

Correlations Between Chemical Structure, Stress-Induced Crystallization, and Deformation Behavior of Polyurethane Elastomers*

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Synopsis

The deformation behavior of polyurethane elastomers depends strongly on physical interactions.

In this paper the stress-induced crystallization of the polyester or polyether segments is investigated in several polyurethane elastomer systems having different chemical structure for the soft segments. The correlation between the tensile properties (hysteresis loss, extension set, modulus) and the stress-induced crystallization is discussed.

INTRODUCTION

Many of the differences between the deformation behavior of polyurethane elastomers and ideal rubber elasticity are caused by physical interactions between adjacent molecules. Although it is well known that segmented polyurethane elastomers are physically crosslinked by a system of hydrogen bridges in the hard-segment regions, it is not such common knowledge that the so-called chemically crosslinked polyurethane elastomers also may contain physical crosslinks. During deformation these crosslinking areas undergo a certain rearrangement which causes stress softening and leads to permanent deformation. This fact has been reported by several authors.¹⁻⁶

In addition to the effects mentioned above, physical interactions take place in the soft regions of the elastomers. Polydiols can usually be crystallized and are often solids at room temperature. Incorporating the polydiols into elastomers has the effect of slightly depressing the melting point and lowering the crystallization rate, so that in many cases an undeformed elastomer shows little or no crystallization. During extension, however, the molecules become parallel, and the crystallization is accelerated.

We have concerned ourselves in this paper with the correlation between the stress-induced crystallization and the tensile properties of polyurethane

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elastomers. Various methods were used to measure these effects in a variety of elastomeric systems.

DEFORMATION CALORIMETRY

The theory of deformation calorimetry is already given in several papers.⁸⁻¹¹ The apparatus used for our measurements is described in detail elsewhere.¹⁰ The following remarks will therefore be sufficient to discuss the results of deformation calorimetry given in this paper.

The samples are elongated stepwise, and the deformation energy dA and the deformation heat dQ for each step are measured.

a. In the case of pure entropy elasticity, the internal energy is constant, and therefore

$$\frac{dQ}{dA} = -1.$$

b. An increase in the internal energy during deformation gives

$$\frac{dQ}{dA} > -1.$$

c. In the case of stress-induced crystallization, the internal energy decreases, and we get

$$\frac{dQ}{dA} < -1.$$

With deformation calorimetry in the described manner, it is not possible to separate the crystallization from other effects which diminish the internal energy, though in most cases these effects are small when compared with the heat of fusion. So we may regard the ratio dQ/dA as a measure of stress-induced crystallization.

RESULTS OF DEFORMATION CALORIMETRY

The influence of some chemical parameters on the stress-induced crystallization has been already dealt with.^{2,10} To complete the picture it seems useful to give a short outline of these results here.

Figure 1 shows $d(Q/A)$ diagrams obtained from elastomers which are based on caprolactone polyester. The diisocyanate is 4,4'-MDI, and a bishydrazide was used as chain extender. To get elastomers of equal stiffness, the low molecular weight polyester was extended with MDI. This prepolymer was mixed in various ratios with the high molecular weight polyester. Figure 1 shows a strong decrease in the internal energy on stretching the elastomer based on the long-chain polyester ($d(Q/A)$ much smaller than -1). X-Ray diffraction proved that stress-induced crystallization had occurred. With increasing MDI content in the polydiol, the

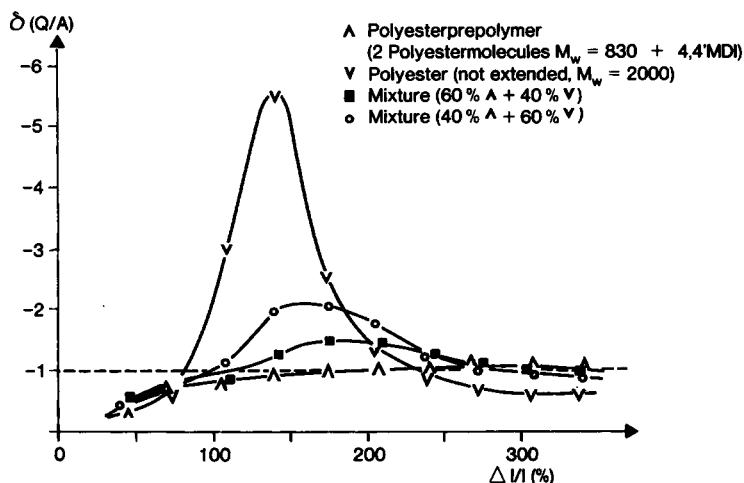


Fig. 1. Stress-induced crystallization as a function of isocyanate content in the soft segments.

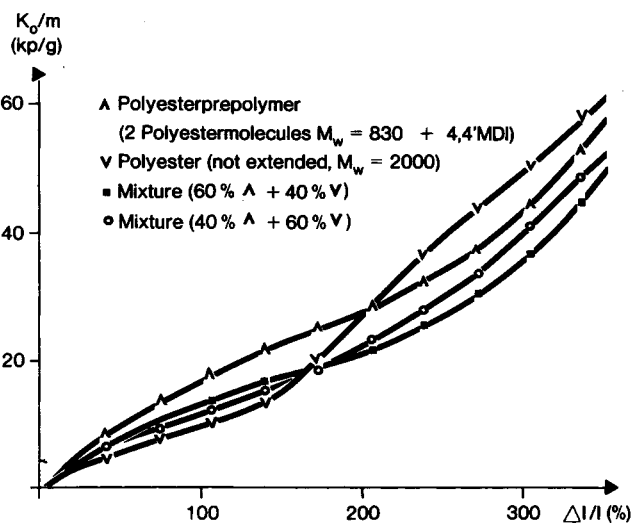


Fig. 2. Correlation between isocyanate content in the soft segments and tensile properties.

crystallization becomes weaker and is completely suppressed in the short-chain polyester.

The influence of the stress-induced crystallization on the tensile properties is shown in Figure 2. The short-chain sample has a higher initial modulus than the long-chain sample because the chain segment mobility is reduced by the bulky MDI molecules. During elongation, however, this relation is inverted on account of the stress-induced crystallization.

Another series of different polydiols was used to produce the elastomers shown in Figure 3. The isocyanate and the chain extender were identical to those used in the series mentioned above. The strongest crystallization is observed in the elastomer based on poly(hexamethylene adipate) but be-

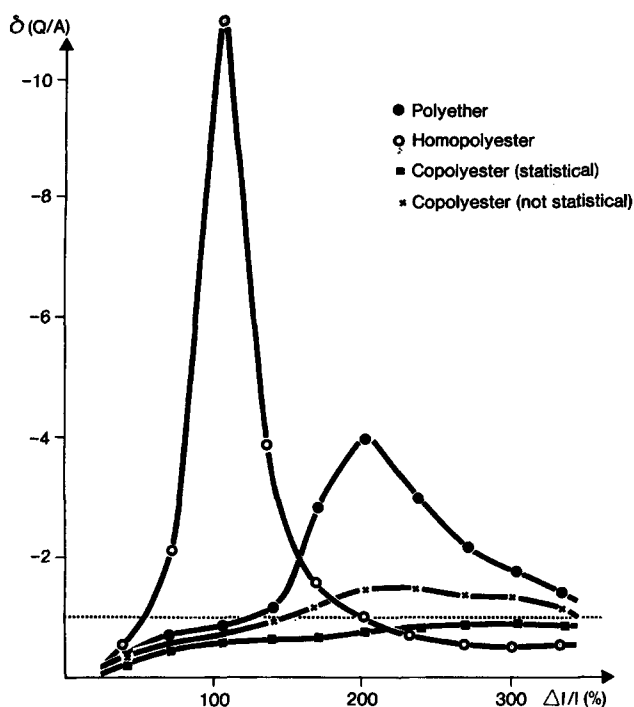


Fig. 3. Influence of the chemical structure on the stress-induced crystallization.

comes weaker when poly(tetramethylene ether) is used as polydiol. The copolyester from hexamethylene glycol, neopentylene glycol, and adipic acid shows very faint crystallization. This small amount could be due to the composition of this polydiol being only partially statistical. No crystallization is observed in the elastomer based on the statistical copolyester poly(ethylene-neopentylene adipate).

Both series show that stress-induced crystallization can be suppressed by sufficient chemical irregularity of the polydiol. Similar behavior is observed upon differential thermal analysis (DTA) of the pure polyesters (Fig. 4). While the homopolymer has a melting point of 50°C and a large heat of fusion, the copolyester (not statistical) melts at 18°C and has a smaller heat of fusion.

The stress-induced crystallization has a marked influence on the mechanical hysteresis under periodic deformation. Figure 5 shows the relative hysteresis loss as a function of temperature for the elastomers based on homopolymer, polyether, and the very weak crystallizing copolyester. With regard to the mechanical loss, there is no difference between the polydiols when the temperature is above the melting point of the homopolymer; but when it falls below this temperature, the loss factor increases with increasing stress-induced crystallization. This effect is probably due to a continuous rearrangement of the stress-induced crystallites caused by the periodic deformation. Furthermore, the stress-strain diagrams show

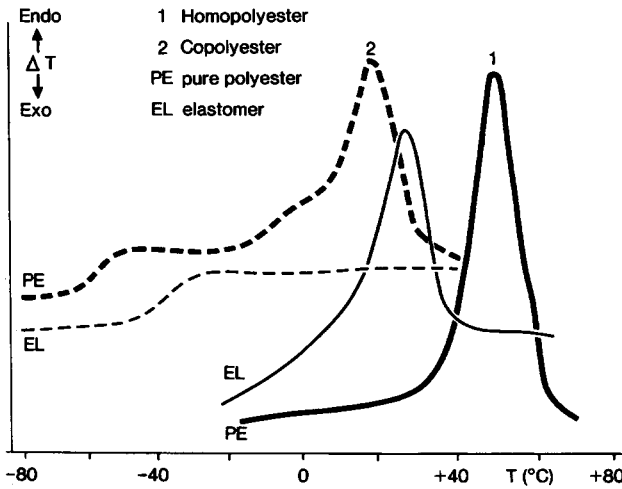


Fig. 4. DTA diagrams of two different polyesters and their corresponding elastomers.

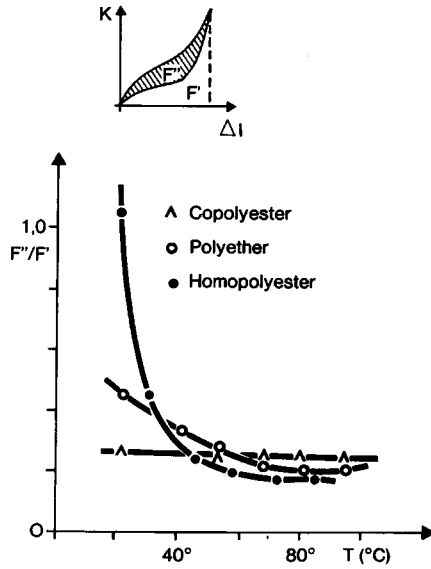


Fig. 5. Relative hysteresis loss as a function of temperature.

a correlation between residual elongation and crystallization. In the next section this correlation will be considered.

**INFLUENCE OF ISOCYANATE CONTENT AND CHEMICAL
CROSSLINKING ON THE EXTENSION SET**

Material

The elastomers are based on poly(ethylene adipate) and cured with naphthylene-1,5-diisocyanate and 1,4-butanediol. The NCO/OH ratio is

varied from 1 to 1.24, and three types of elastomers are made: Type 30 means 30 parts diisocyanate per 100 parts polyester; type 18 contains 18 parts diisocyanate per 100 parts polyester; in type 18/40, 40% of the butanediol is replaced by trimethylolpropane in order to obtain additional chemical crosslinking.

Measurements

Figure 6 shows the relaxation of a type 30 sample which was extended by 300% and held in this state for 5 min at room temperature. Thirty min after unloading, the residual elongation reaches the almost constant value of 80%. This extension set has two main causes: stress-induced crystallization and plastic deformations. These two parts can be separated by increasing the temperature: between 20°C and 50°C, a considerable shrinkage takes place. The DTA shows an endothermic transition in the same temperature interval. It is therefore justified to regard this part $\Delta\epsilon$ of the extension set as caused by stress-induced crystallites, which prevent the oriented molecules from recoiling completely. The rest of the extension set may well be due to rearrangements of chemical crosslinks and hard-

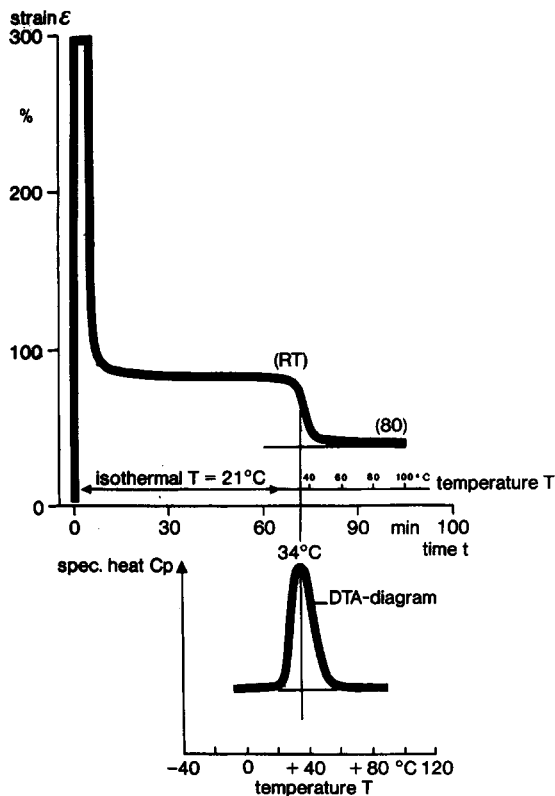


Fig. 6. Residual extension as a function of time and temperature.

segment regions. It has been reported (ref. 12 in Bonart and Morbitzer²) that in natural rubber this plastic deformation vanishes after swelling the sample, thus ruling out the cause as chain fracture.

In Figure 7 we see the complete extension set and its plastic portion as a function of the NCO/OH ratio. The results were obtained in the following manner: The samples were stretched by 300% and held under load for 30 min. After unloading and relaxation of the sample for 30 min, the residual elongation ϵ_R was measured. Then the sample was heated to 80°C and held at this temperature for another 30 min. After cooling to room temperature, the plastic portion of the extension set (ϵ_R at 80°C) could be obtained.

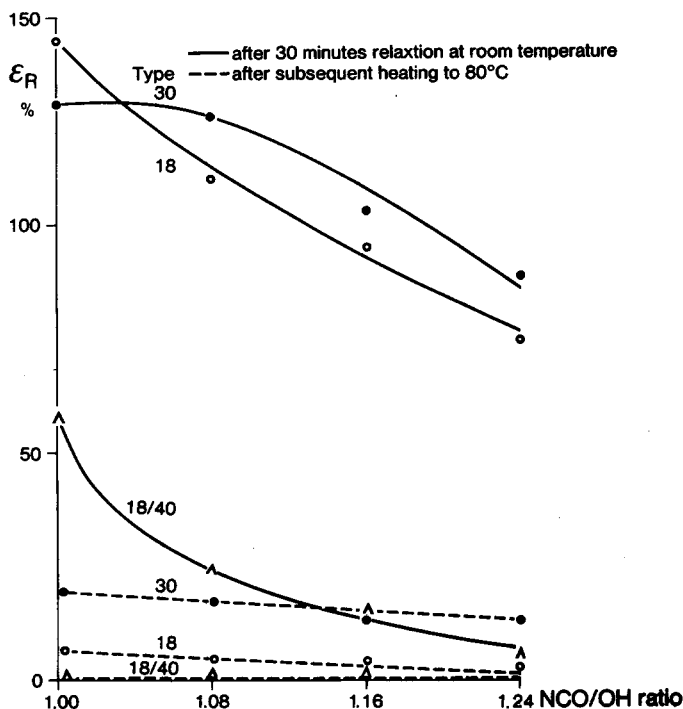


Fig. 7. Residual extension ϵ_R after initial elongation of 300%.

From Figure 7 it is clear that most of the extension set is due to crystallization, which might be also an important factor in the discussion of compression set measurements.

The stress-induced crystallization is aided by decreasing the NCO/OH ratio and increasing the hardness. The addition of trimethylol propane has an effect similar to increasing the NCO/OH ratio. This is quite reasonable because in both cases the density of chemical crosslinking is raised, thereby hindering the alignment of polyester molecules. Similar results are obtained when a constant load is applied instead of a constant initial elongation (Fig. 8).

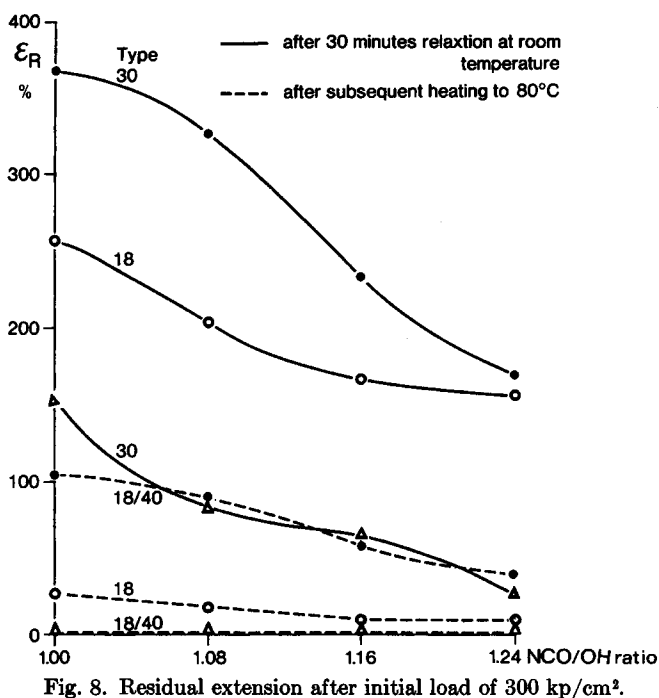


Fig. 8. Residual extension after initial load of 300 kp/cm².

According to a theory of Flory,¹² the retractive force of a sample under constant elongation decreases with advancing crystallization, an effect which may be enlarged by relaxation and flow. Figure 9 shows that the decrease of the retractive force occurs for several hours with a corresponding increase in the extension set. Most of the crystallization, however, takes place during the deformation.

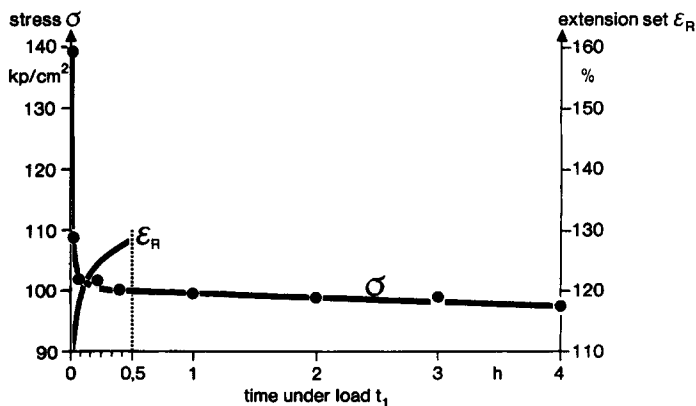


Fig. 9. Stress relaxation and extension set of type 30 elastomer as a function of time under load.

The applied load has a very strong influence on the extension set (Fig. 10). Beneath the yield point (taken from stress-strain diagrams not shown in this paper—the yielding begins at a strain of about 50% for this sample), the extension set is very small but increases considerably at higher loads. From theory we should expect a linear correlation between stress and chain segment orientation and therefore a linear correlation between stress and crystallization. In contrast to this, we find a linear correlation between strain and crystallization. This result is somewhat surprising but does agree with measurements carried out by other authors who found a linear

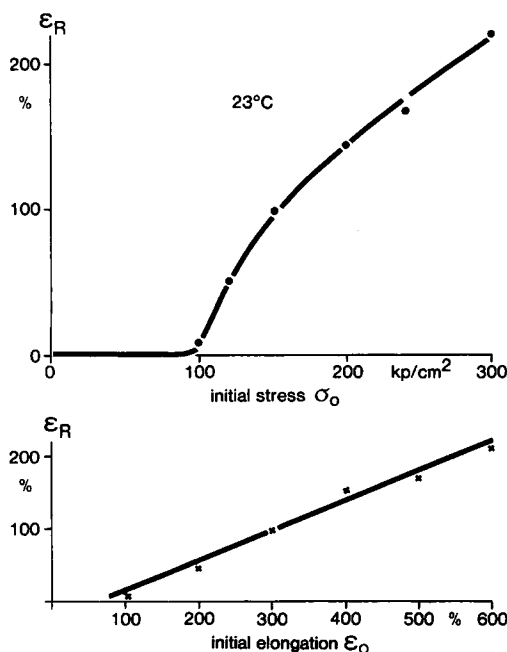


Fig. 10. Extension set ϵ_R of type 30 elastomer as a function of unitial elongation and initial stress.

correlation between molecular orientation and strain in polyurethane elastomers and in styrene-butadiene rubber.⁴⁻⁷ There is as yet no adequate explanation for this irregularity. We feel it must depend on the domain structure of segmented elastomers.

Plotting the heat of fusion ΔH (taken from DSC measurements) versus ϵ shows only a slight increase of ΔH at high values of ϵ (Fig. 11). We must conclude that the crystallites previously generated are rearranged ore, melted and recrystallized at high elongations. In this way different residual elongations can be fixed by similar amounts of crystallinity. These results are confirmed by the conclusions drawn from the hysteresis behavior mentioned in the foregoing section.

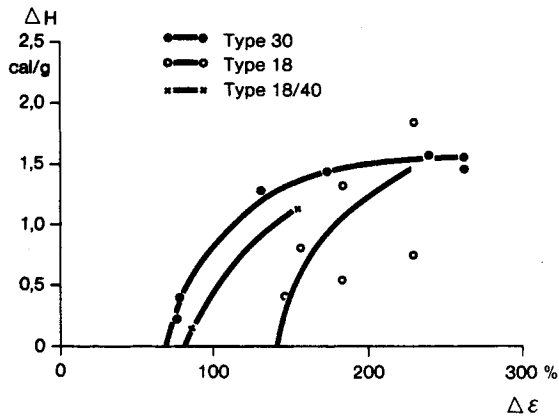


Fig. 11. Correlation between heat of fusion ΔH and the residual extension $\Delta \epsilon$.

CRYSTALLIZATION KINETICS IN A PERIODICALLY DEFORMED SAMPLE

Instead of measuring the retractive force under constant elongation, the tensile properties may be recorded during continuous periodic deformation. The elastomer used for the following experiments was based on a poly(butylene adipate) extended with a dimerised TDI and cured with an excess of a diamine. Figure 12 shows a series of stress-strain diagrams. The first deformation of a "virgin sample" causes a considerable stress softening due to the destruction of polyester crystals which had formed before deformation. Heating to 50°C and then cooling slowly to room temperature restores the sample to its original state (Fig. 12b).

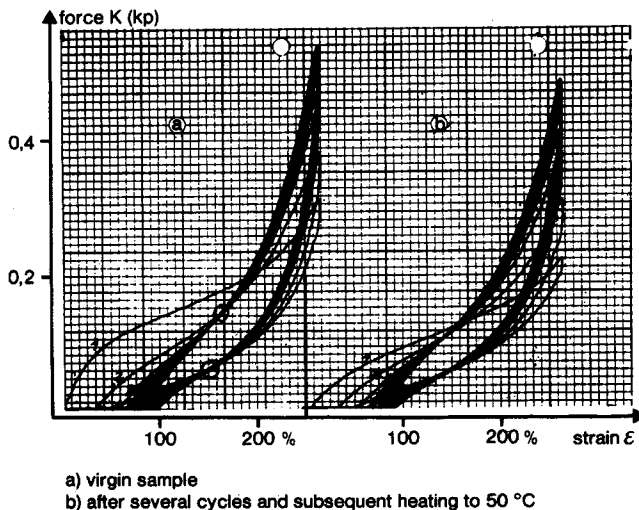


Fig. 12. Change of tensile properties caused by repeated loading and unloading.

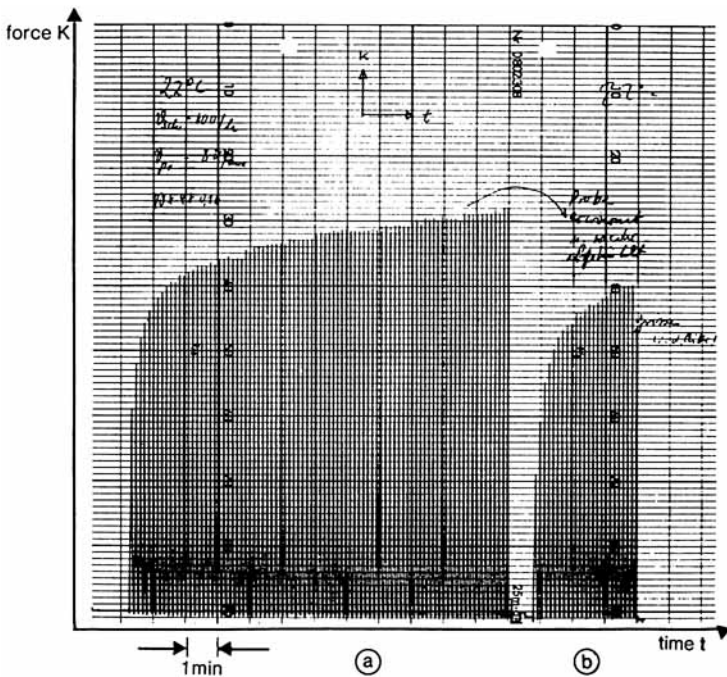


Fig. 13. Increase in maximum force during periodic deformation.

The residual extension increases on increasing the number of deformation cycles (i.e., the time), a phenomenon which gives information on crystallization kinetics. In contrast to the behavior under constant elongation, we now find an increase of the retractive force with time (Figs. 12 and 13). This means that the crystallites do not form during maximum elongation but mainly at medium deformation values. They thus constitute a secondary physical crosslinking network, which makes no contribution to the retractive force when the elongation is about 150%. In excess of this elongation, the secondary network delivers an additional retractive force and below it, diminishes the retractive force of the sample, thus helping us to understand the extension set caused by crystallization. Furthermore, the model gives a simple explanation for the points of intersection observed in the σ, ϵ -diagrams at elongations of about 150%. The conclusion that crystallization takes place mainly at this elongation is confirmed by deformation calorimetry. Figure 14 shows the maximum crystallization at an extension of 150%.

It should be mentioned that similar effects were found in elastomers of quite different chemical structure. In some cases the intersection point was observed at higher elongations than the maximum of stress-induced crystallization. This depends both on the rearrangement or recrystallization of the stress-induced crystallites and on the rearrangement of hard-segment regions.

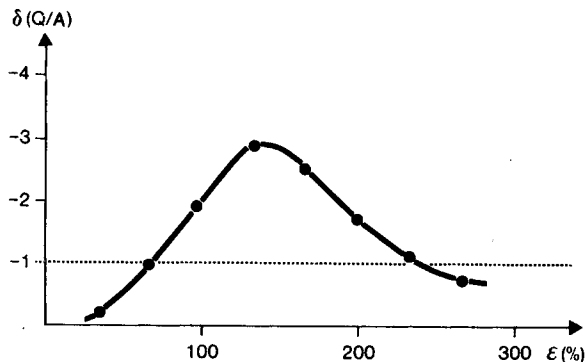


Fig. 14. Stress-induced crystallization as a function of elongation ϵ .

CONCLUSIONS

We set out to show that stress-induced crystallization occurs in a great variety of polyurethane elastomers when the sample temperature is below the melting point of the extended polydiol. All tensile properties are influenced by this effect, especially the extension set. The stress-induced crystallization depends on the chemical structure and regularity of the polydiol used as the soft segment of the elastomer.

The practical importance of stress-induced crystallization will depend upon the application of the manufactured polyurethane. Crystallization effects can improve tensile strength and tear resistance. In addition, the mechanical loss at high strain amplitudes is strongly influenced, which may be useful for special applications. The high extension set caused by these same effects will, however, be undesirable in most cases. The most satisfying compromise, therefore, has to be found for every application of polyurethane elastomers.

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