



CONDITIONS FOR REALIZATION OF MECHANICAL AND THERMOMECHANICAL PROPERTIES IN POLY(EPOXY URETHANE ISOCYANURATES) BEARING CARBON AND GLASS FILLERS

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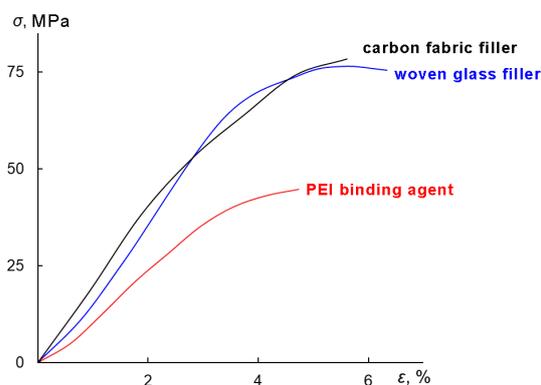
Abstract

The new poly(epoxy urethane isocyanurates) are synthesized in three main steps, which include the reactions of 2,4-toluene diisocyanate with oligoepoxide and 2,4-toluene diisocyanate with poly(tetramethylene oxide). The resulting polymers are used as binding agents for the preparation of composite materials. The following types of fillers are explored: dispersed fillers (A-35 carbon soot), woven glass fillers (Style 120 E-glass), and carbon materials (UVIS-T-22R). The addition of carbon soot and an increase of its content in the composition lead to an increase in the elastic modulus almost by 84% upon heating from the initial temperature to 105 °C, which is in accord with the properties of the binding agent (83%). For the composites based on the woven glass and carbon materials, these changes occur within 47% and 33%, respectively. An increase in the Brinell hardness upon filling with the woven glass and carbon materials exceeds 15%, and that of the Shore hardness—27%. The thermomechanical analysis reveals two relaxation transitions at *ca.* 80 °C and 200 °C. The chemical structures of the copolymers responsible for these transitions are defined using the Cascade computer program (INEOS RAS).

Key words: network polymers, poly(epoxy urethane isocyanurates), polymer composite materials, carbon black powder, reinforcing fillers, mechanical properties, thermomechanical properties.

Introduction

Nowadays, the prediction of physical properties of poly(epoxy urethane) polymers [1–3] is based on the use of the models and computation schemes which enable the calculation of a large number of various properties based on the chemical structures of polymer networks. A rational basis for the development of new polymer composite materials from poly(epoxy urethane) systems can be the experimental data obtained earlier in the Laboratory for Polymer Materials of INEOS RAS [4, 5]. The main goal of this work was to develop a synthetic approach to polymer networks for production of composites with dispersed (carbon soot), woven glass, and carbon fillers, which would ensure the improvement of mechanical properties of the resulting polymer materials in a wide temperature range. For this purpose, a polycyclotrimerization process should be carried out with an optimal ratio of the initial reagents that can be defined by computational methods and would provide the structures of the required chemical compositions. Obviously, the properties of the resulting composites are mainly determined by the structure of a matrix polymer; however, the introduction of the fillers and other additives may also significantly affect the mechanical characteristics of the resulting composites.



Experimental

The target poly(epoxy urethane isocyanurate) (PEI) binding agents (prepregs) were obtained using a three-step approach followed by compression molding. The syntheses were carried out using oligoepoxide, 2,4-toluene diisocyanate (TDI), polytetramethylene oxide (PTMO), and dimethylbenzylamine (DMBA). The oligoepoxide based on a diglycidyl ether of 4,4'-dihydroxy-2,2-diphenylpropane (CHS-EPOXY 520) contained the hydroxy groups of the oligomerized epoxide, which were able to react with TDI; refractive index $n_D^{25} = 1.575$. TDI with the following characteristics was used: 98% content of 2,4-toluene diisocyanate, $n_D^{25} = 1.567$. PTMO with $M = 1000$ represented a white solid, which at T above room temperature converted to a viscous transparent liquid; the hydroxyl value $\text{mg KOH/g} = 0.05$, $n_D^{20} = 1.463$. DMBA is a catalytic curing agent which was used to accelerate the oligoepoxide curing; $n_D^{20} = 1.501$.

The target PEIs were obtained in three main steps, which included the reactions of a 3.5-fold excess of TDI with the oligoepoxide and a 2.6-fold excess of TDI with PTMO, resulting in isocyanate urethanes and urethane forpolymers. The processes for two systems were conducted simultaneously but in different vessels at 75 °C for 30–35 min. The reaction of the

resulting isocyanate urethane and urethane forpolymer in the presence of DMBA as a catalytic curing agent (0.2%) upon heating above 80 °C afforded PEI copolymers which served as the binding agents in the subsequent production of composites.

The thermal processing of the binding agents was carried out in a closed press mold in the temperature range from 80 to 130 °C (with the temperature step of 15 °C) for ~160 min (with the time step of 40 min) at the specific pressure $P_{sp} = 4.3$ MPa. The process was completed by the unforced cooling of the mold without disconnection of the mold plates; the pressure was also allowed to reduce spontaneously (sample reference code I-S). The experiment was performed on a Hydra laboratory hydraulic press.

In the first case, the composite samples represented disperse-filled materials that were obtained by the addition of carbon soot (technical carbon of A-35 trademark synthesized according to the published procedure [6]). In the second case, woven glass (Style 120 E-glass) and carbon (UVIS-T-22R) materials were used as the fillers [7, 8]. Table 1 lists the names and types of the fillers.

The modification of polymer samples with carbon soot was carried out by dry blending of the binding agent with the additive followed by crushing of the resulting agglomerates upon ultrasonic (US) treatment. The latter was performed on a MEF 391.1 ultrasonic disperser at 4–5 mA for 2–3 min. The filling degree of the binding agent varied from 0.5 to 5.0 wt % (samples I-S-CDF_{0.5}, I-S-CDF_{2.5}, and I-S-CDF₅, Table 1).

The samples of the woven glass and carbon materials impregnated with the binding agent were obtained according to the following procedure. The fabrics were processed by dipping into a tank of the binding agent. The resulting prepregs were preliminarily cured at ~80 °C for 35 min; then, curing was continued at the temperature up to ~130 °C at $P_{sp} = 4.3$ MPa. The samples obtained were allowed to cool spontaneously to 50 °C without disconnection of the mold plates upon pressure reduction. The filling degrees of the compositions and the number of prepreg layers are presented in Table 1.

During the reactions, the refractive indices of the resulting systems (n_D^{30}) were measured. This was important for their further control up to the step of polymer production. The experiments were carried out with an IRF-22 refractometer.

Table 1. Filler types, contents, and reference codes

Filler type	Filler content, wt %	Sample reference code ^a	Number of prepreg layers
Technical carbon, A-35	0.5	I-S-CDF _{0.5}	–
Technical carbon, A-35	2.5	I-S-CDF _{2.5}	–
Technical carbon, A-35	5.0	I-S-CDF ₅	–
Woven glass, style 120 E-glass	17	I-S-WG ₁₇	10
Carbon fabric, UVIS-T-22R	25	I-S-CF ₂₅	6

^a I-S corresponds to the PEI binding agent; CDF refers to the technical carbon additive, WG refers to the woven glass filler, and CF refers to the carbon fabric filler. The subscript indices indicate the filling degree of the binding agent.

The titrimetric analysis revealed that the content of isocyanate groups in the initial TDI–oligoepoxide system is ~22.4 wt % and that in the resulting isocyanate urethane is ~14.7 wt %. In the initial TDI–PTMO system this value composes 7.8 wt %, while in the resulting urethane forpolymer—6.7 wt %. The TDI–oligoepoxide + TDI–PTMO system contains initially ~16.62 wt % and after heating (for ~40 min) ~13.6 wt %. The titrimetric data were used to perform the corresponding calculations. The measurements were conducted on a CG805 laboratory pH-meter using hydrogen and calomel electrodes.

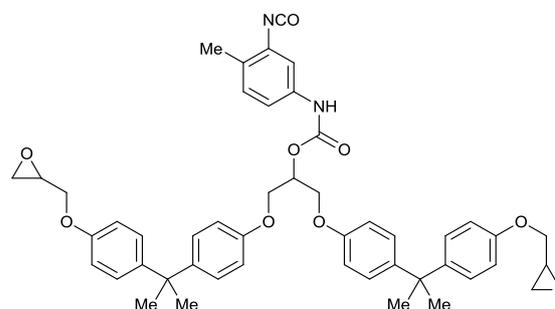
The experiments on compression strength were carried out for all the samples in the temperature range from 20 to 105 °C (with the temperature step of 20 °C). The deformation rate in all the experiments was 0.187 mL/min. The static modulus (E) was determined based on the stress–strain curves at compression. The dependence of E on the growth of the curing temperature, in particular, at different experiment temperatures was analyzed. The measurements were performed on a Dubov–Regel unit with a special program for the registration of experimental data [9, 10].

The microhardness was measured using a Vostok-7 unit (the Shore D hardness) and a TP-1 hardness measuring instrument (the Brinell hardness, H_B). The indentation load was 5 kg (Shore D) and 12 kg (H_B), respectively.

The data of thermomechanical analysis were used to define the experimental glass-transition point T_g . The latter enabled evaluation of chemical compositions of the microphases using the computational schemes. Modeling of the physical properties of the polymers was made using the Cascade computer program. TMA experiments were carried out upon a linear increase of the temperature in the range of 20–400 °C with the heating rate of 1 deg/min. The load was 100 g per a punch with the diameter of 2 mm. The experiment was carried out on a Q400 thermomechanical analyzer.

Results and discussion

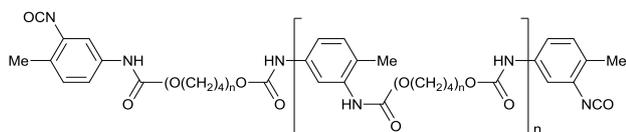
The reaction of an excess of TDI (3.5 mol) with oligoepoxide [11–13] affords isocyanate urethanes of the following chemical structure, which represent the products of addition of TDI to the oligomerized epoxide with hydroxy groups at $n > 1$:



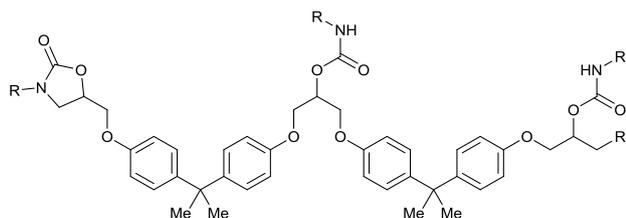
The initial toluene diisocyanate remains in the reaction mixture in the amount of 2.3 mol. These data were obtained from the titrimetric analysis. The refractive index n_D^{30} of the resulting isocyanate urethane is within the limits of 1.5708.

The interaction of an excess of TDI (2.6 mol) with PTMO results in the urethane forpolymer. According to the titrimetric

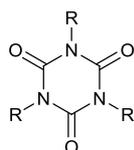
analysis, the content of TDI in the product composes 2.2 mol. The refractive index of the resulting forpolymer is 1.5063. It has the following structure:



Further interaction of the isocyanate urethane with the urethane forpolymer at the temperature above 80 °C can lead to opening of the epoxide cycles under the action of isocyanates [14–19], resulting in the copolymers of the following structure:



The subsequent temperature rise and addition of DMBA lead to the cyclotrimerization of residual NCO groups, which affords the following copolymers:



The chemical structures of substituents R are presented in Table 2.

The effect of the fillers in all experiments can be demonstrated during the analysis of the stress–strain curves at compression. As can be seen from Fig. 1, stress–strain curves

Table 2. Chemical structures of the substituents R

Structures

at compression 2 and 3, strongly differ from curve 1 for sample I-S: slope angles of the linear regions increase until the yield point σ_y . The fast growth of the strength and elastic modulus is observed upon filling with the woven glass and carbon materials; the value of E for samples I-S-WG₁₇ and I-S-CF₂₅ is above 2000 MPa, whereas the value of E for sample I-S composes 1000 MPa. Hence, an increase in σ_y and E upon filling with the woven materials exceeds 40% and 30%, respectively (*vide infra*). This can be explained by the fact that the sample rigidity increases owing to the introduction of the stronger and more rigid continuous fillers into the polymer basis.

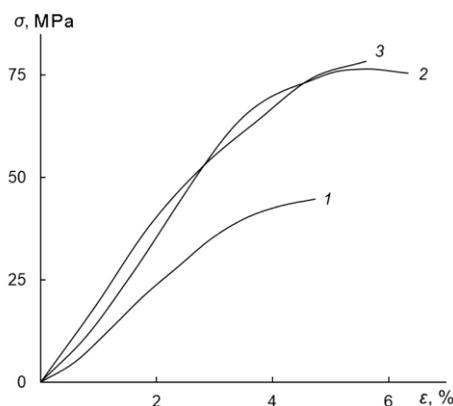


Figure 1. Initial regions of the stress–strain curves at compression obtained at the deformation rate of 0.187 mm/min and $T = 20$ °C: I-S (1), I-S-WG₁₇ (2), I-S-CF₂₅ (3).

Let us consider another example of the effect of dispersed additives on the mentioned properties. Figure 2 shows the stress–strain curves at compression of samples I-S, I-S-CDF_{0.5}, I-S-CDF_{2.5}, and I-S-CDF₅ and the stress–strain curves at compression of sample I-S for comparison. In this case, it is obvious that the character of curves 2–4 is almost the same as that of sample I-S (the elastic moduli are almost the same).

Let us consider the dependence of σ_y on the temperature. The experiments were carried out in the range of 20–105 °C. At the experiment temperatures not exceeding 50 °C, the values of σ_y for samples I-S-WG₁₇ and I-S-CF₂₅ remain almost ($\pm 3\%$)

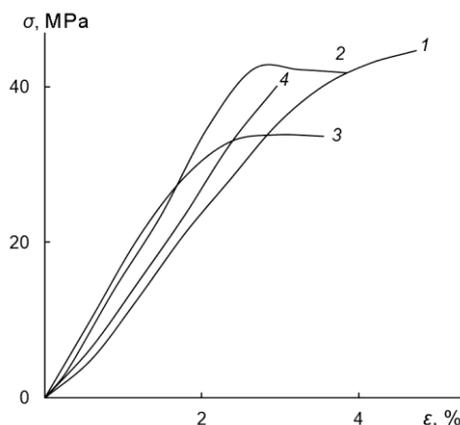


Figure 2. Initial regions of the stress–strain curves at compression obtained at the deformation rate of 0.187 mm/min and $T = 20$ °C: I-S (1), I-S-CDF_{0.5} (2), I-S-CDF_{2.5} (3), I-S-CDF₅ (4). Curve 1 is shown for comparison.

unchanged (Fig. 3); then, during a temperature rise to 105 °C, σ_y reduces from the value at the initial experiment temperature of 20 °C (curves 2 and 3, Fig. 3) by 47% and 33%, respectively. The yield point of sample I-S changes insignificantly until 50 °C (within 15%) and, then, declines drastically as the experiment temperature increases; the growth reaches 82% from the value of σ_y at the initial temperature (curve 1).

The experimental dependences of σ_y (Fig. 4) for the disperse-filled composites show that, at the content of the dry additive from 0.5 to 5 wt %, the value σ_y almost does not change and range from 3 to 10% depending on the experiment temperature. As can be seen from Fig. 4, the yield point essentially reduces, more than by 75%, with an increase in the experiment temperature to 105 °C.

It was established that the value of E for sample I-S reduces to 230 MPa at 105 °C from the initial magnitude of 1400 MPa at 20 °C (Fig. 5, curve 1). This composes 83% reduction. In turn, for the composite samples with the woven glass and carbon materials, the values of E reach 675 and 1057 MPa at 105 °C, while the initial magnitudes are 2000 and 2100 MPa at 20 °C, respectively (curves 2 and 3). Herein, the reductions of E compose 66 and 50%. It should also be noted that the characters of curves 2 and 3, depicted in Fig. 4, feature almost a linear reduction of E during stepwise heating to 105 °C.

It is obvious that in the case of filling with technical carbon, such a dispersed filler can form a separate microphase and affect, thereby, the mechanism of curing and, consequently, the

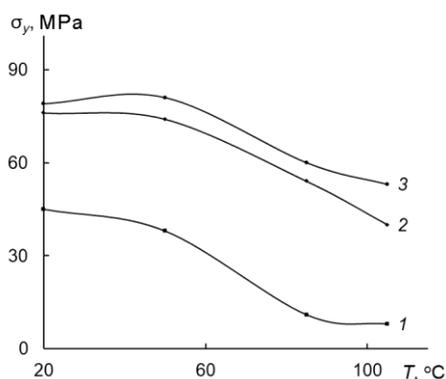


Figure 3. Dependence of the yield point on the temperature for the samples I-S (1), I-S-WG₁₇ (2), and I-S-CF₂₅ (3).

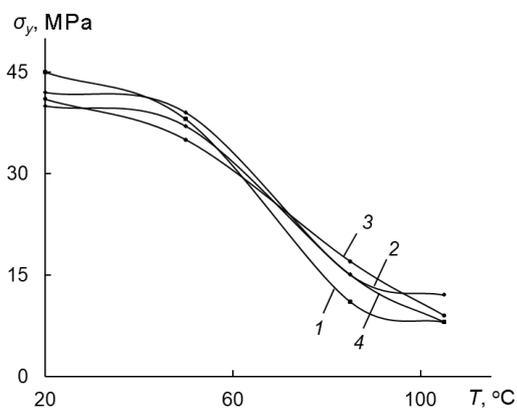


Figure 4. Dependence of the yield point on the temperature for the samples: I-S (1), I-S-CDF_{0.5} (2), I-S-CDF_{2.5} (3), I-S-CDF₅ (4). Curve 1 is shown for comparison.

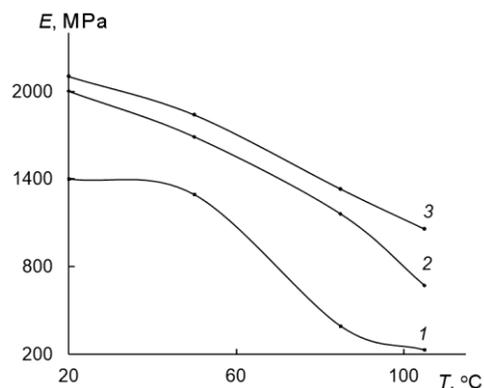
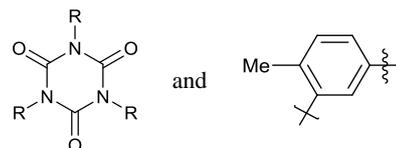


Figure 5. Dependence of the elastic modulus on the temperature during compression: I-S (1), I-S-WG₁₇ (2), I-S-CF₂₅ (3). Curve 1 is shown for comparison.

final properties of polymers. To confirm this, the compatibility of technical carbon with the polymer-forming systems was computed. The calculations were carried out using the Cascade program (INEOS RAS). The compatibility criterion consists of two parts: the left part A and the right part B . The detailed description of the compatibility criterion is presented in the previously published monographs [2–3, 20, 21]. If $A < B$, the polymers are compatible; if $A > B$, the polymers are incompatible.

For the following polymer-forming system



the molar volume V_m is 305 cm³/mol, the solubility parameter δ is 21.7 (J/cm³)^{0.5}, and the surface energy γ is 41.5 mN/m. For technical carbon, the molar volume V_m is 44.6 cm³/mol, the solubility parameter δ is 23.5 (J/cm³)^{0.5}, and the surface energy γ is 71.2 mN/m.

The introduction of the polymer-forming system under consideration into technical carbon leads to incompatibility. The parameters are as follows: $A = 1.17$, $B = 0.31$. The introduction of technical carbon into the polymer-forming system also affords incompatibility: $A = 0.85$, $B = 0.26$. The incompatibility of technical carbon with the polymer-forming system leads to interfacial layering.

The mechanical properties of composites depend not only on the chemical composition of a matrix but also on the character of additives, which modify the final structure. The experimental dependences of E for samples I-S-CDF_{0.5}, I-S-CDF_{2.5}, and I-S-CDF₅ show a considerable reduction in its values (Fig. 6), more than by 84%, with a temperature rise to 105 °C (curves 2–4).

The effect of the fillers on the hardness of the resulting composites can be observed from the Brinell and Shore (Shore D) hardness diagrams. The change of H_B upon filling with the woven glass and carbon materials exceeds 15% (Fig. 7), and that of the Shore (D) hardness—more than by 27%. The low hardness values in the case of the disperse-filled composites (Fig. 7) can be associated with the fact that the disperse carbon particles aggregate into a microphase, which violates the uniformity of the composite structure.

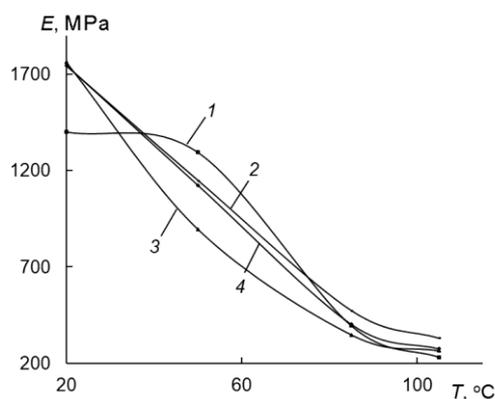


Figure 6. Dependence of the compression elastic modulus on the temperature: I-S (1), I-S-CDF_{0.5} (2), I-S-CDF_{2.5} (3), I-S-CDF₅ (4). Curve 1 is shown for comparison.

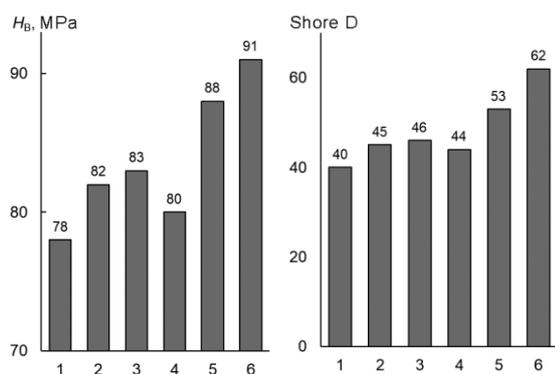


Figure 7. Brinell and Shore (D) hardness diagrams for the composite samples: I-S (1), I-S-CDF_{0.5} (2), I-S-CDF_{2.5} (3), I-S-CDF₅ (4), I-S-WG₁₇ (5), I-S-CF₂₅ (6).

The results of thermomechanical analysis and the calculated data allowed us to define the glass-transition points (T_g) of the resulting binding agents based on I-S.

A principle of the description of T_g of the resulting polymers is described in Refs. [2, 3, 20, 21]. It consists in different effects of the linear fragments, which connect the cross-linked points and the cross-linked points themselves on T_g . The value of T_g can be calculated using equation (1):

$$T_g = \frac{\sum_i \Delta V_i}{(\sum_i a_i \Delta V_i + \sum_j b_j)_l + (\sum_i K_i \Delta V_i)_{cr.p}} \quad (1)$$

where $\sum_i \Delta V_i$ is the van der Waals volume of the repeating unit of a polymer network; $(\sum_i a_i \Delta V_i + \sum_j b_j)_l$ is a set of atomic constant for the repeating unit of the chains between cross-linked points; $(\sum_i K_i \Delta V_i)_{cr.p}$ is a set of atomic constants for the network cross-linked points (for the physical meaning of parameters a_i , b_j , and K_i , see Refs. [2, 3, 20, 21]).

The onset point of the intensive thermal degradation can be defined from the following relation:

$$T_d = \frac{\sum_i \Delta V_i}{\sum_i K_i \Delta V_i} \quad (2)$$

where K_i are the atomic constants connected with the parameters of the Morse potential, $K_i = \frac{63}{2} \frac{R}{(ad_0 E)_i}$; a and d_0 are the parameters of the Morse potential, and E is the energy of a

chemical bond.

For copolymers, the following relation is valid:

$$T_g = \frac{\sum_{k=1}^{k=n} a_k (\sum_i \Delta V_i)_k}{\sum_{k=1}^{k=n} a_k \frac{(\sum_i \Delta V_i)_k}{T_{g,k}} + 0.03 \sum_{k=1}^{k=n} a_k (1 - a_k)} \quad (3)$$

where a_k is the molar fraction of component k , n is the number of components, $T_{g,k}$ is the glass-transition point of component k , and $\sum_i \Delta V_i$ is the van der Waals volume of component k .

The chemical structures of the copolymers and the calculated weight fractions of each repeating unit are presented in Table 3.

Table 3. Calculated weight fractions of I-S binding agent sample

Chemical structures	Weight fractions of each structure corresponding to the temperature relaxation transition, %	
	1	2
I	23.0	0.0
II	16.0	0.0
III	32.0	60.0
IV	29.0	40.0

The weight fractions of the sample of I-S binding agent are defined so that the calculated value of T_g coincides with the experimental one for each microphase, which consists of structures I–IV depicted below:

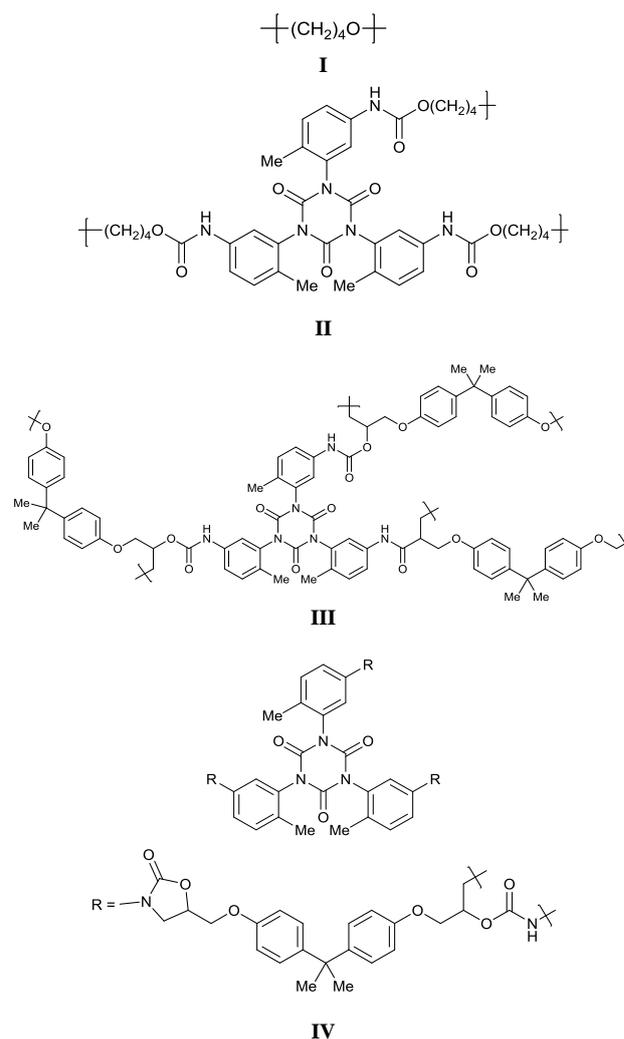


Table 4 lists the experimental values of T_g and those calculated by formulae (1)–(3) and some other properties of the resulting binding agent.

Table 4. Experimental and calculated values of the glass-transition points T_g and other properties of the sample of I-S binding agent

M , g/mol	$\sum_i \Delta V_i$, nm ³	ρ , kg/m ³	T_g^a , K ^a	T_g^b , K ^b	T_d , K	n	C_σ , B	δ , (J/cm ³) ^{1/2}	γ , mN/m
263	0.251	1170	348	350	653	1.48	165	20.8	35.9
1490	1.38	1230	478	475	656	1.58	154	21.4	32.5

^a T_g is defined computationally;

^b T_g is defined experimentally;

$\sum_i \Delta V_i$ is the van der Waals volume of the repeating unit of the copolymer, T_d is the onset point of intensive thermal degradation, n is the refractive index, C_σ is the stress-optical coefficient, δ is the solubility parameter, γ is the surface energy, M is the molar mass of the repeating unit, and T_g is the glass transition point.

The results of TMA show that the first relaxation temperature transition for the sample of I-S binding agent is observed at 353 K (Fig. 8). According to the calculations, a microphase responsible for this transition is formed based on structures I–IV. The following transition observed at ca. 473 K is manifested for the microphase formed by structures III and IV. The analogous TM curves were obtained for all other samples. The additives and fillers do not affect significantly the relaxation transitions under consideration.

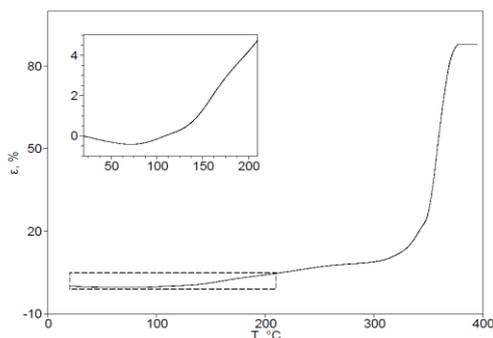


Figure 8. Dependence of the strain on the temperature for the sample of I-S binding agent. The measurements were carried out during a linear increase of the temperature with the rate of 1 deg/min.

Conclusions

The performed experiments and calculations allowed us to gain insight into the effect of the fillers on mechanical and thermal properties of the network epoxy urethane isocyanurate polymers (PEI binding agents). The experimental results showed that the elastic modulus of the PEI sample is 1420 MPa and reaches the values of 2000 and 2100 MPa for the composite samples filled with the woven glass and carbon materials by 17% and 25%, respectively. The elastic moduli of these samples relax over 180 min to 650 MPa and 1100 MPa; consequently, the relaxation processes can be very sensitive to the presence of these types of fillers. A part of the relaxation moduli reduces from 82% for the PEI sample to 67% and 48% for the composite samples. Upon filling of the binding agent with dispersed carbon, at room temperature the elastic modulus increases from 1420 MPa to 1750 MPa; however, at 105 °C the elastic moduli acquires almost the same values. This can be caused by the fact

that the filling degree is not high and reaches maximum 5%.

The effect of variation of the Brinell hardness upon filling with the woven glass and carbon materials exceeds 15%, and that of the Shore (D) hardness is more than 27%. The low hardness values in the case of the disperse-filled composite samples can be associated with the fact that the disperse carbon particles aggregate into a microphase, which violates the composite structure uniformity.

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References

1. A. A. Askadskii, U. I. Matveev, *Chemical Structure and Physical Properties of Polymers*, Khimya, Moscow, **1983** [in Russian].
2. A. A. Askadskii, V. I. Kondrashchenko, *Computational Materials Science of Polymers*, Nauchnyi Mir, Moscow, **1999** [in Russian].
3. A. A. Askadskii, *Computational Materials Science of Polymers*, Cambridge Int. Sci. Publ., Cambridge, **2003**.
4. A. A. Askadskii, L. M. Goleneva, E. S. Afanas'ev, M. D. Petunova, *Rev. J. Chem.*, **2012**, 2, 105–152. DOI: 10.1134/S207997801202001X
5. A. A. Askadskii, L. M. Goleneva, K. V. Konstantinov, K. A. Bychko, *Russ. Polym. News*, **2001**, 6 (2), 6–11.
6. K. B. Galitseyskii, M. D. Petunova, E. S. Afanasiev, M. V. Staroghitskii, O. V. Kovriga, A. A. Askadskii, *Plast. Massy*, **2017**, 7–8, 18–23. DOI: 10.35164/0554-2901-2017-7-8-18-23
7. A. A. Askadskii, L. M. Goleneva, E. S. Afanas'ev, M. D. Petunova, *Rev. J. Chem.*, **2012**, 2, 263–314. DOI: 10.1134/S2079978012030028
8. A. A. Askadskii, K. V. Konstantinov, L. M. Goleneva, K. A. Bychko, *Vysokomol. Soedin., Ser. A*, **2002**, 44, 335–342.
9. V. R. Regel, G. V. Berezhkova, G. A. Dubov, *Zavod. Lab.*, **1959**, 25, 101.
10. V. R. Regel, *J. Tech. Pap.*, **1955**, 25, 2542.
11. M. D. Petunova, A. A. Askadskii, L. M. Goleneva, G. G. Nikiforova, L. A. Vasserman, O. V. Kovriga, V. A. Markov, *Polym. Sci., Ser. A*, **2011**, 53, 984. DOI: 10.1134/S0965545X11100105
12. M. D. Petunova, *Cand. Dissertation*, Moscow, IPS RAS, **2011**.
13. M. D. Petunova, A. A. Askadskii, M. G. Ezernitskaya, T. A. Babushkina, T. P. Klimova, O. V. Kovriga, *Polym. Sci., Ser. B*, **2012**, 54, 361–374. DOI: 10.1134/S1560090412070044
14. I. A. Bulgakova, *Cand. Dissertation*, Moscow, IPS RAS, **1983**.
15. F. V. Morev, N. R. Prokopchuk, E. T. Krut'kov, *Trudy BGTU*, **2012**, 4, 88–91.
16. RU Patent 2111994 C1, **1998**.
17. M. V. Sycheva, R. M. Garipov, R. Ya. Deberdeev, *Vestn. Kazan Tekhnol. Univ.*, **2010**, 9, 364–368.
18. M. A. Sytina, F. M. Gurdzhi, USSR Inventor's Certificate no. 150622, *Byull. Izobret.*, **1967**, no. 9.
19. T. I. Kadurina, V. A. Prokopenko, C. I. Omel'chenko, *Lakokras. Mater. Ikh Primen.*, **1985**, 4, 5–7.
20. A. A. Askadskii, *Physical Properties of Polymers, Prediction and Control*, Gordon and Breach Publ., Amsterdam, **1996**.
21. A. A. Askadskii, A. R. Khokhlov, *Introduction to Physical Chemistry of Polymers*, Nauchnyi Mir, Moscow, **2009** [in Russian].