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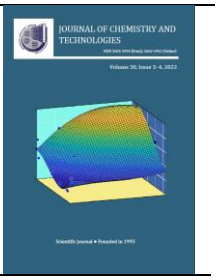

UDC 678.686

INFLUENCE OF POLYOXYPROPYLENETRIAMIN AND CONTENT OF OXIRANE RINGS ON PROPERTIES OF EPOXY-POLYSULFIDE COMPOSITES

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Abstract

The possibilities of controlling the deformation-strength, adhesive and dynamic mechanical properties of epoxy-polysulfide composites based on the products of the preliminary thioetherification reaction (PRTE) with the help of small additions of polyoxypropylenetriamine and changing the concentration of oxirane cycles in the epoxy resin are determined. It has been established that the introduction of polyoxypropylenetriamine into compositions based on the products of the preliminary reaction of thioetherification of epoxy resin with liquid polysulfide rubber (thiokol) leads to an increase in adhesive and cohesive strength, strain at break, and the work of destruction of the material. The effect is achieved both by adding polyoxypropylenetriamine to a mixture of epoxy resin with liquid thiol during PRTE, and by using it as a co-hardener when curing PRTE with diethylenetriamine. It has been shown that the presence of polyoxypropylenetriamine in the PRTE product has a significant effect on the dynamic mechanical characteristics of the cured composition. The introduction of polyoxypropylenetriamine contributes to a noticeable increase in the dynamic modulus of elasticity in the region of the glassy state of the composite and the molecular weight of the chain section between the nodes of the chemical network, as well as the maximum value of the mechanical loss tangent and loss modulus. An extreme dependence of the adhesive shear strength of adhesive joints made using PRTE products on the content of epoxy groups in the resin has been revealed. The effect of strengthening adhesive joints due to modification with polysulfide rubber is most pronounced for epoxy resins, in which the content of oxirane cycles ranges from 8 to 15 %.

Key words: epoxy resins; polysulfide rubber; a preliminary thioetherification reaction; polyoxypropylenetriamine; deformation-strength, adhesive and dynamic mechanical properties; epoxy group content.

ВПЛИВ ПОЛІОКСИПРОПІЛЕНТРІАМІНУ ТА ВМІСТУ ОКСИРАНОВИХ ЦИКЛІВ НА ВЛАСТИВОСТІ ЕПОКСИДНО-ПОЛІСУЛЬФІДНИХ КОМПОЗИТІВ

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Анотація

Визначено можливості регулювання деформаційно-міцнісних, адгезійних та динамічних механічних властивостей епоксидно-полісульфідних композитів на основі продуктів попередньої реакції тіоетерифікації (ПРТЕ) за допомогою малих добавок поліоксипропілентріаміну та зміною вмісту оксиранових циклів в епоксидній смолі. Встановлено, що введення поліоксипропілентріаміну в композиції на основі продуктів попередньої реакції тіоетерифікації епоксидної смоли з рідким полісульфідним каучуком (тіоколом) приводить до збільшення адгезійної і когезійної міцності, деформації при розриві і роботи руйнування матеріалу. Ефект досягається як додаванням поліоксипропілентріаміну в суміш епоксидної смоли з рідким тіоколом в процесі проведення ПРТЕ, так і за його використання в якості співотверджувача. Показано, що присутність поліоксипропілентріаміну в продукті ПРТЕ значно впливає на динамічні механічні характеристики отвердженої композиції. Введення поліоксипропілентриаміну сприяє помітному збільшенню динамічного модуля пружності в області склоподібного стану композиту і молекулярної маси ділянки ланцюга між вузлами хімічної сітки, а також максимального значення тангенса кута механічних втрат і модуля втрат. Виявлено екстремальну залежність адгезійної міцності при зсуві клейових з'єднань, виконаних з використанням продуктів ПРТЕ, від вмісту епоксидних груп в смолі. Ефект зміцнення клейових з'єднань за рахунок модифікації полісульфідним каучуком найбільшою мірою проявляється для епоксидних смол, у яких вміст оксиранових циклів становить від 8 до 15 %.

Ключові слова: епоксидні смоли; полісульфідний каучук; попередня реакція тіоетерифікації; поліоксипропілентриамін; деформаційно-міцнісні, адгезійні та динамічні механічні властивості; вміст епоксидних груп.

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Introduction

In practice, epoxy polymers (EP) are always modified to improve processing properties and reduce cost [1–6]. However, the main goal of EP modification is to strengthen them [7–9], which, first of all, involves an increase in the degree of resistance of the material to external forces and destructive factors.

Modification for the purpose of strengthening should be based on the regularities of the relationship of properties with the structure of the polymer. Modification of the properties of any material is essentially a modification of its structure. The concept of "structure" acquires a specific meaning only with an indication of the scale level of organization of its elements.

In densely networked polymers, including epoxy ones, such levels are molecular, topological, and supramolecular [10–13].

All three levels are linked in genetic sequence, although the relationship between them is not unambiguous. The molecular level reflects the chemical structure of a repeating unit (network fragment, node) consisting of oligomer molecules directly linked to each other (in the case of catalytic homopolymerization of epoxides) or through curing agent molecules during polycondensation (polyaddition), leading to the formation of a networked heteropolymer. The primary level is decisive in all properties of the polymer body.

Intermolecular interaction (van der Waals, hydrogen, donor-acceptor bonds), which affects the main technical properties of glassy epoxy polymers, depends on the chemical structure.

The main way to vary the chemical structure of the epoxy polymer is to change that of the original oligomer and its hardener. This is the basis of chemical modification, the practical possibilities of which are very great, since dozens of types of epoxy resins and (even more) hardeners produced on an industrial scale allow one to create a huge number of their combinations. The next level, topological, is superimposed on the molecular level [14]. Here, the organization of macromolecules, the nature of the bonding of chain sections without regard to their specific chemical nature, is of decisive importance. "Linear", "branched", "reticulated" polymer - these concepts distinguish different types of topological structure.

A characteristic manifestation of the topology of network polymers, regardless of their chemical structure, is their insolubility and inability to irreversibly deform the flow. The main parameters of the network structure are the functionality of the nodes, their concentration (n_c), and the length of the internodal segment (M_s) [15].

At the same time, a network polymer is not one giant macromolecule equal to the volume of a cured product (block). In fact, this is a system of densely cross-linked and close-packed aggregates (~1012 in molecular weight), connected, as a rule, by “through” chains that are rarer in concentration [10, 12]. In addition to the latter, the polymer contains small linear and branched molecules that are not linked to the network and can be extracted (sol fraction). If the molecular structure of the network polymer is determined by the chemical structure of the epoxy oligomer and hardener, then the topological level depends on the stoichiometric reaction conditions, as well as temperature-time and other curing parameters [16–21].

Previously, it has been shown [22] that in order to improve the adhesion and physico-mechanical properties of compositions based on epoxy resin and polysulfide rubber cured without heat treatment, it is necessary to carry out a preliminary thioetherification reaction (PRTE) due to the interaction of mercaptan groups of rubber and oxirane cycles of epoxy resin at elevated temperature, and then use the product of this reaction to cure at room temperature. The composite materials based on thioetherification reaction products are shown to be significantly superior to analogs based on mechanical mixtures of epoxy resin and thiokol in terms of cohesive and adhesive strength, deformation capacity, fracture work, and specific impact strength.

A systematic study of the possibility of controlling the deformation-strength, adhesive and dynamic mechanical properties of epoxy-polysulfide composites based on the products of the preliminary thioetherification reaction (PRTE) by varying the concentration of polysulfide rubber, as well as changing the amount of hardener and using a mineral filler was also carried out [23]. It has been established that an increase in the content of rubber in the product of the preliminary reaction of thioetherification results in an increasing the indicators of cohesive and adhesive strength, strain at break, and the work of destruction of the material. It is assumed that the increase in the complex of properties is associated with the formation of higher molecular weight products as the rubber content in the composition subjected to PTE increases. The formation of such products is confirmed by the data of dynamic mechanical spectrometry. It has been shown that it is possible to effectively control the deformation-strength characteristics of epoxy-polysulfide mixtures by changing the amount of hardener introduced, i.e. by changing the ratio of amine and epoxy groups. When the content of the DETA hardener increased, the tensile strength, strain at break, and the work of destruction of the material increase very significantly. It has been established that the introduction of a filler into an epoxy system containing a large amount of rubber leads to an increase in cohesive strength with a relatively small decrease in adhesive strength and strain at break.

The introduction of both diluents and plasticizers into the products of the preliminary reaction of thioetherification of epoxy resins and polysulfide rubbers was found [24] to lead to an increase in the parameters of tensile strength and deformation ability. The greatest hardening effect is achieved with the use of polyester MHF-9 and glycidyl ether of diethylene glycol DEG-1, the smallest effect being observed with the introduction of the plasticizer EDOS. It has been established that the introduction of plasticizers contributes to a certain increase in adhesive strength, but much less compared to cohesive strength. In this case, the adhesive and cohesive characteristics change antibatically. The method of dynamic mechanical spectrometry has shown that the presence of diluents and plasticizers in epoxy-polysulfide composite materials leads to a decrease in the temperatures of the maximum values of the mechanical loss tangent, the loss modulus, the initial and final sections of the transition of the material from the glassy to the highly elastic state, as well as the density of the chemical network in the epoxy matrix.

In continuation of the previous research, the aim of this work is to study the possibility of controlling the deformation-strength, adhesion, and dynamic mechanical properties of epoxy-polysulfide composites based on the products of the preliminary thioetherification reaction with the help of small additions of polyoxypropylenetriamine and changing the concentration of oxirane cycles in the epoxy resin.

Models and methods

The objects of study were epoxy-diane resins of the Epikote brand produced by the Hexion company [25], the properties of which are given in Table 1, and polysulfide rubber (liquid thiokol brand I with a viscosity of 28 Pa·s at 25 °C, the content of sulfhydryl groups of 3.1 %). The combination of epoxy resin and thiokol was carried out at 160 °C for 2 h with thorough mixing with the addition of T-403 grade polyoxypropylenetriamine (manufactured by Huntsman Chemicals) in an amount not exceeding 0.1 of the stoichiometric amount. The compositions were cured with diethylenetriamine DETA according to two modes: I – 25 °C/24 h +50 °C/8 h (curing at a moderate temperature) and II –25 °C/24 h + 120 °C/3 h (curing with heat treatment at elevated temperature). In some cases, polyoxypropylenetriamine was used as a co-hardener.

Table 1

Properties of epoxy resins

Parameter	Resin grade				
	Epikote-828	Epikote-834	Alloy of Epikote-834 and Epikote-1001 in the ratio of 2 : 1	Epikote-1001	Epikote-1004
Epoxide equivalent, g/equ	189	248	298	494	907
Mass content of epoxide groups, %	22.8	17.3	14.4	8.7	4.7
Molecular mass	380	495	550	640	1830
Dynamical viscosity, Pa·s at 25°C	12.7	-	-	-	-
Dynamical viscosity in 40 wt. % solution of methylethylketone, mPa·s, at 25 °C	-	2.2	3.6	5.9	14.7

The mechanical properties under uniaxial tension (tensile strength σ_t and deformation at rupture ε_s) were measured by an automatic tensile testing machine C610H from Labthink instruments Co. Ltd. The elastic modulus (E) was determined by the slope of the initial portion of the σ - ε curve. The area under the stress-strain curve was considered as a measure of the fracture work (A_f).

The techniques of determination of adhesion strength in shear (τ_{sh}) and tear off (σ_{to}) was corresponded to the State Standards 14759 and 14760, respectively. The surfaces for gluing steel samples (Steel 3) were prepared by a grinding plate using electrocorundum to achieve an uniform roughness, then they being degreased with acetone.

Dynamic mechanical characteristics (dynamic modulus of elasticity E', loss modulus E'', and tangent of the angle of mechanical losses tg δ) were determined by DMA 983 unit of the DuPont 9900 thermoanalytical complex on 25x4x2 mm samples when heated at a rate of 10°C/min. The rubber elasticity modulus ($E_{r.e.}$) was measured at a temperature which surpasses the glass transition temperature of the polymer T_g by 50°C.

The molecular weight of the chain section between the nodes of the chemical network (M_c) was determined as follows:

$$M_c = 3\rho RT / E_{r.e.},$$

where R is the absolute gas constant; T refers to an absolute temperature; ρ is considered as the density of the polymer.

Density of nodes of the chemical network (n_c) was calculated by the following formula:

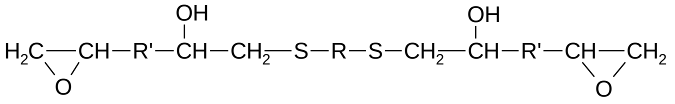
$$n_c = \frac{\rho}{M_c}$$

The density of the samples was determined according to the gradient column method by State Standard 15139.

Results of research and their analysis

The results of studies that were obtained using polyoxypropylenetriamine T-403 as part of epoxy-polysulfide compositions are given in Fig. 1. It can be seen that the effect of increasing the deformation-strength properties, as well as the adhesion strength, manifests itself both in the case when the T-403 hardener is present in the epoxy-polysulfide composition during the PRTE, and when it is used as a co-curing agent with DETA for curing the PRTE product. At the same time, the deformation-strength characteristics are somewhat higher when the T-403 hardener is used as a co-hardener, and the adhesive strength, on the contrary, is greater when the T-403 hardener is used to obtain the PRTE product.

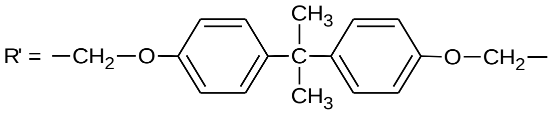
The reaction scheme in the first case can be represented as follows. Initially, as a result of the PRTE reaction, product (1) is formed:



$$H_2C(O)CH{-}R'{-}CH(OH){-}CH_2{-}S{-}R{-}S{-}CH_2{-}CH(OH){-}R'{-}CH(O)CH_2$$

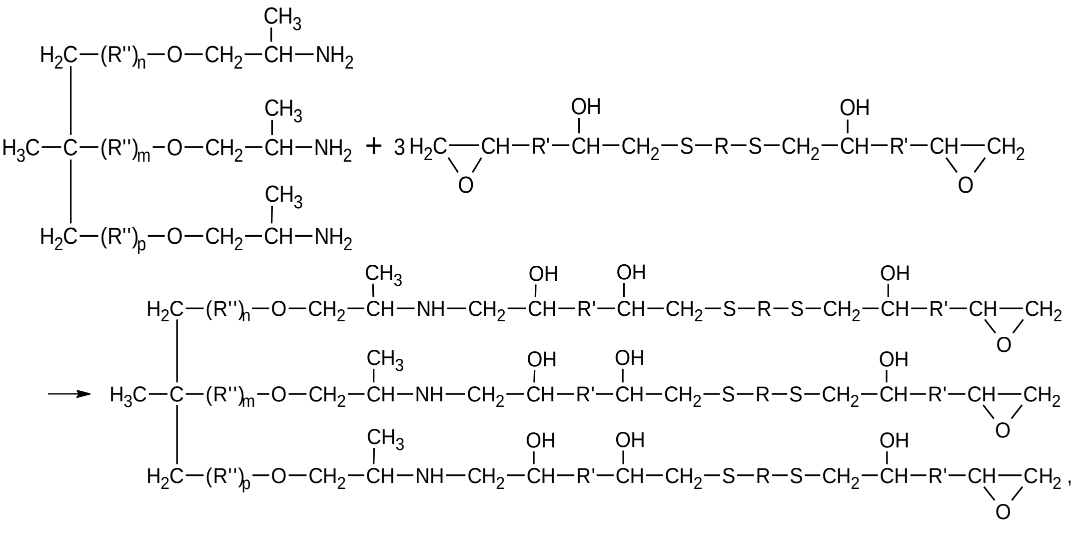
where

$$R = \left(C_2H_4{-}O{-}CH_2{-}O{-}C_2H_4{-}S{-}S\right)_n C_2H_4{-}O{-}CH_2{-}O{-}C_2H_4\ ,$$

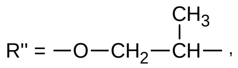


Further, part of the epoxy groups of this product reacts with the primary amine groups of the T-403 hardener. In this case, the following structures among others, are possible to form:

form:

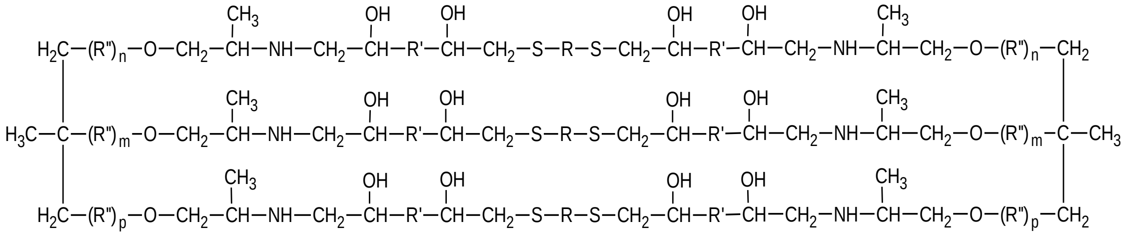


where (2)

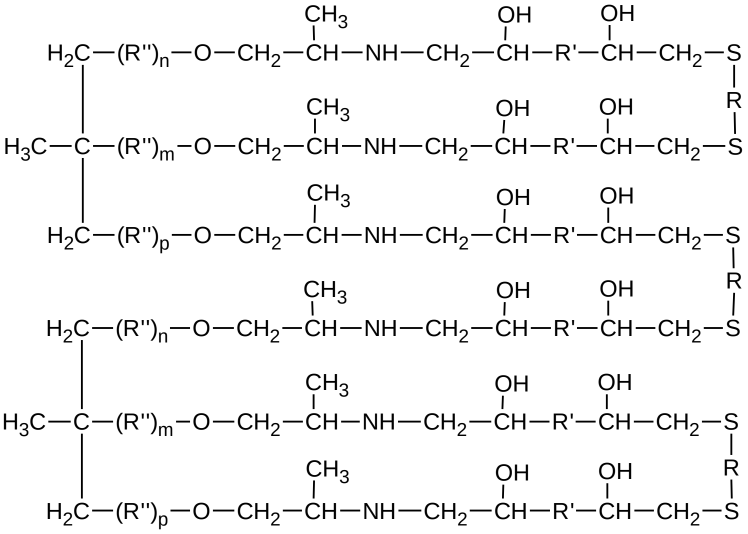


$$R'' = -O-CH_2-\overset{CH_3}{\overset{|}{C}H}-,$$

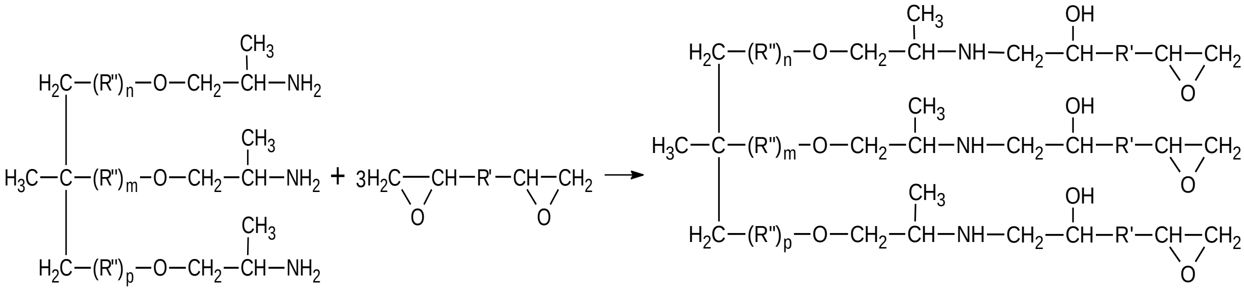
and also (3):



and (4):



In the case when the T-403 hardener is directly involved in the PRTE, the sequence of reactions is obviously different, but, in the end, compounds are formed that are similar in structure (2)–(4). At the first stage, the reaction of the interaction of the primary amines of polyoxypropylenetriamine with the epoxy groups of the resin occurs:



(5)

Next, the epoxy groups of compound (5) enter into a thioetherification reaction with the mercaptan groups of thiokol.

As follows from the data in Fig. 1, there is an optimal content of polyoxypropylenetriamine in the composition, equal to ~ 4 pts. wt. per 100 pts. wt. epoxy resin, regardless of the method of its introduction: directly into the mixture of resin and thiokol during the PRTE (at 160°C) or as a co-curing agent during the curing of the PRTE product at ambient temperature. When this optimum amount of polyoxypropylenetriamine is exceeded, the parameters of cohesive and adhesive strength are markedly reduced. It should be noted that the deformation-strength characteristics are somewhat higher when the T-403 hardener is used as a co-curing agent in the curing of PRTE, and the adhesive strength, on the contrary, is greater when polyoxypropylenetriamine is used directly in the preparation of the PRTE product.

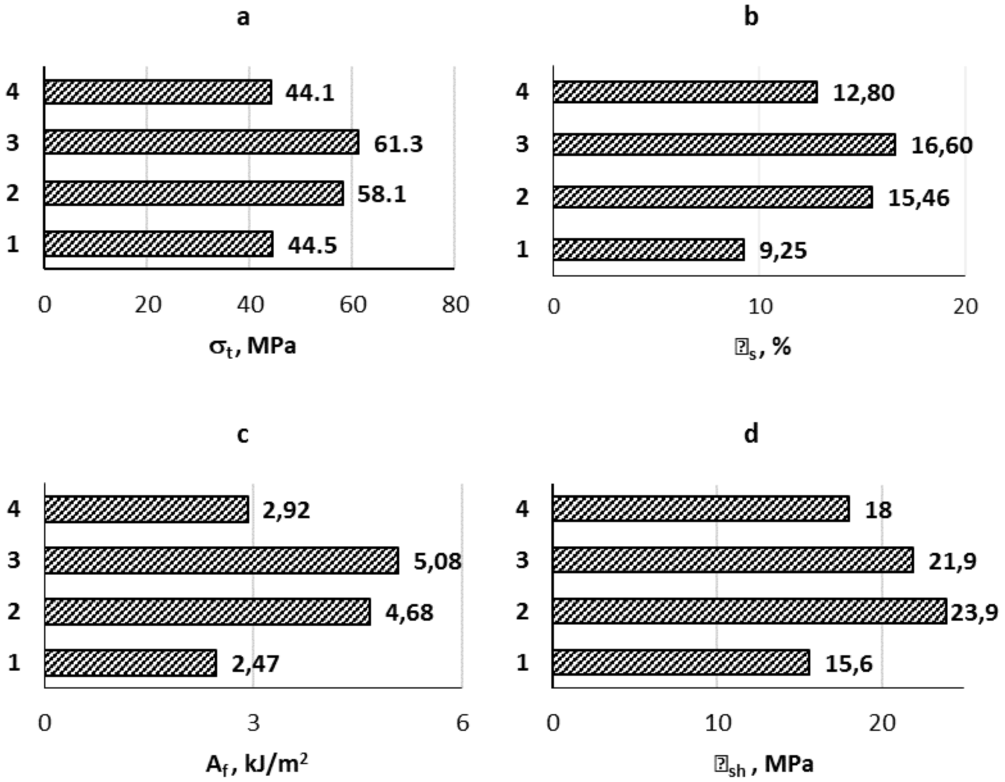


Fig. 1. Dependences of tensile strength σ_t (a), strain at break ε_s (b), work of destruction A_f (c) and adhesive shear strength τ_{sh} (d) on the amount of T-403 hardener: 1 – basic composition based on PRTE product (100 pts. wt. of Epikote-828 and 20 pts. wt. of thiokol), cured 12 pts. wt. DETA; 2 – PRTE product containing 4 pts. wt. T-403 and cured 12 pts. wt. DETA; 3 - PRTE product, cured 12 pts. wt. DETA and 4 pts. wt. T-403; 4 - PRTE product, cured 9.6 pts. wt. DETA and 16.8 pts. wt. T-403

At high concentrations of thiokol in the PRTE product, the strengthening effect with the addition of the T-403 hardener is also clearly exhibited (Fig. 2), but the relative magnitude of the effect is somewhat lower compared to the composition containing a smaller amount of polysulfide rubber. So, with the same addition of polyoxy-propylenetriamine (4 pts. wt. per 100 pts. wt. epoxy resin), the adhesive strength for compositions containing 100 pts. wt. thiocol increases by 22.5 % (from 19.1 to 23.4 MPa), while for a composition containing 20 pts. wt. thiokol (Fig. 1) – by 53.2 % (from 15.6 to 23.9 MPa).

The dynamic mechanical characteristics of the cured composition are rather significantly affected by the presence of polyoxypropylenetriamine T-403 in the PRTE product. It can be seen (Table 2) that the introduction of polyoxypropylenetriamine noticeably increases the dynamic modulus of elasticity measured at 25 °C (in the glassy state) and the molecular weight M_c, as well as the maximum values of the mechanical loss tangent tgδ_m and the loss modulus E''_m. At the same time, with an increase in the content of polyoxypropylenetriamine in the system, the density of cross-linking (frequency of the spatial grid) and the temperatures of the initial T_g^i and final sections T_g^f of the transition from the glassy to the highly elastic state, as well as the temperatures of the maximum value of tgδ and the maximum value of the loss modulus E''_m, decrease. The observed effects can be explained by the fact that in the presence of polyoxypropylenetriamine, longer chain sections are formed between the network nodes. Due to the increased flexibility, they can be packed more tightly, which contributes to an increase in the dynamic modulus of elasticity in the glassy state. On the contrary, during the transition to a highly elastic state, these long sections cause large losses of mechanical energy, which is reflected in an increase in the values of tg δ_m and E''_m. The disadvantage of compositions containing polyoxypropylenetriamine is a decrease in their water resistance as the concentration of the additive increases (Table 2).

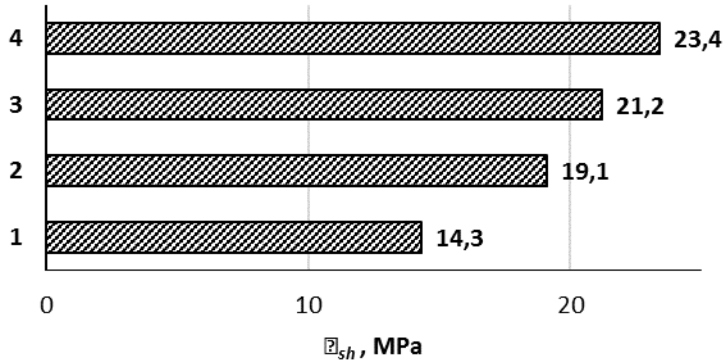


Fig. 2. Dependence of adhesive shear strength τ_{sh} on the conditions of combination of thiokol and epoxy resin on the amount of polyoxypropylenetriamine in the PRTE product. The ratio of resin and thiokol is 100 per 100 pts. wt. 1 - mechanical mixture; 2–4 – PRTE products containing polyoxypropylenetriamine in the amount of: 0 (2); 2 (3) and 4 (4) pts. wt. per 100 pts. wt. EO

Table 2

Properties of epoxy-polysulfide compositions¹ vs. combination conditions and amount of polyoxypropylenetriamine

Property	Mechanical mixture	PRTE products involving T-403, pts. wt.		
		0	2	4
Dynamic elastity modulus, E' at 25°C, GPa	299.3/374.2²⁾	344.1/425.6	474/613	603/645
Molecular weight of chain segment between cross-linking, M_c, kg/kmol	1202/864	1485/1065	1628/1563	2718/2593
Density of nodes of the chemical network, n_c, kmol/m³	0.91/1.27	0.75/1.03	0.68/0.70	0.41/0.42
The temperature of the initial section of the transition from the glassy state to the highly elastic, T_g^i, °C	52.4/57.4	42.7/51.5	34.6/47.1	33.8/37.7
The temperature of the final section of the transition from the glassy state to the highly elastic, T_g^f, °C	82.1/98.9	80.9/88.6	69.8/81.7	63.4/66.8
Maximal value of tangent of the angle of mechanical losses, tg δ_m	0.293/0.261	0.420/0.417	0.460/0.456	0.774/0.702
Temperature of maximal value tg δ_m, °C	81.8/99.1	80.3/89.3	69.2/82.8	66.9/69.1
Maximal value of loss modulus, E''_m, MPa	20.76/21.92	33.47/35.49	45.10/45.45	93.70/83.11
Temperature $T_{E''m}$, °C	80.76/89.52	72.90/75.19	61.03/68.13	42.51/49.92
Water uptake, W, %	1.46	1.30	1.69	2.39

Notes:

¹⁾ Mixture ratio: 100 pts. wt. Epikote-828 + 100 pts. wt. thiokol; ²⁾ before the line - the samples are cured according to mode I; after the line - according to mode II.

The dependence of the adhesive strength vs. the content of epoxy groups (EG) in the original and thiokol-modified resins is given in Fig. 3. It can be seen that for the original (non-rubber-containing) resins, τ_v increases monotonically with an increase in the EG concentration (and, accordingly, a decrease in the molecular weight of the resin) for both curing modes, while for modified resins cured according to mode I, the dependence of τ_v on the EG content has the shape of the curve with a maximum (curve 3), which practically degenerates after the heat treatment of the composition (curve 4).

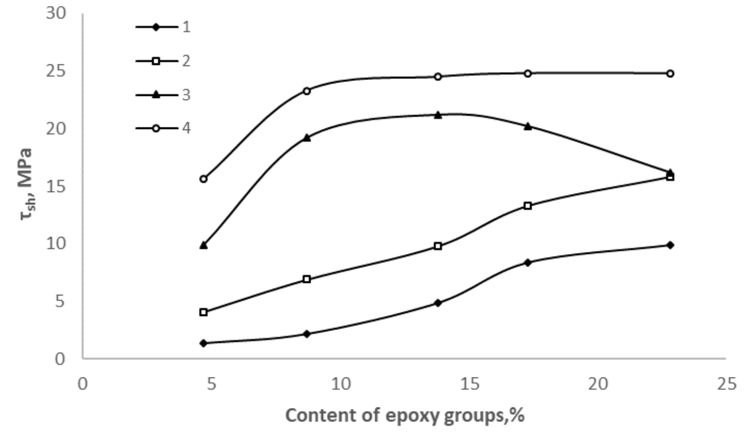


Fig. 3. Dependence of τ_{sh} on the content of epoxy groups for initial resins (1, 2) and PRTE products which include 100 pts. wt. resin and 60 pts. wt. thiokol (3, 4). Composition curing modes: I (1, 3) and II (2, 4)

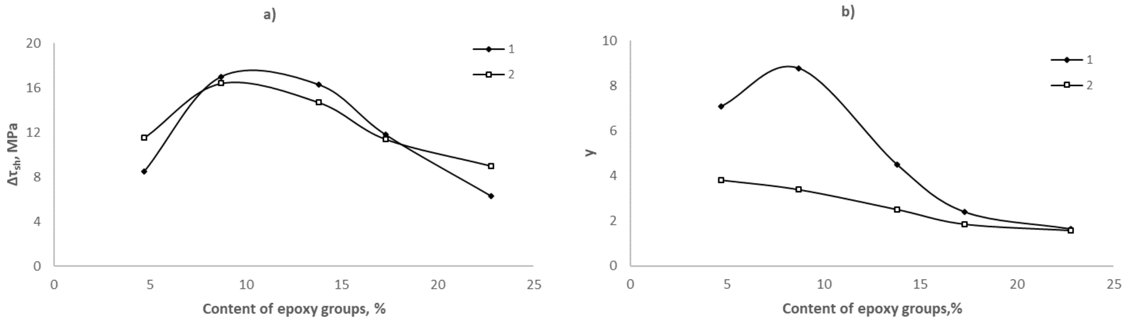


Fig. 4 Absolute $\Delta\tau_{sh}$ (a) and relative γ (b) increase of the adhesive strength vs. content of epoxide groups EG for the compositions cured by modes I (1) and II (2)

As follows from the data in Fig. 3, the effect of shear hardening of adhesive joints due to the modification of resins with thiokol is most pronounced when the content of EG is from ~8 to ~15 pts. wt. The maximum increment $\Delta\tau = \tau_{prte} - \tau_{ref}$ is about 17 MPa (or 8.7 times in value $\gamma = \tau_{prte}/\tau_{ref}$ for samples cured according to mode I, and about 3.5 times for samples cured according to mode II (Fig. 4).

Conclusions

1. As a result of the study, the possibilities of controlling the deformation-strength, adhesive and dynamic mechanical properties of epoxy-thiokol composites based on the products of the preliminary thioetherification reaction with the help of small additions of polyoxy-propylenetriamine and changing the concentration of oxirane cycles in the epoxy resin were determined.
2. It has been established that the introduction of polyoxypropylenetriamine into adhesive compositions based on the products of the preliminary reaction of thioetherification of epoxy resin with liquid polysulfide rubber leads to an increase in adhesive and cohesive strength, strain at break, and the work of destruction of the material. The effect is achieved both by adding polyoxypropylenetriamine to a mixture of epoxy resin with liquid thiol during PRTE, and by using it as a co-hardener when curing PRTE with diethylenetriamine.
3. It has been shown that the presence of polyoxypropylenetriamine in the PRTE product has a significant effect on the dynamic mechanical characteristics of the cured composition. The introduction of polyoxypropylenetriamine contributes to a noticeable increase in the dynamic modulus of elasticity in the region of the glassy state of the composite and the molecular weight of the chain section between the nodes of the chemical network, as well as the maximum value of the mechanical loss tangent and loss modulus.
4. An extreme dependence of the adhesive shear strength of adhesive joints made using PRTE products on the content of epoxy groups in the resin has been revealed. The effect of hardening adhesive joints due to modification with thiokol is most notably for epoxy resins, in which the content of oxirane cycles is ranged from 8 to 15%.

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