Macromol. Symp. ***147***, *127–137 (1999)*

TENSILE DEFORMATION BEHAVIOUR OF THE POLYMER PHASE OF FLEXIBLE POLYURETHANE FOAMS AND POLYURETHANE ELASTOMERS

Evert van der Heide*, Otto L.J. van Asselen, Gerwin W.H. Ingenbleek and Constant A.J. Putman

Shell Research and Technology Centre, Amsterdam, P.O. Box 38000,
1030 BN Amsterdam, Shell International Chemicals B.V., Netherlands

SUMMARY: The change in micromorphology of the polymer phase (single strut) of a flexible polyurethane foam during deformation has been investigated by attenuated total reflection infrared spectroscopy - linear dichroism and by atomic force microscopy. Deformation and, therefore, orientation take place mainly in the soft rubbery phase. This two-phase elastic deformation process has been translated into a mathematical model, which correctly predicts the shape of a single-strut stress-strain curve. The theory also predicts the ultimate shape of stress-strain curves of polyurethane elastomers at various hard phase contents and of low-density polyethylene at various temperatures. Deviations from the elastic behaviour could be ascribed to yielding in combination with the rubbery behaviour.

Introduction

Mechanical properties of flexible polyurethane (PU) foams mainly depend on the mechanical behaviour of the polymer phase in combination with the cell structure. The effects of mechanical properties of the polymer phase and cell structure effects are difficult to separate, as it is not known to which extent these parameters can be varied independently. The very small size of polymer parts (struts) which compose a flexible foam complicates investigations into the mechanical behaviour of the polymer phase, independent of cell structure effects. Solid plaques have been prepared to evaluate the polymer stress-strain behaviour1) but this approach is hampered by the uncertainty to which extent the plaques represent the polymer phase of the foams from which they were prepared.

Hard polyurea-urethane domains, phase-separated from the rubbery polyether or polyester phase, are present in the polymer phase. The micromorphology is formed by spinodal decomposition during foaming2) and, recently, images of structures of size of 50 - 200 nm as well as 5-nm-sized domains have been measured by electron microscopy3). The presence of a

CCC 1022-1360/99/$ 17.50+.50/0

combination of a hard phase and a rubbery phase is not limited to PU foams. The chemically closely related PU elastomers also exhibit a phase-separated structure[4,5)]. The same applies to semicrystalline polymers, which are composed of hard crystallites embedded in a rubbery amorphous phase (e.g., polyethylene[6)]).

A two-phase composite structure usually gives rise to a relatively steep initial increase in stress during strain, the slope (Young's modulus) being mainly dependent on the presence of the hard phase. With increasing strain, the slope of the curve gradually decreases and the contribution of the rubber phase becomes more significant at the expense of the hard-phase contribution. At high strains, the influence of the rubber phase on the stress-strain behaviour can be described by the well-known Mooney - Rivlin equation[7,8)].

The description of the gradual transition from Young's modulus to rubber modulus or, in general, the non-linear stress-strain behaviour, has been the subject of ongoing debate. Stress-strain curves can be described in many different ways by means of equations of various mathematical structure[9)]. Recently developed models include a stochastic discrete model of breaking chains during straining[10)] and a fundamental microstructural model of entangled or crosslinked chains in rubbers or semicrystalline polymers[11)]. In addition, models based on molecular orientation have been proposed[12,13)]. These models all provide quantitative stress-strain relationships on the basis of the assumptions made and are able to describe experimental stress-strain data. However, for most theories, a number of parameters have to be determined separately or to be estimated before stress-strain curves can be fitted.

In this paper, we describe investigations into the gradual transition from Young's modulus to rubbery behaviour during tensile deformation of the polymer phase of a PU foam. The applicability of the results in other two-phase composite polymers will be discussed as well.

Theory

The chemical and physical interactions in the non-deformed state representative for stress development during straining can be assumed to be statistically distributed, which results in an average orientation $\langle\cos^2(\theta)\rangle$ of 1/3, θ being the angle between the draw direction and the specific interaction. During deformation, the interactions rotate into the draw direction and, assuming affine deformation (Kuhn network), the average orientation can be expressed as a function of elongation[12,13)], λ (Eq. (1)).

$$\left\langle \cos^2(\theta)\right\rangle = \frac{\lambda^3}{\lambda^3-1}\left[1-\frac{1}{\sqrt{(\lambda^3-1)}}\tan^{-1}\left\{\sqrt{(\lambda^3-1)}\right\}\right] \tag{1}$$

$$\left\langle \cos^2(\theta)\right\rangle = \frac{1}{3}f_c + f_r = \frac{1}{3}\left(1+2f_r\right) \tag{2}$$

In a field of uniaxial stress and assuming uniform stress distribution, the soft phase will deform to a much higher extent than the hard phase. This strain anisotropy easily results in break-up of the original co-continuous phase into clusters, with zones of soft material in between deformed in the tensile direction. Continuation of straining results in continuation of the break-up of clusters and the phase of the *deformed* soft material will increase at the expense of the clusters composed of the hard material and *non-deformed* rubber.

The average angle of orientation within a cluster can be assumed to be constant and comparable with the situation before deformation ($\langle\cos^2(\theta)\rangle = 1/3$), whereas the stress-carrying chains within the deformed zone will be oriented into the tensile direction ($\langle\cos^2(\theta)\rangle = 1$) (Fig. 1). The average orientation can now be expressed as a function of the fractions of clusters and of the *deformed* rubber, f_c and f_r, respectively (Eq. (2)).

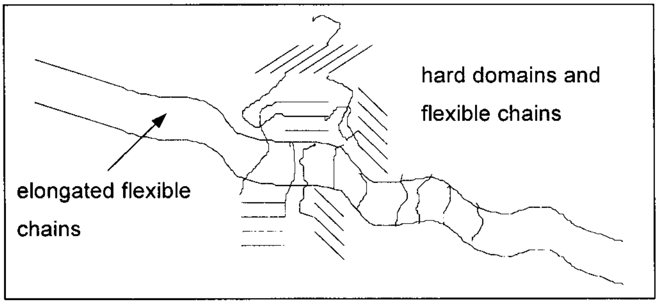

Figure 1. Schematic indication of two-phase deformation behaviour in tensile deformation

$$\frac{1}{E} = f_r\frac{1}{E_r(\lambda)} + \left(1-f_r\right)\frac{1}{E_c} \tag{3}$$

$$E_r(\lambda) = \frac{\rho.R.T}{M_c}\left(2\lambda+\frac{1}{\lambda^2}\right)\left(1+2.5\varphi+14.1\varphi^2\right) = G_r\left(2\lambda+\frac{1}{\lambda^2}\right) \tag{4}$$

$$E = \left[\frac{1}{E_c} - \left\{\frac{3}{2}\frac{\lambda^3}{\left(\lambda^3-1\right)}\left[1-\frac{1}{\sqrt{(\lambda^3-1)}}\tan^{-1}\left\{\sqrt{(\lambda^3-1)}\right\}\right]-\frac{1}{2}\right\}\left(\frac{1}{E_c}-\frac{1}{E_r(\lambda)}\right)\right]^{-1} \tag{5}$$

$$\sigma = \lambda f = \int_1^{\lambda} E\,\mathrm{d}l \tag{6}$$

In the absence of deformation inside clusters, the modulus of the cluster phase, E_c, corresponds to the Young's modulus of the non-deformed polymer. During elongation, the polymer modulus, E, defined as the tangent of the stress-strain curve, $d\sigma/d\lambda$, can be expressed as a serial combination of E_c and E_r, the modulus of the *deformed* rubber phase (Eq. (3)). E_r depends on strain and on the hard phase content[14], φ (Eq. (4)). ρ, R and T are the density, gas constant and absolute temperature respectively, whereas G_r is defined as the rubber shear modulus including the Guth-Smallwood filler content correction. Combination of Eqs (1), (2) and (3) results in E as a function of λ, with E_c and E_r as variables (Eq. (5)). From E, the *true* stress (σ) and, assuming constant volume, the *nominal* or *engineering* stress (f) can easily be derived[9] (Eq. (6)).

Results and discussion

Single-strut deformation

During the deformation of a single strut obtained from a flexible polyurethane foam with 31.5 wt.-% of hard domain, the polymer chains become oriented. The orientation of the units can be investigated by infrared-attenuated-total-reflection linear dichroism[1]; the results are depicted in Fig. 2.

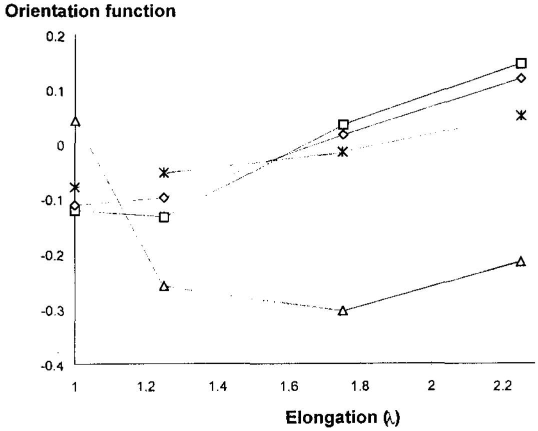

Figure 2. Orientation of units in a single strut during elongation, measured by IR dichroism

Δ C=O urea, □ C=O urethane, ◇ CH_3, ✶ - C-O-C-

The orientation already present without deformation might be due to elongation during foaming, or to some pre-extension during sample preparation. The rubber phase, represented by the ether and methyl groups of the polyol, gradually becomes oriented on average during deformation. The hard segments within hard domains, represented by the didentate hydrogen-bonded urea carbonyl group, first orient perpendicular to the tensile direction, which indicates orientation of complete domains[1]. At increasing deformations, the domains start to break and individual hard segments become oriented into the tensile direction, which results in a minimum in the orientation function. Urethane groups can be present in the rubber phase as well as in the interphase between rubber and hard domains. The behaviour of the urethane units closely resembles the rubber orientation, although some effects of the hard domains cannot be excluded (Fig. 2).

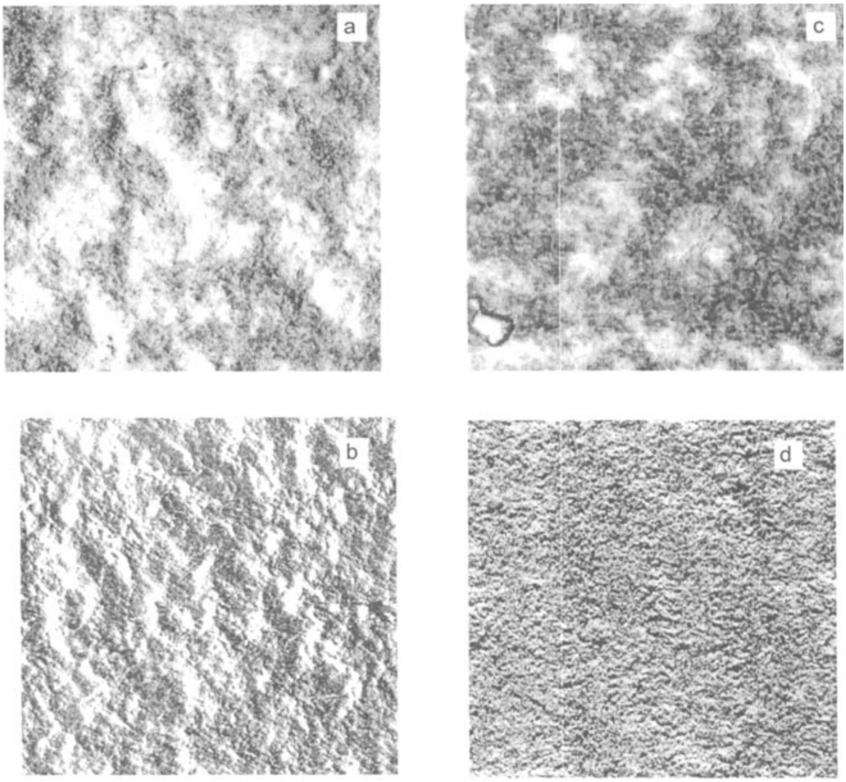

Figure 3. Atomic force micrographs of single struts before deformation (a,c) and after about 50 % (b) and about 100 % (d) deformation (vertical). (a,b): 31.5 wt.-% hard domains; (c,d): 30.5 wt.-% hard domains, 7 wt.-% EO (random). Size: (a,c,d) 2 x 2 μm, (b) 5 x 5 μm

The changes in micromorphology during deformation are clearly visible in Fig. 3. Without deformation, the hard domains with a size of about 5 nm are visible, in addition to larger structures with sizes of 50 - 200 nm (Figs. 3a and 3c), in line with literature[3]. After some deformation, clusters rotated into the vertical tensile direction can be observed (Fig. 3b), whereas at about 100 % elongation, an alternating pattern of the soft black phase and hard white phase perpendicular to the vertical tensile direction is present. A typical stress-strain curve of a single strut is depicted in Fig. 4.

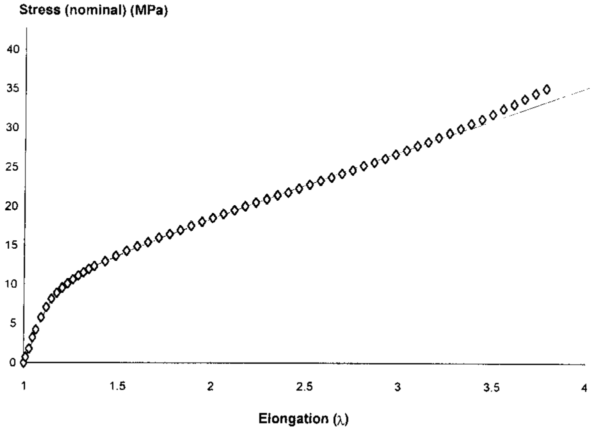

Figure 4. Single-strut stress-strain curve (hard domain content 31.5 wt.-%)

Dashed line: theoretical curve (E_c = 70 MPa, G_r = 8.5 MPa), solid line: discontinuity, pure rubbery behaviour above λ = 1.2

The shape of the curve is correctly predicted by Eq. (6), with values of 70 MPa and 8.5 MPa for E_c and G_r, respectively. This last value corresponds to M_c = 1020, which resembles the expected value of 1000 for a three-functional polyol of molecular weight of 3000. A deviation between the predicted and measured stress is seen above λ = 1.2. Assuming a discontinuous transition from the two-phase behaviour (Eq. (6)) to the pure rubbery behaviour at λ = 1.2, the stress-strain curve can be recalculated, which results in a quantitatively correct prediction of stress during elongation. This discontinuity might be due to the initiation of yielding of hard domains at λ = 1.2, which is not in conflict with Fig. 2.

Elastomers

An increase in the hard phase content in PU elastomers, e.g., by addition of NaCl as a filler, results in an increase in Young's modulus[15)]. The stress-strain curves of 10, 21 and 31 vol.-% have previously been described with success by a model of breaking chains[10)]. These curves can be fitted by the present model as well (Fig. 5). A reduction in G_r is observed, which might be due to the interference of sodium ions with the hydrogen bridges in the hard domains. At 42 vol.-% of NaCl, the theoretical curve obtained by extrapolation of E_c and G_r of the other curves predicts a decrease in stress at high strains, due to a combination of strong reduction in stiffness and transversal contraction[16)]. This stress instability predicts a decrease in stress after reaching the yield point, which is indeed observed (Fig. 5).

A more convenient way to increase the hard phase content is increasing the amount of isocyanate and chain extender (Fig. 6). The stress-strain curve for a linear poly(propylene oxide)diol (PPG)-based PU elastomer at the 20 wt.-% hard segment content is predicted perfectly. The deviation between experimental data and theoretical fits increases with increasing hard segment contents, due to the occurrence of yielding at $\lambda = 1.17$. A decrease in M_c from about 15 000 to about 2500 is found, comparable with the used soft chain length of 2000. The decrease might be due to increasing resistance of the physically crosslinked network to straining.

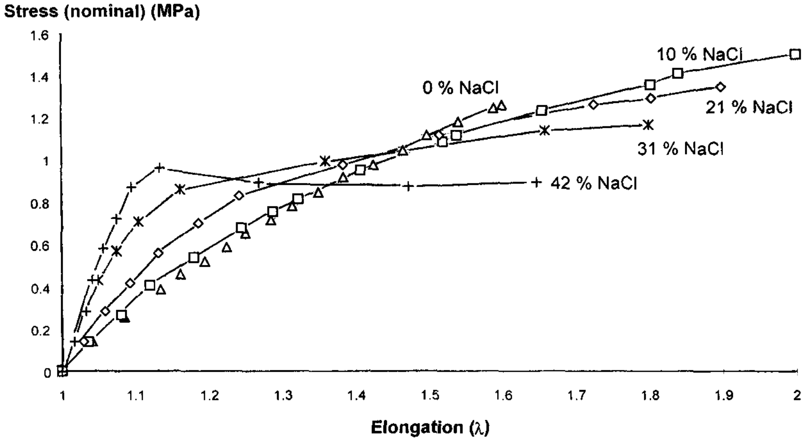

Figure 5. Stress-strain curves for linear PPG-PU elastomers with various NaCl contents (the volume percentages are indicated)[15]. Dashed lines: theoretical fits. (For fit parameters, see Table 1.)

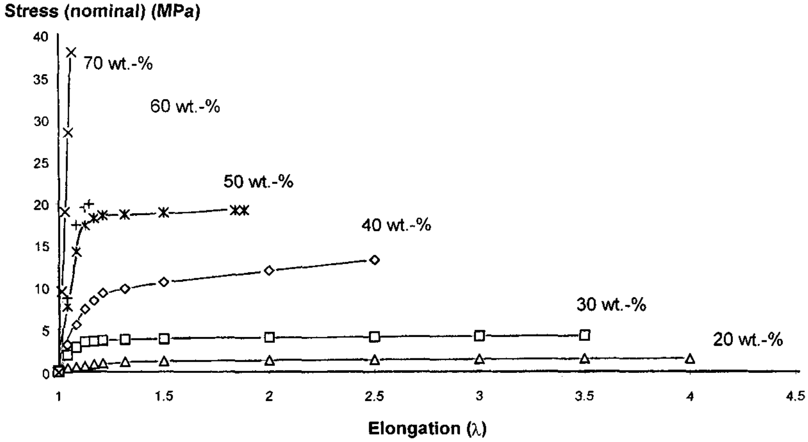

Figure 6. Stress-strain curves for linear PPG-PU elastomers with indicated hard segment contents[17]. (For fit parameters, see Table 1.)

A comparable trend, but at much higher stress levels, can be observed for crosslinked PPG-based PU elastomers, prepared by reaction injection moulding[4)] (Fig. 7). At low hard segment contents, M_c is about 2000, which closely corresponds to the expected value of 1900 for a trifunctional polyol with molecular weight of 5700[4)]. At increasing hard segment contents, M_c tends to decrease to 1000 indicating increasing immobilisation of soft segments, which has been indeed observed[4,17)]. In these elastomers, yielding is observed above $\lambda = 1.09$. The slope of the curves after yielding is higher than expected for a pure rubbery behaviour (Eq. (4)), which makes a critical evaluation of the applicability of the Mooney-Rivlin theory in PU elastomers worthwhile[7,8)]. The stress-strain curves tend to increase at high elongations and to approach the theoretical fits, without reaching them.

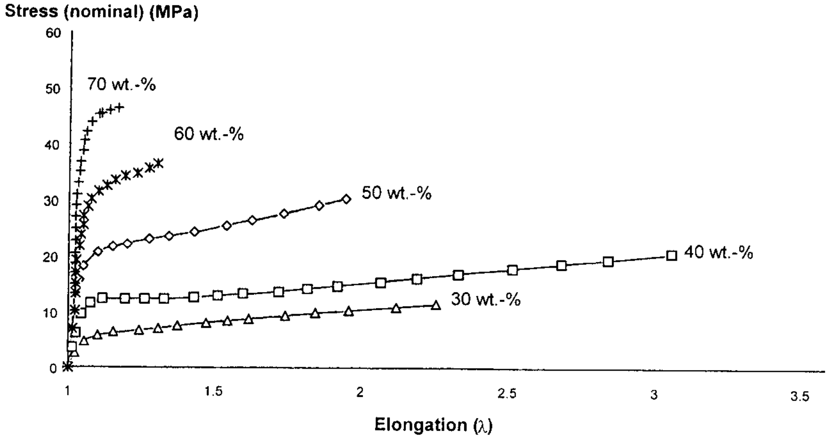

Figure 7. Stress-strain curves for crosslinked PPG-PU elastomers and trifunctional PPG with indicated hard segment contents[4)]. (For fit parameters, see Table 1.)

Semicrystalline polymers

Semicrystalline polymers also exhibit a two-phase deformation behaviour[6)]. The stress-strain curves of low-density polyethylene (LDPE) at various temperatures have been correctly described by complete distributions of orientation during deformation[12)] and can be predicted by the present theory as well (Fig. 8).

The decrease in G_r with increasing temperature (Table 1) is due to a combination of reduction in crystallinity[12)] and increase in temperature. At 70 °C, hardly any difference between experimental and theoretical data is found. At decreasing temperatures, an increasing deviation at strains between $\lambda = 1.15$ and 1.75 is observed, which indicates the occurrence of yielding. The slope of the stress-strain curves just above $\lambda = 1.15$ corresponds to 3.5 times G_r, which is yet unexplained. If the original theoretical curve is exceeded, as indicated at 20 °C in Fig. 8, the yielding stops and the elastic deformation process continues to proceed up to high strains. At temperatures below 50 °C, even a decrease in stress is observed, due to the combination of a decrease in stiffness and transversal contraction[16)].

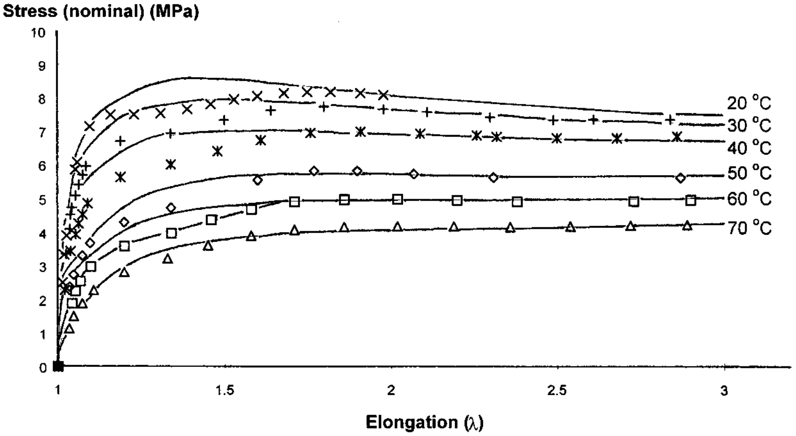

Figure 8. Stress-strain curves of LDPE at the temperatures indicated[12)]. (For fit parameters, see Table 1.)

Table 1. Young's moduli and rubber shear moduli of PPG - PU elastomers and LDPE

PPG-PU[a]			PPG-PU[b]			PPG-PU[c]			LDPE[d]		
NaCl conc. vol.-%	E_c MPa	G_r MPa	hard-segment content wt.-%	E_c MPa	G_r MPa	hard-segment content. wt.-%	E_c MPa	G_r MPa	temp. °C	E_c MPa	G_r MPa
0	-	1.05	20	15	0.23	30	160	2.6	20	400	0.84
10	3.9	0.57	30	70	0.8	40	300	3.6	30	280	0.85
21	6.1	0.33	40	100	2.8	50	560	4.9	40	180	0.84
31	14	0.18	50	300	4.2	60	960	6.4	50	105	0.76
42	55	0.1	60	350	6				60	75	0.70
									70	44	0.64

[a] Fig. 5 (Ref. 15); [b] Fig. 6 (Ref. 17); [c] Fig. 7 (Ref. 4); [d] Fig. 8 (Ref. 12).

Experimental

Flexible foam

A foam, comprising a trifunctional PO-based polyol of molecular weight 3.000, toluene diisocyanate (index 115), 3.8 parts of water per hundred parts of polyol, appropriate surfactant and catalysts, is made on a Vinking laboratory slabstock machine as 50 x 50 x 35 cm blocks. Auxiliary chemicals were brought together with the base polyol in a manifold and then mixed at 3000 rpm. The foam is subsequently placed in a forced-circulation air oven at 85 °C for 5 min and left to cure for at least 48 h before cutting.

Atomic force microscopy

A single strut, oriented in the ascending direction, was glued with epoxy resin at both ends on an aluminium foil, elongated, embedded in a PMMA resin and cut in the longitudinal direction with a diamond knife. The phase-imaged micrographs were obtained with an atomic force nanoscope 3 (Digital Instruments) operated in the tapping mode.

Single-strut stress-strain measurements

The tensile equipment was home-made, with a 300-mN load amplifier. Load calibration was performed with known weights. A strut, oriented in the ascending direction, was been isolated and mounted in the grips of the tensile equipment at a defined distance between the grips. The strut was deformed by a stepping-motor driver and the load was registered as a function of time (LabTech Notebook software). An Olympus SZH-ILLB or Olympus BH-2 microscope, equipped with a photographic or video camera, was used to follow the process visually. After breaking the strut, the cross-sectional area was measured by microscopy. Reproducibility was within 5 - 10 %, depending on the load range measured.

Single-strut IR attenuated total reflection spectroscopy

A thin piece of a flexible foam was mounted on a flat drawing bench and, in the middle, struts were cut off until one strut oriented in the ascending direction was left. The foam was drawn and fixed, put into a Nicolet Magna 550 infrared spectroscope, operating with OMNIC software, and the strut length was determined *in situ*. The attenuated total reflection (ATR) objective, zinc selenide (ZnSe), with a circular upper aperture 100 μm in diameter, was focused and brought into contact with the strut. The contact was checked by the interferogram intensity. Polarised-light (1200 lines/mm of ZnSe wire-grid polariser) IR spectra were recorded at 0°- and 90°-polarised light with the strut in the tensile direction. The measurement was repeated at the same site after 90° rotation of the sample. The time between stretching and measuring was between 5 and 45 min. Within this time interval, the orientation was found to be more or less constant, in accord with literature1).

Conclusions

During deformation of a single strut of a flexible polyurethane foam, mainly the rubber phase is deformed. A theory developed from this two-phase deformation behaviour correctly describes the shape of the stress-strain curve of a single strut. Ultimate stress-strain curves for PPG-PU elastomers and for LDPE were predicted. Deviations from ideal elastic behaviour are ascribed to yielding and to the rubber crosslink density.

References

1) J.C. Moreland, G.L. Wilkes and R.B. Turner, *J. Appl. Polym. Sci.* **43**, 801 (1991)

2) M.J. Elwell, A.J. Ryan, H.J.M. Grunbauer and H.C. van Lieshout, *Macromolecules* **29**, 2960 (1996)

3) R. Neff, A. Adedeji, C.W. Macosko and A.J. Ryan, *J. Polym. Sci., Part B: Polym. Phys.* **36**, 573 (1998)

4) J.L. Stanford, in: R.F.T. Stepto, *Polymer Networks. Principles of Their Formation, Structure and Properties*, Blackie, London 1998, p.125

5) R.S. McLean and B.B. Sauer, *Macromolecules* **30**, 8314 (1997)

6) I.L. Hay and A. Keller, *Kolloid-Z. Z. Polym.* **204**, 43 (1965)

7) O. Thomas, R.D. Priester, Jr., K.J. Hinze and D.D. Latham, *J. Polym. Sci., Part B: Polym. Phys.* **32**, 2155 (1994); H. Ishihara, I. Kimura and N. Yoshihara, *J. Macromol. Sci., Part B* **22**, 713 (1983)

8) J.E. Mark and B. Erman, in: R.F.T. Stepto, *Polymer Networks. Principles of Their Formation, Structure and Properties*, Blackie, London 1998, p.215.

9) I.M. Ward and D.W. Hadley, *An Introduction to the Mechanical Properties of Solid Polymers*, Wiley, Chichester 1997

10) V.V. Moshev and S.E. Evlampeva, *Polym. Eng. Sci.* **37**, 1348 (1997)

11) J. Bicerano, N.K. Grant, J.T. Seitz and K. Pant, *J. Polym. Sci., Part B: Polym. Phys.* **35**, 2715 (1997)

12) H.G. Kilian, W. Knechtel, B. Heise and M. Zrinyi, *Prog. Colloid Polym. Sci.* **92**, 60 (1993)

13) P.A. Irvine and P. Smith, *Macromolecules* **19**, 240 (1986)

14) K. te Nijenhuis, *Adv. Polym. Sci.* **130**, 1 (1997)

15) F.R. Schwarzl, H.W. Bree and C.J. Nederveen, in: *Proc. 4th Int. Congress on Rheology*, August 26-30, 1963, E.H. Lee (Ed.), Interscience, New York 1965, p.241

16) P.I. Vincent, *Polymer* **1**, 7 (1960)

17) Z.S. Chen, W.P. Yang and C.W. Macosco, *Rubber Chem. Technol.* **61**, 86, (1987)