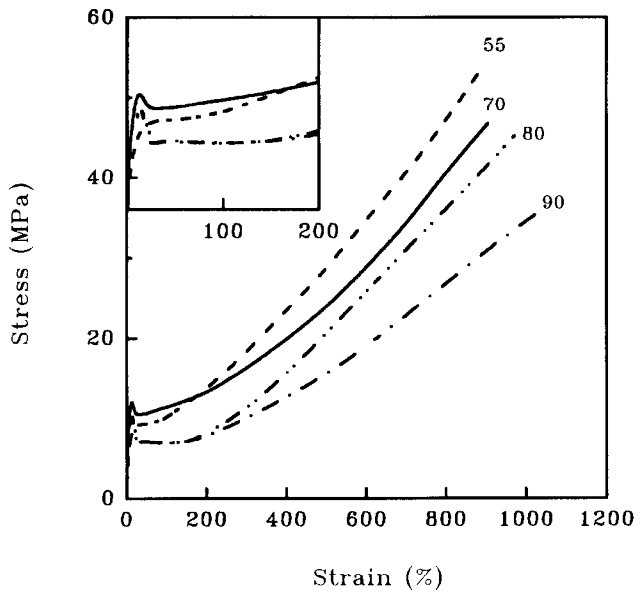


Figure 15 Stress–strain curves of PCL 8000 based PUs at 25°C

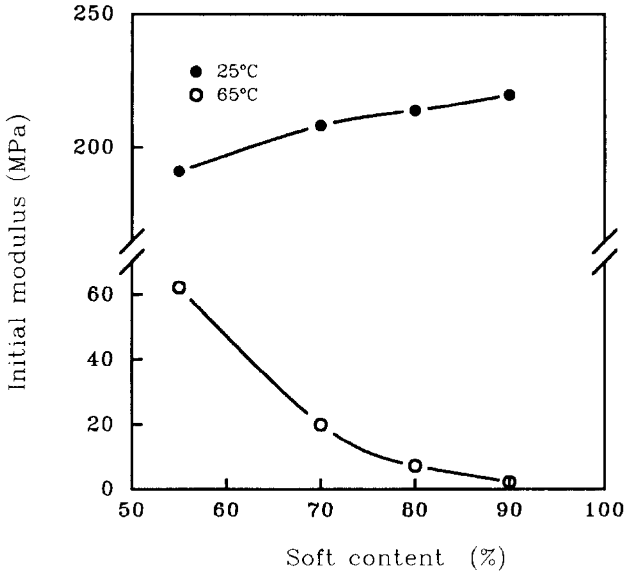


Figure 17 Initial moduli of PCL 8000 based PUs at 25 and 65°C

accompanied by strain hardening in homogeneous deformation (low soft segment PU) are not recovered by simple unloading at low temperature. They can be recovered upon heating to high temperature.

Figure 10 shows the stress–strain behaviour of PCL 2000 based PUs at 65°C. Tensile strength, elongation at break as well as the initial modulus are significantly decreased with increasing soft segment content. Above the T_m of soft segment, hard segments are totally responsible for carrying the load. Since hard segment content decreases with increasing soft segment content, the decrease in tensile properties is expected. Regarding the application of these PUs to shape memory materials, much easier deformation at high temperature becomes possible with PUs containing more soft segments. Comparison of the tensile behaviour at two different temperatures indicates that yielding is readily possible with high soft segment content at low temperature, and with high hard segment content at high temperature. Certainly yielding is more feasible at low temperature, and with a higher rate of deformation[14,15].

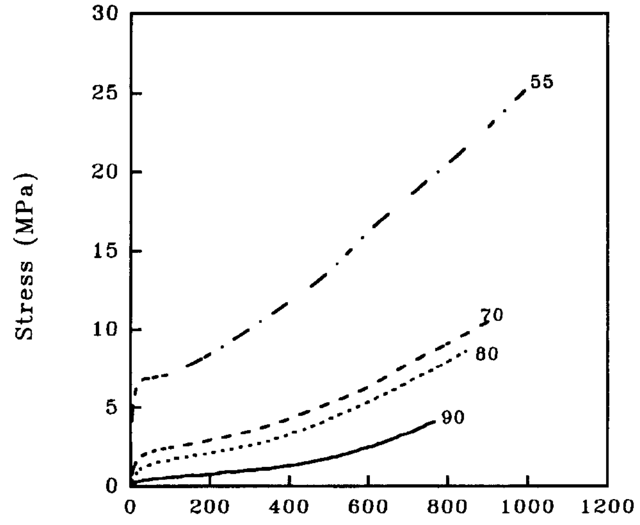


Figure 16 Stress–strain curves of PCL 8000 based PUs at 65°C

Figure 11 shows the initial moduli of these materials at 25°C and 65°C. Tensile modulus increases and decreases with soft segment content at low and high temperature, respectively. However, the magnitude of increase at low temperature is much greater than the decrease at high temperature, implying that soft segment–hard segment phase separation greatly contributes to the increased initial modulus.

Figure 12 shows the room temperature tensile behaviour of PCL 4000 based PUs carrying different soft segment contents. The stress–strain behaviour of these materials is generally similar to that of PCL 2000 based PUs. For example, upper yield points are obtained with high soft segment content. However, one notable difference is that the yield strength of these materials (10–16 MPa) are much greater than those of PCL 2000 based PUs (< 6 MPa). The greater yield strength of these materials should come from the well organized structures of PUs leading to greater phase separation and soft segment crystallizations.

Figure 13 shows the stress–strain behaviour of PCL 4000 based PUs at 65°C. Like PCL 2000 based PUs, tensile modulus, strength, and elongation at break are all significantly decreased with increasing soft segment content. In fact, high soft segment PUs (85 and 90%) were of hardly measurable strength. No upper yield point is observed, and a higher modulus is obtained with low soft segment content, a contradiction to the lower temperature properties.

Figure 14 shows the initial moduli of PCL 4000 based PUs as a function of soft segment content. Apparently the same tendency with PCL 2000 based PUs is obtained. That is, room temperature modulus increases and high temperature modulus decreases with increasing soft segment content. As the soft segment content increases from 50 to 90%, the room temperature modulus

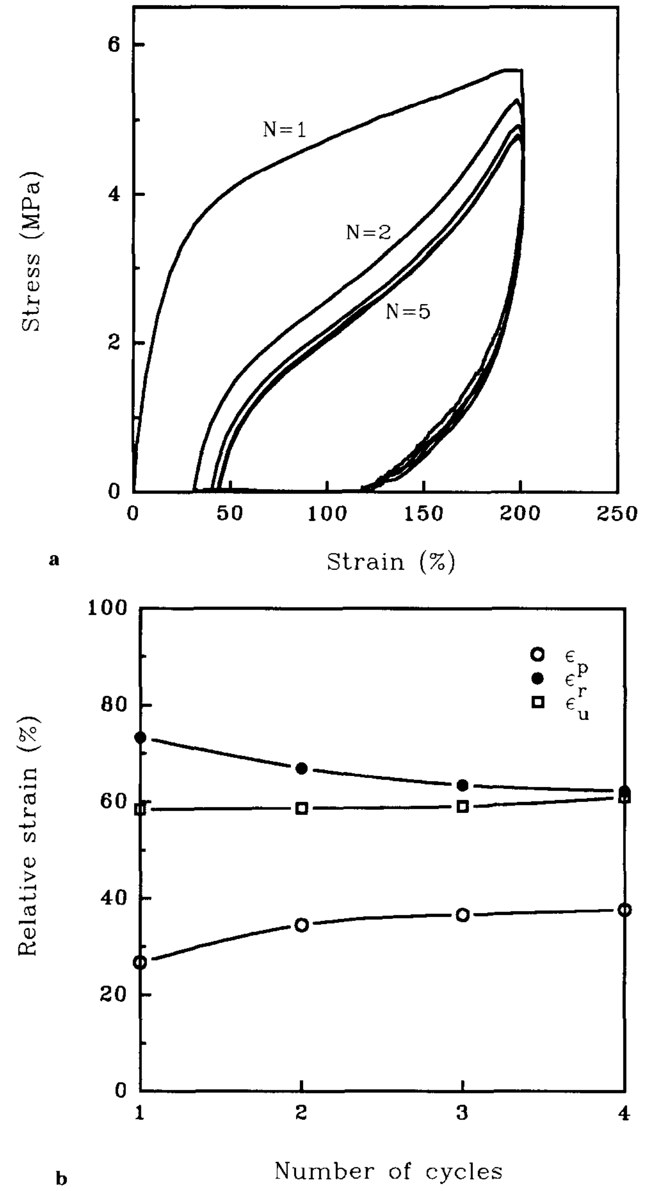


Figure 18 Cyclic tensile behaviour of PCL 2000 based PUs containing 55% soft segment: (a) stress–strain curves; (b) cyclic dependence of strains

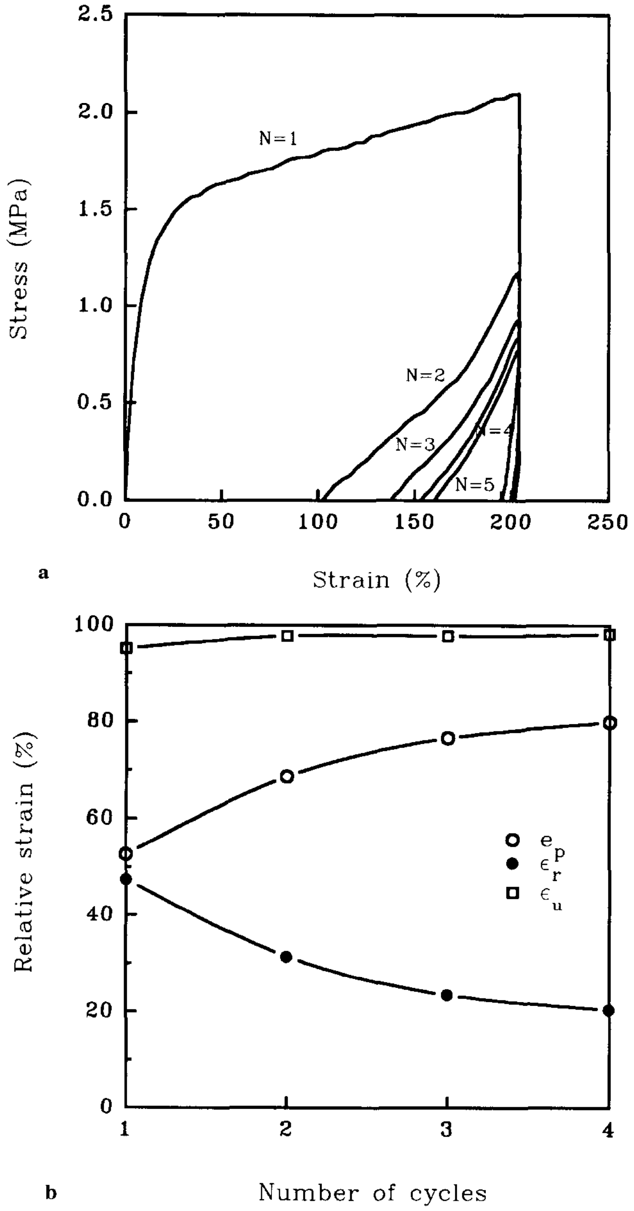


Figure 19 Cyclic tensile behaviour of PCL 2000 based PUs containing 70% soft segment: (a) stress–strain curves; (b) cyclic dependence of strains

increases by over four times, which is much greater than the decrease of the high temperature modulus. While comparing with PCL 2000 based PUs, the modulus of PCL 4000 based PUs is approximately twice as large. This is due to the greater phase separa-tion and hence soft segment crystallization of PCL 4000 based PUs, evidenced from the X-ray and d.s.c. data.

Figure 15 shows the room temperature tensile behaviour of PCL 8000 based PUs containing various contents of soft segments. The stress–strain behaviour is similar to those based on PCL 2000 and PCL 4000. Tensile strength decreases and elongation at break increases with increasing soft segment content. Yield is relatively well defined with high soft segment content. The lowest soft segment content (55%) also defines a yield, but with no necking. The yield strength is higher than PCL 2000 based PUs, and lower than PCL 4000 based PUs.

Figure 16 shows the stress–strain behaviour of PCL 8000 based PUs at 65°C. Tensile strength, initial modulus, and elongation at break all significantly decrease with increasing soft segment content. However, the lowest soft segment PU (55%) shows a notable retention of tensile properties at high temperature. This is probably a synergistic effect of soft segment crystallization and high hard segment content.

Figure 17 shows the initial moduli of PCL 8000 based PUs as a function of soft segment content. It is seen that the moduli of these materials are higher than those of PCL 4000, which are higher than those of PCL 2000 based PUs. The increase of the modulus with the increase of soft segment length at constant soft segment composition is due to the greater soft segment crystallization owing to the greater phase separations. Surprisingly, the increase of room temperature modulus is much

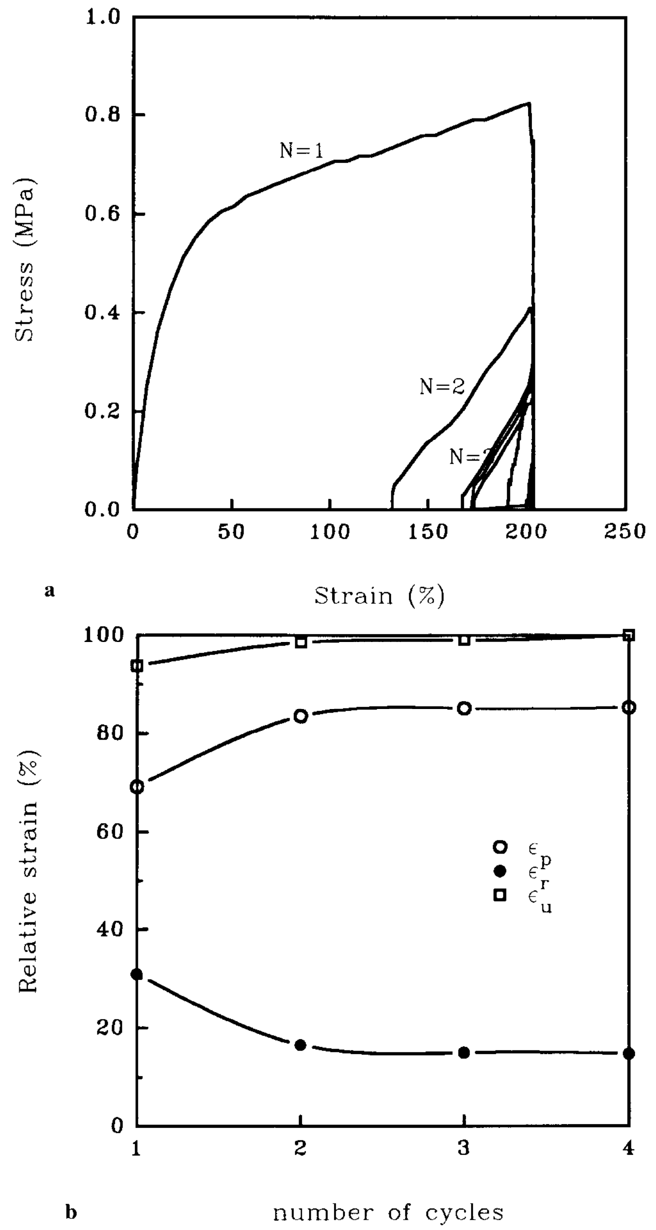


Figure 20 Cyclic tensile behaviour of PCL 2000 based PUs containing 80% soft segment: (a) stress–strain curves; (b) cyclic dependence of strains

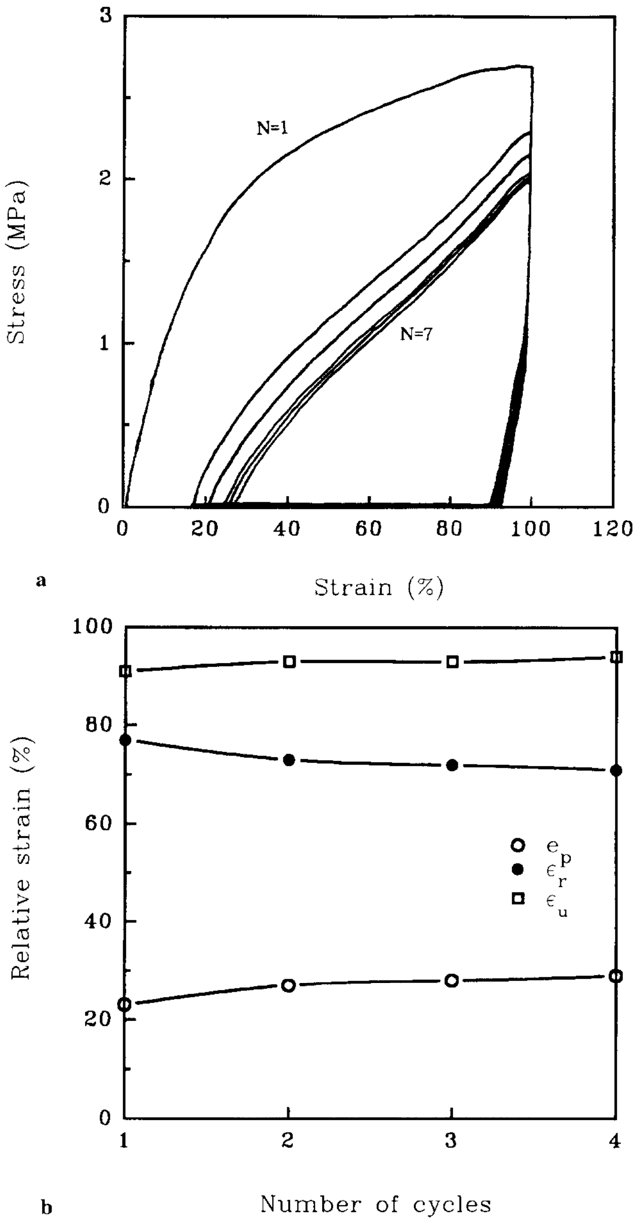


Figure 21 Cyclic tensile behaviour of PCL 4000 based PUs with 100% maximum strain (soft segment content = 70%); (a) stress–strain behaviour; (b) cyclic dependence of strain

smaller than those of PCL 2000 and PCL 4000 based PUs. This implies that the crystallization of long soft segments is not very influenced by the increased soft segment content.

Cyclic tensile properties

PCL 2000 based PUs. *Figures 18–20* show the cyclic stress–strain behaviour of PCL 2000 based PUs, together with the cyclic dependence of various strains. It is seen that the slope of loading curve increases with increasing number of cycles (*N*), implying that resistance to deformation increases with cycling. This cyclic hardening is caused by the orientations of PU segments during extension. However, the variation of cyclic hardening and even the shape of stress–strain curve is mostly confined to the first several cycles and no significant variation is observed with further cycles[4]. The insensitivity of cyclic properties with large *N* can be used to obtain a uniform cyclic deformation, prior to their practical applications. Regarding the cyclic dependence of various strains, ε_u is least sensitive and only marginally increased with *N* due to the strain hardening effect. Residual strain increases with *N* due mainly to the decreased recoverable strain.

On the other hand, with the increase of soft segment content (from 55 to 80%), ε_u is significantly increased from below 60% to over 90%, accompanied by the decrease in recoverable strain from over 70% to below 30%. The increase and decrease of these two types of strains resulted in the increased residual strain. Since the slope of stress–strain curve during cooling represents the elastic modulus of glassy state, the increase of ε_u with

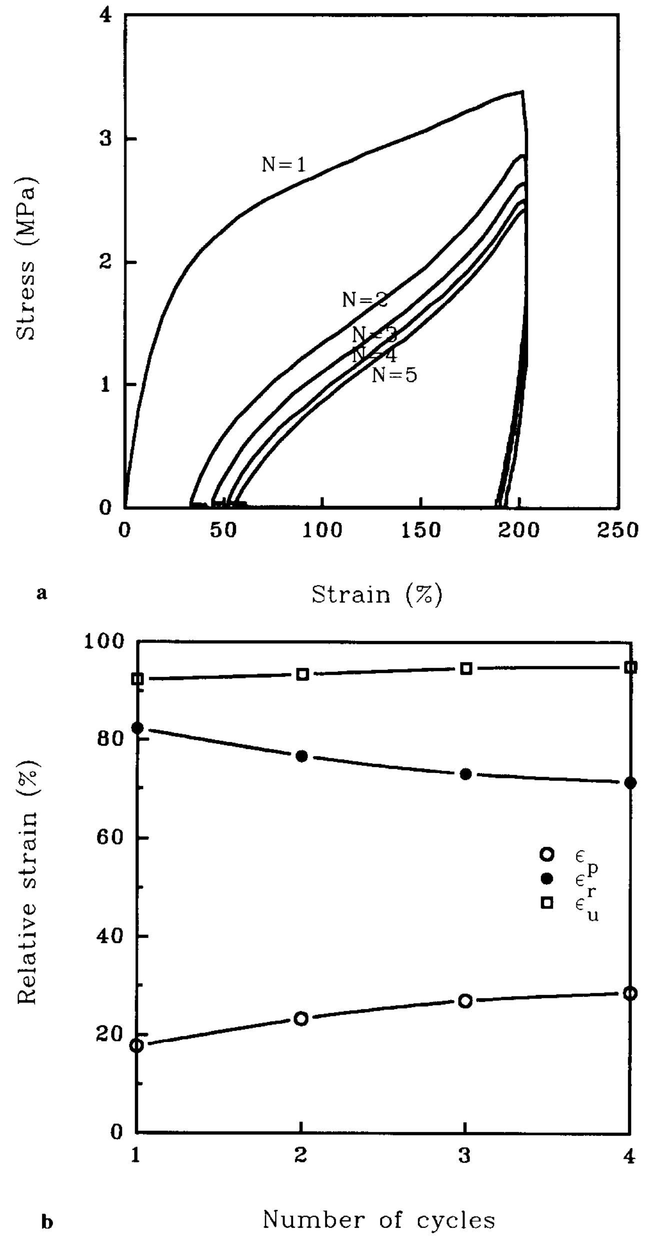


Figure 22 Cyclic tensile behaviour of PCL 4000 bases PUs with 200% maximum strain (soft segment content = 70%): (a) stress–strain behaviour; (b) cyclic dependence of strain

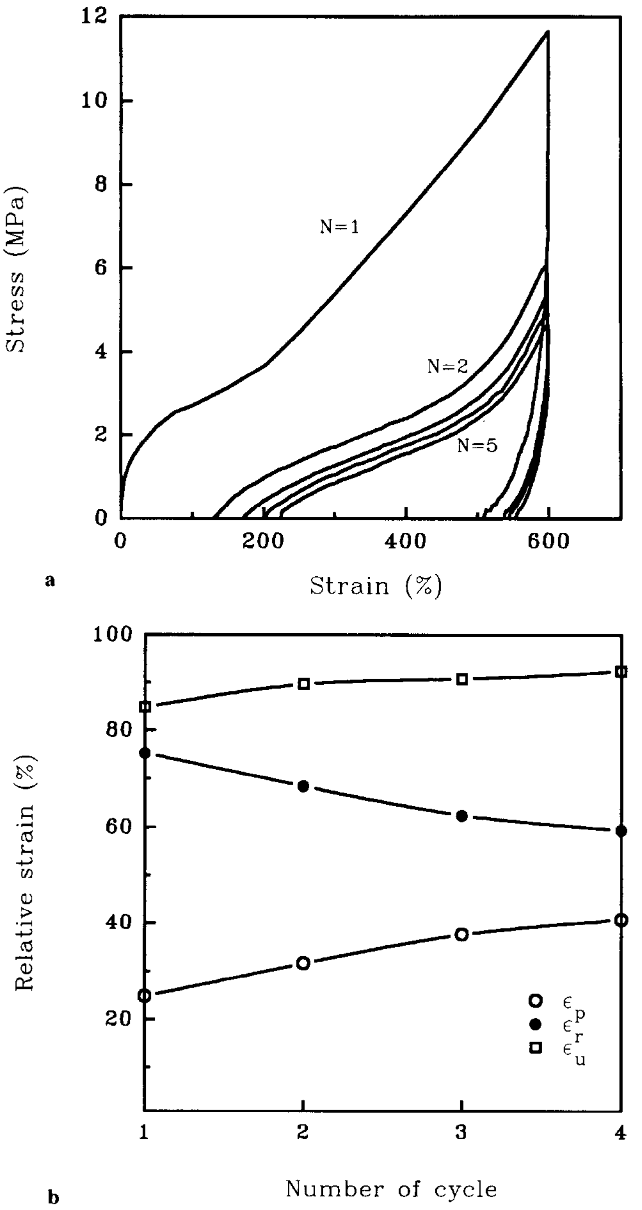


Figure 23 Cyclic tensile behaviour of PCL 4000 based PUs with 600% maximum strain (soft segment of content = 70%: (a) stress–strain behaviour; (b) cyclic dependence of strain

increasing soft segment content is caused by the increased soft segment crystallization. During heating and standing at high temperature under no load, the oriented and crystallized polymer segments are melted and randomized, and the original shape is recovered via a mechanism similar to the entropy elasticity of crosslinked rubbers. In crosslinked materials, elasticity is introduced due to the existence of chemical crosslinks. However in linear PUs, there are no chemical crosslinks, instead hard segments act as effective crosslinks. Therefore, with decreased hard segment contents, elastic recoil should decrease leaving a larger residual strain.

PCL 4000 based PUs. *Figures 21–23* show the cyclic tensile behaviour and cyclic dependence of various strains of PCL 4000 based PUs with different value of maximum strains, i.e. 100, 200, and 600%. During loading at high temperature, higher maximum strain should give more orientations of polymer chains, as noted from the increased slope of loading curve. This would give a higher elastic modulus during the subsequent cooling under a constant strain. Then, a larger rate of increase of ε_u with N is expected with a larger ε_m, which is confirmed in our experiments. The recovery strain generally increases with increasing ε_m (*Figure 24*). However, at large N the difference between ε_u and ε_r decreases with increasing ε_m. Therefore in order to obtain a uniform cyclic recovery deformation, lower maximum strain is preferred.

PCL 8000 based PUs. *Figures 25–27* show the cyclic tensile behaviour of PCL 8000 based PUs together with the cyclic dependence of various strains. With the

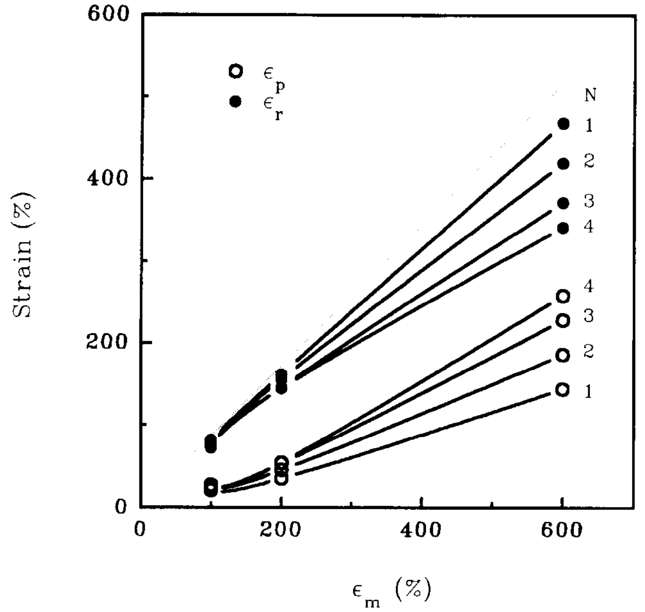


Figure 24 Effect of maximum strain on ε_p and ε_u for PCL 4000 based PUs (soft segment content = 70%)

increase in soft segment content, ε_u increases from about 90% to over 99%, which is significantly higher than those of PCL 2000 based PUs (60–90%). In contrast to the PCL 2000 based PUs, the recovery strain increases and hence the residual strain decreases with the increase in soft segment content. In addition, the increase of residual strain with *N* is also significantly decreased with increasing soft segment content.

Increases of both soft segment content and soft segment molecular weight contribute to the phase separation and soft segment crystallization. These two factors contribute to the increased elastic modulus during cooling, leading to the increase in ε_u. However, the increased recovery strain is mainly due to the increased rubbery state modulus which is achieved by the increased soft segment molecular weight. It has been shown that rubbery state modulus increases with soft segment molecular weight but decreases with soft segment content (*Figures 6* and *8*).

CONCLUSIONS

Over 15 different types of segmented polyurethanes were formulated from polycaprolactone diol, 4,4′-diphenylmethane diisocyanate, and 1,4-butanediol, and tested for shape memory effects in terms of tensile cyclic properties, dynamic mechanical and mechanical properties. It was found that the shape memory characteristics of the segment polyurethanes having crystallizable soft segments are closely related to the temperature-dependent dynamic mechanical properties of the materials. A large glassy state modulus led to large shape fixity upon cooling and unloading, whereas a large rubbery state modulus led to large shape recovery upon heating and standing at high temperature. Large shape fixity allows precise shaping and large shape recovery leaves little hysteresis, and hence these properties are highly desirable for shape memory materials. On the other hand, the glassy state and rubbery state moduli strongly depended on the soft segment length and content. Increase in soft segment length increased glass state as well as rubbery state moduli due to the increased soft segment crystallizations. However, an increase in soft segment content resulted in increased glassy state modulus and decreased rubbery state modulus. The increased glassy state modulus is caused by the increased soft segment–hard segment phase separation, whereas the decreased rubbery state modulus is mainly due to the decreased hard segment content.

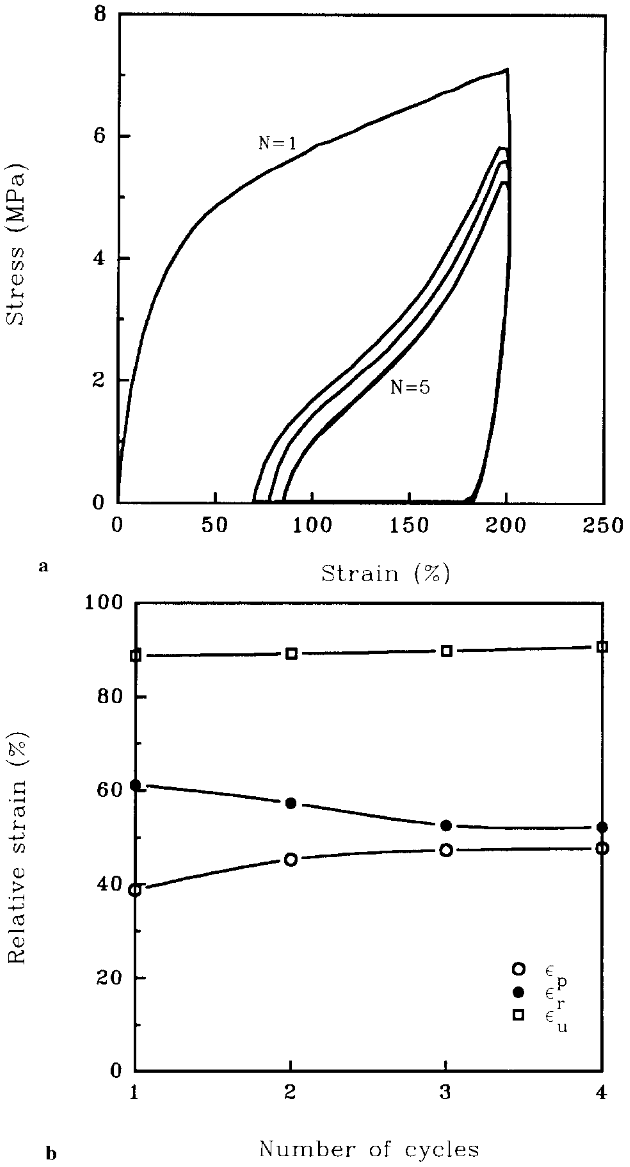


Figure 25 Cyclic tensile behaviour of PCL 8000 based PUs containing 55% soft segment: (a) stress–strain curve; (b) cyclic dependence of strains

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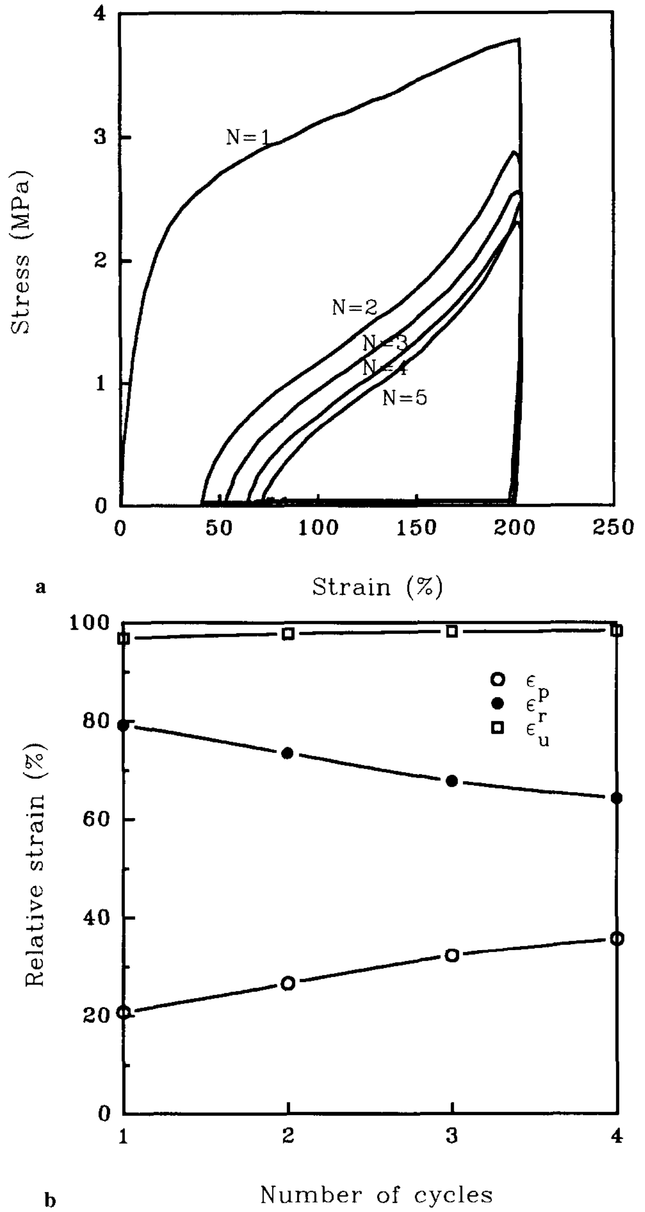

Figure 26 Cyclic tensile behaviour of PCL 8000 based PUs containing 70% soft segment: (a) stress–strain curve; (b) cyclic dependence of strains

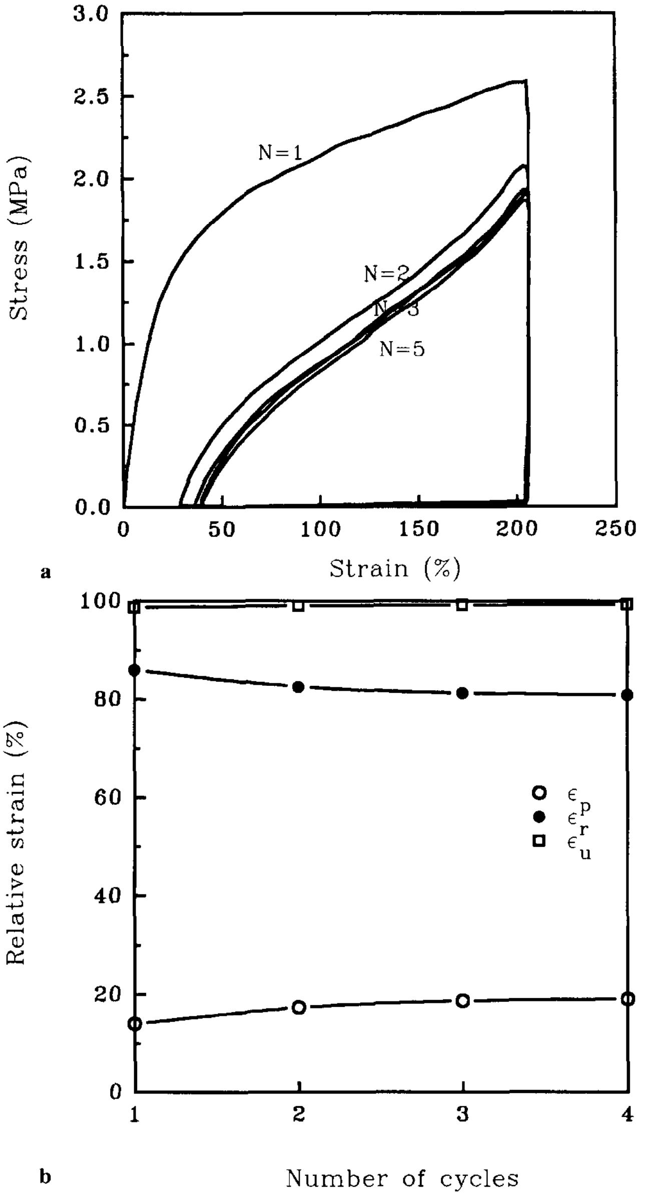

Figure 27 Cyclic tensile behaviour of PCL 8000 based PUs containing 80% soft segment: (a) stress–strain curve; (b) cyclic dependence of strains

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