Structure and properties of polyepoxyurethane-containing isocyanurate polymers

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Abstract. The modification of epoxyurethane-containing isocyanate polymers of a network structure was performed due to variations in the curing temperature and the ratio of diol, diisocyanate components and epoxy resin. When the reaction systems are cured below 100°C, the polymers contain a large number of flexible chain structures and pass into the rubbery state at ~60°C. An increase in the processing temperature above 120°C leads to a significant change in the composition, which affects the properties of the resulting systems, the glass transition temperature of which increases in the limit to 225°C. An experimental change in the elastic modulus associated with an increase in the curing temperature from 80 to 200°C was found. At the processing temperature of 120°C, the Sol fraction content in the samples is decreased and the gel fraction is increased. Yield strength increases by 48%, modulus of elasticity by 107%, Brinell hardness by 40%, Shore hardness by 20 %. The glass transition temperature increases to 225°C.

1. Introduction
This work is devoted to preparation and studying the properties of modified epoxy urethane-containing isocyanurate network polymers. This work is preceded by previous studies [1-4] on this issue, including the study of the strength, deformation and thermal properties of such polymers synthesized on the basis of various oligoetherdiols, iso- and disocyanates and epoxy resin. These properties vary significantly depending on the ratio of diol and isocyanate components. The properties also depend significantly on the reaction temperature and the concentration of the catalyst. The data obtained in [1-4] allowed us to evaluate the effect of the concentration of the polymer cross-linked points formed on the glass transition temperature and apply computational methods for quantitative description of this dependence.

In this paper, the influence of precursor curing temperatures on physical, strength and thermal properties is analyzed. Measurements were made in a wide range of temperatures. The paper uses the previously developed calculation scheme [5-7] for determining the glass transition temperature of copolymers to predict their physical characteristics.

2. Experimental part
The following systems were studied: 1) an epoxy resin cured with 2,4-toluylenediisocyanate (TDI) with a 3.5-fold excess of the latter; 2) polytetramethylene oxide (PTMO) cured with 2,4-toluylenediisocyanate (2.6-fold excess). The synthesis process of systems 1 and 2 was performed...
simultaneously, but in different containers at a temperature of 75°C for 30-35 minutes. The reaction system consisting of a mixture of the products of both reactions in the presence of the catalytic hardener dimethylbenzylamine, equal to 0.2% in terms of the total mass of the system, was subjected to thermal curing. Temperature and time curing mode specified in table 1.

Table 1. Temperature-time mode of sample curing.

| Samples of the copolymers | 80°C | 90°C | 100°C | 110°C | 120°C | 160°C | 200°C |
|---------------------------|------|------|-------|-------|-------|-------|-------|
| SPEUI₁ | 40   | -    | -     | -     | -     | -     | -     |
| SPEUI₁₁ | 40   | 40   | -     | -     | -     | -     | -     |
| SPEUI₁₁₁ | 40   | 40   | 40    | -     | -     | -     | -     |
| SPEUI₁₁₁₁ | 40   | 40   | 40    | 40    | -     | -     | -     |
| SPEUI₁₁₁₁₁ | 60   | 60   | 60    | -     | 60    | -     | -     |
| SPEUI₁₁₁₁₁₁ | 60   | 60   | 60    | -     | 60    | 60    | 60    |
| SPEUI₁₁₁₁₁₁₁ | 60   | 60   | 60    | -     | 60    | 60    | 60    |

Epoxy resin is a product of CHS-EPOXY 520 containing residual hydroxyl groups of phenol, as well as hydroxyl groups of oligomerized epoxy that can react with TDI. PTMO has a molecular mass of $M = 1000$. DMBA is used to accelerate the curing of epoxy resin and is a catalytic hardener. NMR spectra were recorded on a Bruker Avance 400 device with an operating frequency of 400 Hz ($^1$H); the signals of residual protons of deuterosalsvators were used as an internal standard.

IR spectroscopy and titrimetric methods were used for continuous monitoring of the reaction in the TDI-epoxy, TDI-PTMO and epoxy-TDI + TDI-PTMO systems. IR spectra in the region of 440÷4000 cm$^{-1}$ were registered on the Fourier spectrometer "NicoletMagna 750".

The choice of the optimal curing mode was determined by studying changes in the following properties of the system: strength at compression, modulus of elasticity (including at different temperatures), Brinell and Shore D hardness. Thermomechanical, differential-thermal and thermogravimetric methods of analysis were also used.

Measurements of stress-strain curves at compression were performed at different temperatures on the Dubov-Regel device (the device is equipped with special software for electronic registration of experimental data).

Standard methods for determining Shore D and Brinell ($H_b$) hardness were used. The measurement was performed on the Vostok-7 device (Shore D) and the TP-1 hardness tester. The load on the indenter was 5 kg (samples SPEUI₁-SPEUI₁₁ (Shore D)) and 5 and 12 kg ($H_b$) samples SPEUI₁-SPEUI₁₁ and SPEUI₁₁₁-SPEUI₁₁₁ respectively.

According to thermomechanical analysis (TMA), the experimental glass transition temperature $T_g$ was determined, on the basis of which the chemical composition of microphases was estimated. Methods of quantitative description of the dependence of $T_g$ on the chemical composition of microphases using the Cascade computer program (INEOS RAS) were used [5-7]. TMA was performed on a thermomechanical analyzer "Q400 Instrument".

Thermogravimetric analysis (TGA) in combination with differential thermal analysis (DTA) was performed on a derivatograph "Derivatograth-C" in the temperature range of 20-700°C in air at a heating rate of 10 deg/min.

During the Sol analysis, fractions were isolated from samples at the curing depths, which were reached at temperatures of 80, 90, 100, 110, 120, 160 and 200°C. The Sol-fraction separation process was carried out in a continuous way in the Soxlett apparatus using acetone.
3. Results and discussion

Initially, when an excess amount of TDI 3.5 mol interacts with an epoxy resin at \( T \sim 75^\circ C \), isocyanate-epoxyurethane is formed, which is the product of adding TDI to an oligomerized epoxy

\[
\begin{align*}
\text{CH}_3 & - \text{NCO} \\
\text{NH} & - \text{C}=\text{O} \\
\text{O} & - \text{CH}_2 - \text{CH}_2 - \text{O}
\end{align*}
\]

According to NMR data, the ratio of reacted TDI to non-reacted TDI is 1:3.

Based on the data of titrimetric analysis, it is calculated that the initial TDI remains in the reaction system in the amount of 2.3 mol. According to the same analysis, it was determined that the number of epoxy groups in the initial reaction system was \( \sim 14.02 \) wt. %, i.e. their consumption during the reaction does not exceed 16%. Quantitative processing of IR spectra shows that the main bands of the epoxy at 1511, 1247 and 830 cm\(^{-1}\) decrease by \( \sim 12.8, 23.6 \) and 11.2%, respectively, during the reaction 6.

As a result of the interaction of an excess amount of TDI (2.6 mol) with PTMO, we obtain the urethane for polymer of the following structure:

\[
\begin{align*}
\text{H}_3\text{C} & - \text{OCN} \\
\text{NH} - \text{C}(\text{O(CH}_2\text{)}_4)\text{nO} & - \text{C}-\text{HN} \\
\text{NH} - \text{C}(\text{O(CH}_2\text{)}_4)\text{nO} & - \text{C}-\text{HN} \\
\end{align*}
\]

According to NMR data, the ratio of reacted TDI to non-reacted TDI is 1:2.

The TDI content in the resulting product (based on titrimetric data) is \( \sim 2.2 \) mol. IR spectroscopy data confirms a decrease in the peaks of isocyanate groups in the range of \( \sim 16\% \). This also corresponds to titrimetric data, according to which the TDI content is reduced by \( \sim 15\% \).

When further interaction between the urethane prepolymer and isocyanatomethane and add DMBA with increasing temperature epoxyurethaneisocyanurates formed of the following structure:
In the resulting system, initially containing 4.5 mol of TDI, the consumption of the latter, according to titrimetry data, exceeds 18% for more than 40 minutes. Thus, in the resulting epoxyurethanisocyanurate product, the number of TDI moles is reduced to 3.7. The data of titrimetric analysis are confirmed by the results of IR spectroscopy analysis, according to which the decrease in the characteristic peaks of isocyanate groups does not exceed 17%.

In general, the subsequent heating of the polymerizing system from 80°C and higher (see table 1) results in cyclotrimerization of residual NCO groups with the formation of isocyanurates [2-4]:

The chemical formulas of R structures are shown above.

The calculated and experimental data discussed below allow us to draw some conclusions about the choice of the final temperature of the curing process. Calculations of $T_g$ of network polymers were performed using the method [6]. The structural features of the resulting systems were considered taking into account the chemical nature of the repeating units and their quantitative ratio. Based on the chemical structure of linear chains and cross-linked points (table 2), as well as experimental results of TMA and TGA, using the computer program “Cascade” obtained data on the quantitative ratios of the structures that make up each microphase.
Table 2. Chemical structure of repeating units of the copolymer.

|   |   |
|---|---|
| A | ![Chemical structure A](image1.png) |
| B | ![Chemical structure B](image2.png) |
| C | ![Chemical structure C](image3.png) |
| D | ![Chemical structure D](image4.png) |

The calculated values of \( T_g \) and \( T_d \) of the studied samples are shown in table 3 (the table also shows the experimental values of \( T_g \)).
Table 3. Values of glass transition temperature and density of synthesized samples (calculations were made using the computer program “Cascade”, INEOS RAS).

| Samples   | Relaxation transitions | \( M \) (g/mol) | \( \sum \Delta V_i \) (nm\(^3\)) | \( \rho \) (kg/m\(^3\)) | \( T_{g, \text{calculation}} \) | \( T_{d} \) (K) |
|-----------|------------------------|-----------------|-------------------------------|-----------------|----------------------|-----------------|
| SPEUI\(_I\) | I                      | 235             | 0.226                         | 1160            | 332                  | 328             | 653             |
|           | II                     | 763             | 0.708                         | 1220            | 432                  | 433             | 651             |
| SPEUI\(_II\) | I                     | 235             | 0.226                         | 1160            | 332                  | 340             | 653             |
|           | II                     | 448             | 0.420                         | 1200            | 393                  | 393             | 652             |
| SPEUI\(_III\) | I                    | 235             | 0.226                         | 1160            | 332                  | 338             | 653             |
|           | II                    | 508             | 0.475                         | 1200            | 403                  | 407             | 651             |
| SPEUI\(_IV\) | I                     | 235             | 0.226                         | 1160            | 332                  | 338             | 653             |
|           | II                     | 508             | 0.475                         | 1200            | 403                  | 407             | 651             |
| SPEUI\(_V\) | I                      | 263             | 0.251                         | 1170            | 348                  | 350             | 653             |
|           | II                     | 1490            | 1.38                          | 1230            | 478                  | 475             | 656             |
| SPEUI\(_VI\) | I                     | 1360            | 1.26                          | 1230            | 463                  | 464             | 656             |
| SPEUI\(_VII\) | I                     | 1410            | 1.31                          | 1220            | 497                  | 498             | 641             |

The microphase cleavage for the SPEUI\(_I\) sample takes place at \( T \approx 328\)K and \( T \approx 433\)K at the following ratio of structural fragments: \( A = 26.4 \) and \( 4\)%, \( B = 15.8\) and \( 16\)%, \( C = 28.9\) and \( 51\)%, \( D = 28.9\) and \( 29\)%, respectively. For the SPEUI\(_V\) sample, the relaxation transition occurs only at \( T \approx 498\)K, which is \( 170\)K higher than for the SPEUI\(_I\) sample. The composition of microphases is as follows: \( C = 93\%\), \( D = 7\%\).

It was found that the elastic modulus \( E \) decreases from an initial value of 700 MPa at \( 20^\circ\)C to a value of 45 MPa at \( 105^\circ\)C (figure 1, curve 1), which exceeds 93%. The most significant change in the composition of microphases associated with an increase in the final temperature of the curing process by 2.5 times (sample SPEUI\(_V\)) is manifested in the practical loss of structures with increased flexibility (fragments \( C \) with a share of 93\% and \( D \) with a share of 7\% prevail in the composition of microphases). As for \( T_{g, \text{calculation}} \), the highest value is observed here, equal to \(~498\)K (table 3). In this case, the value of \( E \) reaches a value of 900 MPa at a temperature of \( 105^\circ\)C with an initial value of 1450 MPa at \( 20^\circ\)C (figure 1, curve 5). Here, the value \( E \) is reduced by 38\%. If in such a system (meaning the SPEUI\(_V\) sample) the concentration of cross-linked points increases, as indicated by the ratio of structural fragments, then the \( T_{g} \) of the system is higher by \( 170\)K than in the SPEUI\(_I\) sample. The region in which the polymer SPEUI\(_V\) is located in this case corresponds to the glassy state.
Figure 1. Dependence of the elastic modulus of copolymer samples on temperature: 1 – SPEUII, 2 – SPEUIIV, 3 – SPEUV, 4 – SPEUIVI, 5 – SPEUIVII.

The influence of the heat treatment temperature on the strength properties of samples can be seen in the obtained Brinell and Shore hardness dependencies (Shore D). The effect of changes in Brinell hardness with changes in the final temperatures of the curing process exceeds 40% (figure 2, curve 1), and shore hardness – 20% (curve 2).

Figure 2. Dependence of Brinell hardness (1) and Shore hardness (2) on the temperature of the sample curing process. The points correspond to the final temperatures of the curing process of samples SPEUII, SPEUIIV, SPEUUV, SPEUIVI, SPEUIVII.
4. Conclusion

The experiments and calculations carried out in this work allowed us to obtain information about the effect of the curing temperature of the reaction medium consisting of epoxy resin, TDI, PTMO and DMBA on the strength and thermal properties of the resulting epoxyurethane-containing isocyanurate polymers of a network structure. The final curing temperature varied from 80 to 200°C. The dependence of the yield strength at temperature curing of the reaction mixture showed that at the curing temperature of 200°C, the value of $\sigma_y$ acting increases by 48%, elastic modulus increased by 107%, Brinell hardness number increases by 40 %, and Shore hardness by 20%. The glass transition temperature increases to 225°C. As the analysis showed, such a change in strength properties with variations in the curing temperature is associated with a change in the chemical composition of microphases that form polymer systems.

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References

[1] Askadskii A A, Goleneva L M, Konstantinov K V and Bychko K A 2001 Russian Polym. News 6 (2) p 6
[2] Askadskii A A, Goleneva L M, Afanas'ev E S and Petunova M D 2012 Review J. of Chemistry 2 (2) pp 105-152
[3] Askadskii A A, Goleneva L M, Afanas'ev E S and Petunova M D 2012 Review J. of Chemistry 2 (4) pp 263-314
[4] Askadskii A A 1998 Russian Chem. Reviews pp 681–712
[5] Askadskii A A 1996 Physical properties of Polymers. Prediction and Control (Amsterdam: Gordon and Breach Publishers)
[6] Askadskii A A 2003 Computational Materials Science of Polymers (Cambridge: Cambridge International Silence Publishing)
[7] Askadskii A A, Goleneva L M, Konstantinov K V and Bychko K A 2002 Vysokomolek. Soedin. A. 44 (4) p 567 [in Russian].