Short-Term Morphology Relaxation of Thermoplastic Polyurethane Elastomers after Fast Strain Steps

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Strain steps are applied to elastomers in a pneumatic relaxometer and monitored by small-angle X-ray scattering (SAXS). The relaxometer provides a rise time of 13 ms for strain pulses of step height $\Delta \varepsilon = \pm 1$ in strain. The basic character of the 2D SAXS frames is examined and corresponding invariants $Q(t)$ are analyzed. Three thermoplastic polyurethanes (TPU) of hardness 85 Shore A with different soft segments are studied both unannealed and annealed. The first response of all materials is a fast morphology conversion which finishes within $t_{mc} \approx 250$ ms. Because it has been untraceable, it is characterized by a settling stroke $Q(t_{md}) - Q(0)$. The second response is a slow morphology adjustment process which complies with logarithmic relaxation. It is characterized by a relaxation rate $D_Q = Q(10^t)/Q(t) - 1$. Comparison indicates that the nanoscopic morphology relaxation processes appear to have little direct relation to the macroscopic stress relaxation curves. The materials differ with respect to hard-domain morphology stability and morphology recovery. Most unstable is the morphology of the annealed polyether-based material. It forms nanofibrillary entities when strained.

1. Introduction

The ideal elastomer reacts instantly on mechanical stress. With a real material, however, one often has to take into account the time dependence of its response. Seals for example, should be retightened from time to time. The material behaves viscoelastic. The classical experiments of viscoelasticity perturb the material mechanically and record a response that is also in nonlinear viscoelasticity.

In the literature, there are many papers which carry out mechanical stress relaxation experiments and correlate them to scattering data taken during straining, at fixed strains or fixed stresses, but we have found only a few papers that monitor the morphology relaxation of soft matter. Yang et al. stretch an ethylene–propylene elastomer slowly ($\dot{\varepsilon} < 0.003$) to different strains ($\Delta \varepsilon$ between 0.2 and 1.9) and relate the stress relaxation to the morphology relaxation monitored by wide-angle X-ray diffraction. During relaxation they observe increasing crystallinity and study crystal orientation as a function of strain and time. Screen et al. investigate the relaxation of the nanofibrillary structure of rat tendon after strain steps $\Delta \varepsilon$ between 0.02 and 0.08. Their conventional tensile tester approaches the final strain quite slowly ($t_{ex} = 0.2$ s, but then they obtain low-noise scattering patterns as a function of time. Nanofibrils in the material are manifested in the small-angle X-ray scattering (SAXS) pattern by an equatorial reflection of the Heaviside step function. In practice, the rise time $t_\varepsilon$ of the step is $t_\varepsilon > 0$, but it must be much smaller than the relaxation time of the monitored response. With a pneumatic relaxometer, we hope to be able to resolve rapid morphology relaxation processes. Very high deformation rates are necessary because the main part of the nanostructure transformation is very fast and cannot be resolved with cycle time of 1 s.

Between mechanical behavior and structural changes in the material remains hidden. Therefore we, additionally, try to record and analyze the response of the material's morphology. For this purpose, we monitor the classical stress relaxation experiment using X-ray scattering. In a stress relaxation experiment, the material is suddenly strained and the course of the stress $\sigma(t)$ is recorded. The material's response to an ideal step change in strain, $\varepsilon(t) = \varepsilon_0 + \Delta \Theta(t)$, is of great importance also in nonlinear viscoelasticity. $\varepsilon_0$ is a pre-strain, $\Delta \varepsilon$ the height of the step strain and $\Theta(t) = \{0 \text{ if } t < t_c, \ 1 \text{ if } t \geq t_c \}$ with $t_c = 0$ is the Heaviside step function. In practice, the rise time $t_\varepsilon$ of the step is $t_\varepsilon > 0$, but it must be much smaller than the relaxation time of the monitored response. With a pneumatic relaxometer, we hope to be able to resolve rapid morphology relaxation processes.
itself by sharp reflections in the SAXS scattering pattern. The mechanical signal is a square wave ε_{sq}(t) with Δε ≈ 0.5, t_{r} = 0.075 s, a frequency ν_{sq} = 1.1 Hz and a duty cycle of 1:3 simulating human heartbeat. tr is “in milliseconds” and the SAXS images from a large 2D detector show a good S/N ratio. The authors hook on the sharp peaks from the SAXS pattern and track positions and intensities by software. In this way, they correlate the fatigue of the material with changes in the morphology. Two other groups use neutron scattering to monitor slow relaxations in gels.[8,9]

2. Experimental Section

2.1. Materials

3 thermoplastic polyurethane (TPU) materials of identical hardness (85 Shore A) and similar hard segment content (HSC) have been subjected to the feasibility tests. Identical components are the building blocks of the hard segments (methylene diphenyl diisocyanate) and the chain extender (1,4-butanediol).

The materials are labeled by the digits 1–3, and a suffix indicates if the samples have been annealed (“a”) for 20 h at 100 °C or have been left unannealed (“u”). Table 1 presents the varying characteristic data of the materials. The soft segment component of material 1 is a polyether, the soft segments of materials 2 and 3 are polyesters. The mechanical parameters relate to annealed material.

| Materials       | 1a / 1u | 2a / 2u | 3a / 3u |
|-----------------|---------|---------|---------|
| soft segment    | PTHF1000 polycaprolactone diol adipic acid ester |
| HSC [%]         | 29      | 32      | 27      |
| σ_{max} [MPa]   | 48      | 54      | 49      |
| ε_{b} [%]       | 600     | 530     | 660     |

2.2. The Relaxometer

Relaxometers for examining stress relaxation after uniaxial strain-steps have been described early (e.g., Tobolsky[10] p. 143, Vieweg and Braun[11] p. 515). Modern commercial equipment subjects the specimen to a step in shear. Unfortunately, the morphology of a twisted sample can hardly be analyzed using scattering methods. One of us (K.S.) therefore has built a pneumatic relaxometer for uniaxial stretching and use on a synchrotron beamline. Here we report the results of a feasibility study on three polyurethanes.

Figure 1 presents a sketch of the pneumatic step-strain relaxometer built at the IPF, Dresden, Germany.

Small shouldered test bars (DIN 53504, “S3”) with a total length of 35 mm and a thickness of 1.0 mm are used. The reduced section is 12 mm long and 2 mm wide. A grating of fiducial marks is stamped on the specimens. They are clamped with a clamping distance of 20 mm and a prestrain ε_{0} is applied by moving the clamps apart by 4 mm. The stop is set to a stroke distance of 20 mm. In a pretest, a sample of material 1a has been filmed and photographed. The actual elongation has been determined from the distances between the fiducial marks and it is assumed that the measured values ε_{0} = 0.2 and ε_{1} = 1.2 apply to all the samples.

2.3. Synchrotron Beamline Setup

The SAXS monitoring has been carried out at beamline P03 of DESY, Hamburg, Germany. The test setup has provided a microfocus beam of moderate intensity. A 2D PILATUS 300 K 2D detector (DECTRIS, Switzerland) has been placed in a distance of 4000 mm behind the sample with large lateral offset. Using a X-ray wavelength λ = 0.1 nm and assuming fiber symmetry, the small detector monitors the scattering intensity I(s) in only a relatively small volume of reciprocal space. This volume is characterized by the relations 0.006 nm^{-1} < |s_{12}| < 0.16 nm^{-1} and 0.006 nm^{-1} < |s_{3}| < 0.13 nm^{-1}. s = (s_{12}, s_{3}) is the scattering vector in reciprocal

![Figure 1. The IPF uniaxial step-strain relaxometer. The gap on the right is the stroke distance defining the strain step Δε. Directly to the left is the pneumatic cylinder (speed: 800 mm s^{-1}). The sample is clamped under the end of the swivel arm between the heating heads. Further to the left the load cell is mounted. The prestrain ε_{0} is set with the knurled screw on the left in front of the big triangular bracket. Inset photos show a clamped sample and the setup on the beamline.](image-url)
space with its component $s_3$ pointing in straining direction. $|s| = s = (2/\lambda) \sin \theta$ with the scattering angle $2\theta$. Scattering patterns (frames) have been registered every $100$ ms with an exposure of $t_{ex} = 95$ ms yielding noisy data. A low-noise machine background has been registered with $t_{ex} = 2 s$ and used for background correction considering the different absorption factors in the strained state and in the relaxed state, respectively. A setup better adapted to the experiment would not only have required a high-intensity primary beam, but also a larger SAXS detector. In addition, simultaneous measurement of the 2D WAXS would have been desirable. Nevertheless, for a feasibility study, the microfocus setup is still of some use as long as the noise can be reduced by analysis technique. With sequence averaging, we integrate over time and when calculating projections, for example, rows of pixels are integrated and noise is reduced.

After the end of our test beamtime we have had the opportunity to monitor the relaxation of one material with wide-angle X-ray scattering (WAXS) using also the PILATUS 300 K detector.

The force on the sample has been registered every $10$ ms in arbitrary units. During each experimental run an expansion and contraction step have been triggered manually.

3. Data Evaluation

3.1. Big Data Analysis

The data from the experiments are analyzed using scripts written in Python. The Python libraries FabIO and h5py are used to read the raw scattering data (frames). Within SASKia,[12,13] scripts and commands are nested by the user until an automatic analysis of entire sequences of frames is facilitated. Automation is possible because together with every data set, already calculated intermediate results are saved as attributes.

3.2. Preevaluation of Scattering Patterns

Blind areas of the detector are discriminated by a mask. The scattering patterns are multiplied by the reciprocal of the absorption factor. The machine background is subtracted. A $3 \times 3$ median filter eliminates spikes. The frame is multiplied by the detector mask. The picture is placed on a larger canvas and its logical center is moved to the center of the canvas. The image is rotated so that the equatorial streak is on the horizontal axis, $s_2$, the “equator.” As far as possible, blind pixels are filled from valid mirror pixels. Simultaneously the noise of multiple valid pixels is reduced by averaging. There remains a hole in the center with the radius $s_p = 0.006 \text{ nm}^{-1}$. This hole has to be filled so that the projection curves calculated later become differentiable everywhere. For this purpose, the intensity on the equator is extrapolated into the center by a fourth degree polynomial. Using the method of radial basis functions,[14] a smooth surface is stretched over the polynomial arch, which continues differentiably into the data measured all around.

The WAXS images shown here are raw data that have only been completed symmetrically.

3.3. Simple Analysis of SAXS from Elongated Elastomers

The calculation and study of projections[3,15,16] is a method based on scattering theory, which even reduces the noise of individual 2D frames.

3.3.1. The Longitudinal Projection

Figure 2 shows projections

$$\{I\} = 2\pi \int_0^\pi \sum_l I(l,s_1) ds_1 ds_2$$

of the fiber pattern onto the straining direction, $s_1$, for the first frames after an expansion shot. Bonart[15,16] called such curves “longitudinal scattering intensity.” In our experiments the transverse limit is $s_1 = 0.16 \text{ nm}^{-1}$, which is small but still appears acceptable, because averaged low-noise patterns show that out there the intensity has already dropped sufficiently. In the vicinity of zero the projections look differentiable. At the upper limit of the detector ($s_1 = 0.125 \text{ nm}^{-1}$) the Porod law may already be a fair assumption, but the constant that governs the law cannot be determined. Fits and the analysis of the covariance matrix[17] (“pcov” in Python) return an error of determination of 25%. Thus we would obtain insignificant results if we would transform the short curves $\{I\} = (1) to real space in order to study the sizes of hard domains, their size distribution and arrangement within the soft phase matrix.

3.3.2. The Invariant

Because we cannot extract information about the domain structure from $\{I\} = (1)$, we have to limit ourselves to studying the scattering power (invariant)

$$Q = 2\pi \int_0^\pi \sum_l I(l,s_1) ds_1 = \sum_l \int I(l) d\mathbf{r}$$

of the SAXS. $Q$ is also the integral of the curves shown in Figure 2. We cannot extrapolate the curves to infinity. Therefore we must accept that the $Q$ determined in this study is not complete. So we do not try to evaluate $Q$ in detail, but simply keep in mind its relation to the morphology of a material made from hard and soft domains

$$Q = (\rho_h - \rho_s)^2 v_h (1 - v_h)$$

with $\rho_h$ and $\rho_s$ the electron densities of the hard and the soft phase, respectively. $v_h$ is the volume fraction of the hard domains. In the studied materials $v_h$ is well below 50%. So an increase of $Q$ probably indicates an increase of the hard domain fraction. An increase of the contrast $(\rho_h - \rho_s)$ upon
3.4. Analysis of Relaxation Phenomena

3.4.1. Analysis of Response Functions

A graphical method for comparing different relaxation processes is already established in early polymer physics textbooks.[10,18] For this purpose, the response function of the material is displayed in the semilogarithmic lin-log plot as a function of the logarithm of time. Utilizing such a diagram, the engineer discusses relaxation laws and mechanisms, but also effects that cause deviations from the ideal experiment (Fuss,[19] Figure 5.6). The ideal relaxation [1,10,18] is described by an exponential law and a single relaxation time, and a perturbation with logarithmic relaxation. Theoretical reasoning explains why in practice either the exponential law or the logarithmic law prevails. From logarithmic relaxation data we compute relaxation velocities and propose a four-law or the logarithmic law prevails. From logarithmic relaxation processes it is established in early polymer physics textbooks.[20–23] many materials are found that respond to such a signal with a delay, the definition of the time zero is not critical. For response functions that respond instantaneously, our definition of time is still conservative, but problematic. Such response functions definitely include \( \sigma(t) \) itself, which cannot be differentiated at \( t = 0 \). A deeper look then approaches the moment of discontinuity from both sides.

3.4.2. Definition of Time Zero and Relaxation Start

Let \( t' \) be the external time. Before the strain step has been triggered, the applied prestrain has generated a positive, almost constant force \( F = c \), \( c > 0 \). Then related stress \( \sigma(t') = c/A \) is constant and positive, as well. Ais the sample cross section before the strain step. Consequently, the trigger time \( t_i \), at which the strain step \( \epsilon(t') = \epsilon_0 + \Delta \epsilon_0 \Theta(t' - t_i) \) has taken place is recognized by the change (derivative) of the force response

\[
\sigma(t') = \begin{cases} 
0 & \text{if } t' < t_i \\
\ne & \text{if } t' \geq t_i
\end{cases}
\]

From this moment on, the sled moves until the force shows its next extremum. \( \sigma(t_i + \tau) = 0 \), \( t_i \) is the rise time of the strain step. For our analysis, we conservatively place the time zero on the arrival time of the sled and define

\[
t = t' - t_i
\]

By doing so we anticipate that then the morphological response function has not yet changed.

As long as we consider response functions that react to the signal with a delay, the definition of the time zero is not critical. For response functions that respond instantaneously, our definition of time is still conservative, but problematic. Such response functions definitely include \( \sigma(t) \) itself, which cannot be differentiated at \( t = 0 \). A deeper look then approaches the moment of discontinuity from both sides.

3.4.3. Relaxation Velocity with Logarithmic Relaxation

In order to compare relaxation processes which can be approximated by a linear course in a semilogarithmic lin-log representation,

\[
f(t) = f(t_0) + E_f \ln \left( \frac{t}{t_0} \right)
\]

the corresponding slope \( E_f \) is a measure of the relaxation rate. Closer to human imagination is the decadal measure

\[
D_f = \ln(10) E_f
\]

the relative increment of the function \( f \) per decadal order of magnitude, for example,

\[
D_f = \frac{1}{m - n} \left( \frac{f(10^n u) - f(10^0 u)}{f(10^0 u)} \right) = \frac{f(10^1)}{f(1)} - 1
\]

\( m - n \) are integer numbers. \( u \) is the chosen unit of \( t \). Within \( m - n \) orders of decadal magnitude the value of \( f(t) \) increases by \( 100 \times (m - n) D_f \% \).

4. Results and Discussion

4.1. Step Strain, Sled Movement, and Specimen Straightening

For material 1a we have filmed a test at the synchrotron with a video camera. The video frame sequence does not resolve the sled movement during the expansion shot. Subsequent tests with a high speed camera (4000 frames s\(^{-1}\)) show that the specimen expands under tension within 13 ms by 20 mm, that is, from \( \epsilon = 0.2 \) to the final elongation \( \epsilon = 1.2 \) (\( \dot{\epsilon} \geq 50 \text{s}^{-1} \)). After reaching the end point, a decaying vibration with a maximum amplitude of \( \Delta \epsilon_{\text{rms}} < 3 \times 10^{-3} \) is observed. The force measured...
every 10 ms reaches its registered maximum after a rise time $t_r = 20$ ms.

With the contraction shot, the sled is just as fast, but the sample itself is contracting much slower. Based on the video frames (Figure 3), we estimate a time $t_{st} \approx 250$ ms until the sample is straightened.

### 4.2. Classical Stress Relaxation

The force $F(t)$ has been recorded by the load cell in arbitrary units. In the static state ($\varepsilon = 0$), $F(t) \propto \sigma(t)$ is valid with the stress $\sigma(t) = F(t)/A(t)$ and the sample cross section $A(t) = A$ being constant in the static state, that is, while both the sled is at rest and the sample is tightened between the clamps. Figure 4 presents the response stresses of the materials registered during the

![Figure 3](image-url)

Figure 3. Sequence of video frames taken during a contraction-step experiment of material 1a ($\Delta \epsilon = -1$). Video frame rate 25 fps. Tapering originates from fiducial marks on the specimen.

![Figure 4](image-url)

Figure 4. Lin-log plots of the stress relaxation during the tests at the synchrotron. Arrows indicate the step-strain pulses that have just taken place. Left: $\varepsilon_0 = 0.2$, $\Delta \epsilon = +1$. $F(t) \propto \sigma(t)$ for $t > 20$ ms. Right: $\Delta \epsilon = -1$, $\varepsilon_\infty = 0.2$. During the yellow shaded period $t < t_{st}$, the samples are slack and $F(t) \propto \sigma(t)$ becomes only valid for $t > t_{st}$.
experiments at the synchrotron. In contraction, during the initial period highlighted in yellow the specimen relaxes macroscopically (cf. Figure 3). Within this straightening period it appears difficult to quantify the mechanical relaxation process.

The decay curves (Figure 4a,c) for \( t > t_{250} \) ms after the strain steps appear to satisfy a logarithmic fall-off, even though our observation period is somewhat short. Qualitatively very similar stress relaxation curves have been reported by Andrews et al.\cite{26} on polysisobutylene and by Clarke and Terentjev\cite{22} on polysiloxane elastomers. The latter have termed this behavior “logarithmic relaxation,” and we agree with this terminology.

The relaxation after the contraction steps is presented in Figure 4b.d. Even for \( t > t_{c} \) the curves are strongly curved in the lin-log plot. Here an evaluation according to Equation (6) assuming a logarithmic relaxation is certainly only a zero-order approximation which may only be used to discuss the order of magnitude of velocities \( D_{\sigma} \) in a comparison between stress relaxation and morphology relaxation. In any case, the value \( D_{\sigma} \rightarrow D_{\sigma} \Delta t_{i, j} \) determined in this way depends both on the step height \( \Delta \varepsilon \) and on the time interval \((t_{i, j})\) from which we determine the rate. Also the prestrain \( \varepsilon_{0} = 0.2 \) will affect the determined value of \( D_{\sigma} \). We decide to calculate the initial \( D_{\sigma} \) of the relaxing stress \( \sigma(t) \) using the interval \((t_{i, 10\times t_{i}})\) directly after the specimen straightening.

4.3. The WAXS Test

Figure 5 presents the first four frames after the expansion step. In the first pattern after the step, there is no change at all. So the WAXS response has no discontinuity at the moment of the strain step. It takes 140 ms after the step until the orientation of the polymer chains appears increased. It further increases until the next pattern taken 240 ms after the step, but qualitatively this is the final state. If the detector does not afterglow strongly, this observation indicates that (already) the orientation distribution of the chains responds to the sudden macroscopic strain only with a delay. After the contraction shot we observe the same delay. The latter observation appears less astonishing, because then the macroscopic tightening of the specimen takes 250 ms, as well.

![Figure 5. Material 2a. Sequence of WAXS frames taken during an expansion shot (\( \Delta \varepsilon = +1 \)). Insets show the change of force during the exposure of the corresponding scattering pattern.](image)

4.4. Qualitative: SAXS and Morphology Evolution

Also the SAXS response is continuously differentiable at the moment of the strain steps, that is, it too reacts with a delay. Figure 6 presents SAXS patterns of the annealed materials from the short period \( t \lessapprox 400 \) ms after the step perturbations together with patterns from the final stage of observation labeled “accu.” The noise in these patterns has been reduced by accumulating frames.

For \( t > t_{nc} = 250 \) ms all patterns look the same and the morphologies are stable, in principle. Thus the principal morphology conversion (mc) is very fast. After that, the morphology changes only gradually. The study of the corresponding relaxation requires a quantitative analysis of the scattering patterns. \( t_{nc} = t_{c} \) indicates that changes of the basic morphology evolve in the same time span which the material takes for (straightening in) free relaxation.

Morphology conversions of a very similar type are exhibited in the sequences of the materials with polyester soft-segments (2a and 3a). They are different with material 1a, where the intensity in the long-period reflection collapses after the expansion step, and simultaneously a strong (horizontal) equatorial streak appears. The domain structure degrades in favor of a morphology of nanofibrils that are oriented in the stretching direction. However, the noise-reduced “accu” pattern top left shows that a small fraction of the domains is preserved. This persistent fraction in turn transforms similarly to the domains of materials 2a and 3a. After the contraction step, the equatorial streak collapses in favor of recurring domain scattering. Therefore the formation of non-healing cracks in the polyester-based annealed material is ruled out as an explanation. We do not know what the nature of the needle-like entities is. They may be pores or entities made of matter, the density of which differs from the density around. In the figure, the scattering intensity of material 1a is displayed on a logarithmic scale to make its extreme variation manageable for visualization.

Comparing to the mechanical stress relaxation, Figure 4a,c exhibit that for \( t < t_{mc} \) the \( \sigma(t) \) relaxes much slower than the morphology conversion in all materials. The fundamental mc-process appears to have little direct impact on the stress relaxation.

Figure 7 visualizes the change in the scattering patterns for the unannealed specimens. Obvious differences to the annealed samples are:

1. In the polyester-based material 1u, no dominant fibril morphology is formed at the expense of the domain morphology. Its mc-process can be visualized in linear scaling of the intensity.
2. All the unannealed materials show less discrete scattering and less equatorial scattering. This is not seen by comparing the patterns from the figures, because the pseudo-color scale has been adjusted separately for each experiment to visualize changes in the arrangement of the hard domains.
4.5. Qualitative: Static Morphologies

4.5.1. Morphology before the Experiment

Let us compare in Figures 6 and 7, the patterns in the bottom line, left from the double arrow. Qualitatively the patterns of annealed and unannealed materials look very similar. Thus the primary effect of annealing on the morphology is the already addressed improvement in phase separation without an apparent change in the average hard domain arrangement.

4.5.2. Morphology Long after the Expansion Step

Let us compare in Figures 6, 7 the patterns in the top line, left from the double arrow. Outside the equatorial streak, the scattering is in principal very similar. Correlations among hard domains only exist in the stretching direction. Compared to the morphology before the experiment (bottom patterns), the position of the long-period reflection has changed little. Thus the soft phase between persistent hard domains hardly extends. The change is particularly small for the unannealed materials. In the annealed materials, the polyester-based samples 2a and 3a show a more pronounced increase of the long period.

4.5.3. Morphology Long Time after the Return to \( \varepsilon = 0.2 \)

Let us now consider in Figures 6 and 7, the patterns in the bottom line, right from the double arrow. They are related to the final morphologies that have formed after the contraction steps. The domain scattering has been clearly restored for all samples, but now shows 4 intensity maxima, placed on an almost circular reflection. The differences between annealed and unannealed materials are small.

To explain such patterns it is neither necessary to assume tilting\(^{[27]}\) of lamellar-shaped domains nor the formation of a macrolattice.\(^{[7,28]}\) It is sufficient to assume that some of the hard domains are coupled to a neighbor. Like dumbbells such pairs of hard domains orient during expansion and relax back to a preferred angle during contraction. Such pairs of hard domains have been called “duos” in previous papers.\(^{[12,29]}\)
4.6. Quantitative Evaluation of Morphology Relaxation

Because of the poor quality of the scattering patterns, we can only analyze the scattering power \( Q \) quantitatively. On the one hand, by the calculation of \( Q \) noise is effectively suppressed because one integrates over the reciprocal space. On the other hand, \( Q(\mathbf{t}) \) measures morphology change. The determination of domain size distributions and interdomain distances depends on better data.\[30,31\] Although one can easily extract the equatorial streak in the 2D scattering pattern, the extracted \( Q_{\text{streak}}(\mathbf{t}) \) is both too low and too noisy to draw significant conclusions.

For \( Q(\mathbf{t}) \), Figure 8 shows the initial relaxation behavior of the domain morphology in the same representation in which we have already presented the stress relaxation (Figure 4). In the lin-log plot, the curves appear angular at small \( t \), because there the frame-cycle time (100 ms) is too long. After the shot, \( Q \) initially remains at the old level, but then changes too fast for the temporal resolution of the experiments. The fast process expires at \( t_{\text{mc}} = t_{\sigma} \). We can only characterize it by its settling stroke \( \Delta S(\mathbf{t}) = Q(t_{\text{mc}}) - Q(0) \).

Thereafter we observe a straight line in the lin-log plot for all samples which describes a slow morphology relaxation process. We characterize the slow process according to Equation (8) by relaxation rates \( D_{\theta}^+ \) and \( D_{\theta}^- \) for the expansion and contraction relaxation, respectively. Because of the observed linearity, the determination of the \( D_{\theta}^\pm \) is independent of the choice of the limits \( t_1 > t_{\text{mc}} \) and \( t_2 \) of the interval \( (t_1, t_2) \) in which the linear regression is carried out. In the annealed material (bottom in Figure 8) the invariants \( Q \) are twice as high as in the unannealed materials (top).

Let us first consider the relaxation after the expansion steps (left in Figure 8). The polyester-based materials 2 and 3 change only slightly after the morphology conversion. The unannealed variants 2u and 3u even experience a slow improvement in \( Q \) over time. The polyester-based material 1 reacts more strongly. In the unannealed version, \( Q \) improves over time, but when it is annealed, the domain structure crumbles away rather fast.

After the contraction steps, the quick process leads to a significant increase in \( Q \). In the following slow process \( Q \) continues to increase over time for all samples. Thus the domain morphology recovers for all materials. Quantitatively the relations are reflected in the rate parameters, which are presented in Table 2 both for the morphology relaxation and the mechanical relaxation. The intervals of confidence have been computed from the covariance matrix of the fit.\[17\] In practice, a value \( D_{\sigma}^- = 18 \) means that the SAXS invariant \( Q \) decreases in the period \([0.25 \text{ s}, 2.5 \text{ s}]\) after the expansion step by 18%, and by another 18% in the following interval of decadal order, that is, \([2.5 \text{ s}, 25 \text{ s}]\).

As already discussed above, \( D_\sigma \) is decreasing considerably during the relaxation after the contraction jump (cf. Figure 4). The specified values relate to the beginning of the relaxation process.

4.6.1. Visualization of Two Observed Response Processes in a Diagram

The scattering response of the elastomers is continuously differentiable across the expansion steps. At the spot of X-ray irradiation the specimen reacts delayed by a fast settling that is
followed by a traceable relaxation. We characterize the settling by its settling time $t_{mc}$ and the settling stroke $\Delta \varphi$. Thereafter, the traceable relaxation takes place at a relaxation rate $D_R$. If we measure a response function like $Q(t)$, the question arises how high are the proportions of settling and relaxation in it. The answer to this question can be assessed from the addressed

Figure 8. Lin-log plots of the relaxation of the domain morphology (SAXS scattering power $Q(t)$). Arrows indicate the step-strain pulses that have just taken place. Left: $\varepsilon_0 = 0.2$, $\Delta \varepsilon = +1$. Right: $\Delta \varepsilon = -1$, $\varepsilon_\infty = 0.2$. During the yellow shaded time, the samples are slack.

Table 2. Initial rate parameters $D_J(t, 2.5s)$ (in percent) of stress ($R = \sigma$) and morphology relaxation ($R = Q$) for a strain step $\Delta \varepsilon = 1$ with a prestrain $\varepsilon_0 = 0.2$. A number in parentheses indicates the inaccuracy of the last place meaning, that is, $-9.1(2) \rightarrow -9.1 \pm 0.2$.

| Sample | $\Delta \varepsilon = 1$ | $\Delta \varepsilon = -1$ |
|--------|--------------------------|--------------------------|
|        | "a" annealed             | "u" unannealed           | "a"       | "u"       |
|        | $D_\sigma [%]$ | $D_Q [%]$ | $D_\sigma [%]$ | $D_Q [%]$ | $D_\sigma [%]$ | $D_Q [%]$ |
| 1      | -9.1(2)                 | -18(5)                   | -10.6(1)   | 3(1)      | 15(1)                 | 2.1(2)   |
| 2      | -8.8(2)                 | 0                         | -10.1(2)   | 2(1)      | 36(2)                 | 3.6(2)   |
| 3      | -7.9(2)                 | 0                         | -9.2(2)    | -2(1)     | 17(1)                 | 2.5(3)   |
Finally, the is negative and is mapped on the time interval (0.1, 10) mc. The slope of the material (1a) is labeled for the discussion.

Such relative response path (RRP) diagrams are presented in Figure 9 for the relaxation of the SAXS invariant Q. Both axes are normalized. The time axis is normalized to 10 mc and the Q-axis to the Q of the pristine material. Let us explain the graph of sample 1a, that is, of the annealed polyether-based TPU. Its line segments are labeled in the drawing. We start with the expansion segment. Segment A visualizes the relative loss of Q in the settling interval. The observed settling stroke Δt/Q is negative and is mapped on the time interval (0.1, mc, 10 mc). The slope of segment B visualizes the subsequent relaxation with rate D; thus the line ends at the height Q(10 mc)/Q0. As the virtual contraction step starts, the time is reversed and segment C indicates the corresponding settling stroke Δt/Q. Finally, the slope of segment D visualizes the relaxation with rate D; and the height of the end point indicates the total change of Q in the virtual cycle, that is, the response of the SAXS invariant to the strain signal S(t) = ε0 + Δεt Θ(t)(1 - Θ(t - 10 mc)) after the period t = 20 mc.

4.6.2. Discussion of the RRP Diagrams

With the annealed polyether-based TPU 1a, expansion causes the scattering force of the hard domains to drop to 22% during settling. Another 18% of the value reached is lost in the interval [mc, 10 mc] (cf. also Table 2). Nevertheless, after the contraction segment C) the morphology recovers extremely well already in the settling. After that, even slow relaxation (segment D) is sufficient to completely restore the morphology. The polyether-based annealed materials show a less spectacular response of the morphology on the nanoscale. At high strain there is little change of the settled morphology. Settling after the contraction step is not as effective as that after the expansion step has been, but here the recovery makes a significant contribution over time—although recovery is unable to reach the initial state.

When discussing the unannealed materials it is worth remembering that their Q are only half as high as the Q of the annealed materials. After the expansion step, the relative settling loss of the u-materials is higher than that of the a-materials, but in the slow relaxation it even improves with time. After the contraction step during settling there is little recovery, but the slow relaxation improves the morphology considerably. Nevertheless, the unannealed materials do not return to their initial value. After the virtual cycle the polyester-based TPUs 2u and 3u have lost 15% of their already low scattering power. The polyether-based TPU 1u does better with a loss of only 6%.

4.6.3. Domain Cluster Relaxation and Stress Relaxation

The stress relaxation σ(t) cannot be visualized in an RRP diagram and compared to Q(t) easily, because the response σ(t) is not continuously differentiable at the strain step. Nevertheless, there are several features of both types of responses indicating that σ(t) (Figure 4) cannot easily be related to the morphological relaxation Q(t) (Figure 8) of the TPUs. Even the basic timings of both functions are different. As Q(t) is just beginning to change, a considerable fraction of the relaxation of σ(t) has already expired. As then the slow process runs for both response functions, the comparison of the relaxation rates (Table 2) shows that the constant logarithmic relaxation D of the morphology is generally significantly slower than the initial stress relaxation Dσ. The exception is the annealed polyether-based material 1a after the expansion step, which has developed strong equatorial streak scattering in the fast morphology settling (Q(t < mc)). There we observe Dσ > D for the subsequent slow morphology relaxation process.

The stress relaxation σ(t) of the material correlates little with the relaxation Q(t) of the domain clusters. Therefore, future studies should also examine the relaxation of the unstructured, amorphous soft phase by adding the WAXS.

4.7. Discussion of General Results

It appears remarkable that two morphology transformation processes are found, the first of which is extremely fast. We also have not expected that the stress relaxations σ(t) of the different materials are much more similar to each other than the morphology relaxation curves Q(t). The huge effect of the formation of nanofibrillar entities on the morphology evolution of the annealed polyether-based TPU is not apparent in the stress relaxation. Also interesting is the strict logarithmic relaxation of Q(t) for all materials. The separation of the total morphology change into two relaxation components seems at least of academic interest. It answers the question: How big is the fast settling stroke of the morphology and how much of the further response is contributed by the slow process? If a morphological response deficit measured in a strain-jump cycle were linked to a rebound...
resilience deficiency in mechanics, the determination of the two relaxation components might even be of practical value.

It also appears noteworthy that the annealed materials show a particularly large settling stroke after the contraction jump and then no gradual improvement of the morphology, this in contrast to the unannealed materials. Thus with the annealed materials an impacting ball ball is bouncing back quite well.

5. Conclusions

This feasibility study has given a first impression of the character of the rapid morphology relaxation after strain jumps in elastomers. We have obtained a more detailed picture of the necessary experiment design and even obtained results on a small series of thermoplastic polyurethanes.

We are satisfied with our pneumatic relaxometer in combination with the materials and the sample geometry. We have been surprised that the major change in morphology (hard domain arrangement in the soft matrix) takes place within 250 ms. In future experiments, the frame rate of the X-ray scattering must therefore be increased from 10 to 100 Hz during the first half second after each strain jump and the exposure must be reduced. To make this possible, the frame rate and exposure should be variably programmable within a run. SAXS and WAXS should be measured simultaneously with large area detectors and low signal-to-noise ratio. Only then will it be possible to analyze the important relaxation of both the distances between the hard domains and of the domain orientation. A particular challenge is the registration of the 2D SAXS pattern with a sufficient signal-to-noise ratio in quick succession. Thus this experiment needs the frame rate of the X-ray scattering must therefore be increased from 10 to 100 Hz during the first half second after each strain jump and the exposure must be reduced.

Are there force vibrations in the material after the strain steps? Might a morphology conversion wave run through the sample? Such questions should become answerable if the step-strain experiment is scanned with a high frame rate of both the force and the 2D X-ray scattering.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

elastomers, mechanical relaxation, morphological relaxation, small-angle X-ray scattering (SAXS), strain steps

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