Analytical description of stress-strain dependence for segmented polyurethane ureas swollen in physically aggressive media

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Abstract. The article is devoted to the problem of analytical description of the strain behavior of elastomers under various conditions. It summarizes experimental data on the stress versus strain dependences of polyurethane urea elastomers swollen in two plasticizers. These data can be adequately described using the approach taking into account relaxation properties of elastomers and non-relaxation ones. All factors affecting the strain behavior of investigated elastomers are considered.

1. Introduction

Elastomers based on polyurethane ureas and polyurethanes are widely used in industry due to the advantages of their physic-mechanical properties comparing with usual rubbers. The most complete information about the deformation behavior of these materials can be obtained using the experimental dependence of stress versus strain. Such dependences can be obtained as analytical equations using the previously proposed generalized approach to the theory of elasticity [1, 2].

However, when the mentioned materials are used in physically aggressive media (solvents, plasticizers), their properties significantly vary. It was previously established, for example, that the dependence of the initial modulus of the swollen amorphous cross-linked elastomers on the plasticizer concentration can be described by a complex function. Herewith the parts of the modulus related with chemical bonds and physical ones depend on the plasticizer concentration according a power function with exponent $m$ [3]. This exponent is equal to $1/3$ for chemical bonds, but $m>2$ for physical bonds correspondingly. The value of this exponent is related to the nature of the plasticizer, the polar groups of which are able to interact with the polar groups of the polymer, competing with the formation of interchain physical bonds in the polymer system.

It should be noted that the most important polyurethanes and polyurethane ureas are block-copolymers, i.e. polymers whose polymer chains consist of alternating segments that differ greatly in chemical structure. This difference leads to the phase separation, promoting formation of hard and soft block domains [4]. The domains of hard blocks in such elastomers play, on the one hand, the role of reinforcing filler, and on the other hand, they play the role of spatial network nodes. Under the conditions of swelling hard domains may be partially or completely break down [5].

The target of this work is investigation of the possibility of analytically describing the dependence of stress versus strain for segmented polyurethane urea elastomers swollen in plasticizers.

2. Materials and Methods

We investigated the polyether urethane urea elastomers with different content of hard segments. All of them were made on the basis of oligotetramethylene oxide diol (PTMO-1400) with $M_n = 1400$ g·mol$^{-1}$ and 2,4-toluene diisocyanate (TDI). Methylene-ortho-chloroaniline (MOCA) was used as a chain
extender, and trimethylolpropane (TMP) as a cross-linking agent. Di-2,6-hexyl sebacate (DEHS) and tributyl phosphate (TBP) were used as plasticizers.

Synthesis of elastomers was carried out using two stages. At the first stage of synthesis, a prepolymer was obtained by the reaction between PTMO-1400 and TDI. In this case, the ratio NCO/OH = 2.06 was applied. In the second stage, prepolymers were reacted with mixtures of the aromatic diamine MOCA, PTMO-1400 and TMP. The ratio of components in the synthesis are shown in Table 1. Preparation of the samples was published earlier [6].

Table 1. Molar ratios between components of compositions.

| Series | NCO/OH | PTMO-1400 | TMP | MOCA |
|--------|--------|-----------|-----|------|
| PT-1   | 1.08   | 0.95      | 0.05| 0    |
| PT-2   | 1.08   | 0.75      | 0.05| 0.2  |
| PT-3   | 1.08   | 0.55      | 0.05| 0.4  |
| PT-4   | 1.08   | 0.15      | 0.05| 0.8  |

Cured elastomer samples were cut to obtain rectangular plates for further swelling to achieve a certain swelling degree. The amount of this degree for each sample in the DEHS was chosen so that the values of the polymer volume fraction in the swollen samples \( \phi_2 \) were distributed approximately uniformly in the range of 1\( \approx \)0.66. Subsequently, the swelling in the TBP was carried out to achieve the values of \( \phi_2 \), which were almost equal to the ones swollen in DEHS.

Mechanical testing of elastomers was performed using Instron 3365 testing machine. The tests were carried out at 25\( \pm \)1 °C under three stretching rates 0.0028 s\(^{-1}\), 0.056 s\(^{-1}\), and 0.56 s\(^{-1}\). The relaxation characteristics of the studied samples were determined by the Bartenev-Bryukhanov method [7] under the same stretching ratio \( \lambda = 1.4 \).

3. Results and discussion

As mentioned earlier, the stress versus strain dependence for the cross-linked elastomers can be described using the previously developed approach that takes into account both the relaxation properties and non-relaxation ones of the elastomers. This approach gives the following equation for stretching at a constant rate [2]:

\[
\sigma = E_0(\lambda - \lambda^2) \cdot \left[1 + 3b(\lambda^{-1} - d) + \gamma_1 \alpha^2 (1 - \phi)(\alpha^2 \phi - 2)/(1 - \alpha^2 \phi)^2 \right] + \\
\frac{1}{\nu} \int W \sum_{i=1}^{n} E_i \exp \left(1 - \frac{\lambda}{v \tau_i} \right) d \lambda = \sigma_{el} + \frac{1}{\nu} \int W \sum_{i=1}^{n} E_i \exp \left(1 - \frac{\lambda}{v \tau_i} \right) d \lambda 
\]

where \( \sigma_{el} \) is the highly elastic part of the stress and not related to the relaxation properties of the object, \( \lambda \) is the stretching ratio, \( \nu \) is the stretching rate, \( \tau_i \) is the relaxation time, \( E_i \) is the relaxation parameter with stress dimensionality, \( W \) is the transformation function, \( \alpha \) is the chain inextensibility coefficient, and \( \phi \) is an intermediate function, \( \phi = \lambda^2 + 2\lambda^{-1} \). \( E_0 \) can be considered as a parameter of a relaxation element with an infinite relaxation time and identified as the elastic response of a constant spatial network with a certain density. The change in the freedom degree of polymer segments in the deformation process of polymer chains is taken into account by introducing \( \alpha \) and the \( \gamma_1 \) coefficient reflecting the fraction of polymer chains taking part in the deformation process in an overstressed state.
Parameters $b, d$ are chemical network constants for specific series. Usually $d \approx 0.2$ for unswollen elastomers.

When adapting equation (1) to the case of swollen polymer networks, it is possible to use semi-empirical dependencies of some parameters on the swelling degree. Thus, these dependences were obtained in [8] for the $d$ and $E_i$ quantities. In principle, the question of the swelling effect on the mentioned parameters remains open. However, the approximating analysis of the swelling effect on these parameters can be done using the Bueche approach which relates the strength and tensile properties of polymer networks with the rupture probability of overstressed polymer chains [9].

Let us consider, for example, in the simplest form, swelling of three-dimensional networks within the framework of the Flory’s theory, setting as a constant criterion related to the magnitude of the limiting strain degree, the specific work of strain $A$ performed upon reaching the $\lambda_{\text{max}}$ value:

$$A = \lambda_{\text{max}}^2 + 2\lambda_{\text{max}}^{-1}$$

(2)

Taking into account the fact that a part of the specific work of strain during deformation of swollen networks spend for three-dimensional stretching (during swelling), we can obtain the following formula connecting the values of the maximum stretching ration before swelling and after swelling ($\lambda_{0\text{max}}$ and $\lambda_{\text{max}}$):

$$\lambda_{0\text{max}}^2 + 2\lambda_{0\text{max}}^{-1} = \lambda_{\text{max}}^2 + 2\lambda_{\text{max}}^{-1} + 3(1 - \gamma_2^{-2/3})$$

(3)

Calculations using this equation with transition to $\alpha$ values ($\alpha=1/\lambda_{\text{max}}$), show that the variation in $\alpha$ values during swelling can be neglected within the diapason of small swelling degrees (up to 30%) and for relatively low ultimate stretching values ($\lambda_{0\text{max}} < 7$). Since the $\gamma_i$ parameter plays a subordinate role with respect to $\alpha$, one can also assume its permanent status under swelling in a similar way.

On the other hand, it is obvious that plasticization can affect all the relaxation parameters included in this equation. In this work, we used the approach described in [8], in which the values of the characteristic relaxation times of the polymers under consideration are frozen, which to some extent corresponds to the principle of continuity of the relaxation time spectrum of most polymers. In this case, the swelling effect can be marked only for the parameters of the corresponding relaxation elements having the modulus dimensionality. Let us now consider the dependence of the above mentioned parameters and all the stress versus strain plots on the swelling degree, i.e. on the $\phi_2$ values.

Table 1 shows the relaxation parameters of the studied elastomers and the features of their variation in the swelling process. These variations for the $E_i$ values were considered in the framework of the following dependencies:

$$E_i = E_{i0}\phi_2^m$$

(4)

Generally, a large volume of experimental data was obtained, which made it possible to draw a number of important conclusions. Firstly, the used equation (1), taking into account the concentration correction of the $E_i$ parameters, makes it possible to obtain calculated stress versus strain plots. Parameters of the samples necessary for calculations are given in Tables 2, 3. They were determined according to [1]. As shown in Fig.1, the agreement between the experimental plots and calculated ones is quite satisfactory, which allows us to conclude that the corresponding approach is unconditionally applicable for swollen segmented elastomers.
Figure 1. Comparison of calculated stress versus strain plots for PT-1 (a) and PT-4 series (b) under 0.56 s\(^{-1}\) stretching rate. Solid curves are experimental, dotted ones are calculated using equation (1).

Table 2. Relaxation parameters of the unswollen PT elastomers at 25°C

| Series | \(E_0\), MPa | \(E_1\), MPa | \(E_2\), MPa | \(E_3\), MPa | \(\tau_1\), s \(\times 10^{-3}\) | \(\tau_1\), s \(\times 10^{-2}\) | \(\tau_1\), s |
|--------|-------------|-------------|-------------|-------------|----------------|----------------|---------|
| PT-1   | 0.84        | 0.18        | 0.14        | 0.17        | 1.02           | 1.10           | 10.2    |
| PT-2   | 0.88        | 0.18        | 0.14        | 0.17        | 0.99           | 1.12           | 9.9     |
| PT-3   | 0.93        | 0.18        | 0.14        | 0.17        | 1.01           | 1.11           | 9.5     |
| PT-4   | 2.93        | 0.18        | 0.14        | 0.17        | 1.02           | 1.10           | 9.9     |
| DEHS   | 0.33        | 2.2         | 2.2         | 2.2         |                |                |         |
| \(m\)  | TBP         | 2.3         | 3.5         | 3.5         | 3.5            |                |         |

Also some important conclusion can be made considering values of exponents \(m\) for the \(E_i\) parameters presented in Table 1. The average value of the index \(m\) for the \(E_i\) parameters for samples swollen in DEHS is 2.2, and the same for ones swollen in TBP is 3.5. Similar phenomena for relaxation elements caused by physical bonds have already been described previously [8].

But we can consider now the plasticization effect on the network of strong physical bonds caused by the presence of the hard domains in polyurethane ureas. This network determines the level of the \(E_0\) parameter. One can see that the variation of this value depending on the plasticizer concentration has a completely different character when using DEHS and TBP.
We determined that \( m = 0.33 \) for \( E_0 \) in all samples swollen in DEHS. Also the same \( m \) value for \( E_0 \) was obtained for the PT-1 series swollen in the both plasticizers. But this value has a much higher level for other samples swollen in TBP (\( m =2.3 \)). This fact suggests that DEHS does not practically destroy the network of strong physical bonds in segmented elastomers, the concentration variation in \( E_0 \) value corresponds to the geometric factor characteristic for swelling network of chemical bonds. The PT-1 series samples do not contain hard blocks. The variation of their parameters during swelling corresponds to the amorphous elastomers [8]. TBP, in contrast to DEHS, destroys partially the domains of hard blocks leading to the correspondent degradation of the spatial network in the investigated polymers during swelling. This effect is reflected by the higher level of the \( m \) value for \( E_0 \) parameters for segmented polyurethane urea elastomers.

**Table 3.** Parameters of equation (1) for investigated samples in the unswollen state

| №  | \( \alpha \) | \( \gamma_s \) | \( b \) |
|----|-------------|------------|--------|
| PT-1 | 0.16        | 0.06       | 0.4    |
| PT-2 | 0.16        | 0.06       | 0.4    |
| PT-3 | 0.16        | 0.06       | 0.4    |
| PT-4 | 0.16        | 0.06       | 0.4    |

**4. Conclusion**

It was found that the experimental dependence of stress versus strain for cross-linked segmented elastomers swollen in plasticizers can be successfully described using the equation previously tested for the non-swollen elastomers. Experimental confirmation of this fact was given for four series of segmented polyurethane ureas samples with different chemical structures and network density. The degree of the plasticizer structure influence on the level of variation in the relaxation parameters of the studied elastomers, and the deformation behavior of the swollen elastomers was found as well.

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