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PHYSICOCHEMICAL MODIFICATION OF HEAT-SHRINKABLE EPOXY POLYMERS

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An approach to the physicochemical modification of heat-shrinkable epoxy-diane polymers was considered, these polymers being used as couplings for the repair of polymer pipelines for various functional purposes. The purpose of the modification is to stabilize and improve the performance of the end couplings that are heat-shrinkable. We assessed the prospects of preparation of the products of various profiles by forming cross-linked polymers in a highly elastic state by plunger extrusion via creating favorable conditions for the orientation of interstitial fragments in epoxy-diane polymers. The starting epoxy-diane composition contained rigid and elastic components. The polymers fabricated by hardening of these compositions have both a glass transition temperature, which is convenient for operation, and high deformability in glassy and highly elastic states. We investigated the tensile strength, the elastic modulus, the failure deformation and the flaring deformation of the inner diameter of the preform of epoxy-diane polymers. Physical modification of a liquid filled epoxy-diane composition before mixing with a hardener was performed by using low-frequency ultrasonic treatment. We analyzed the results associated with the effect of combined ultrasonic treatment on the physical-mechanical and service properties of heat-shrinkable epoxy-diane polymers filled with short glass fibers.

Keywords: physicochemical modification, ultrasound, filling, fiberglass, epoxy-diane polymer, heat shrinkage.

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Introduction

Technologies for repairing polymer pipelines of various functional purposes, in particular low and medium pressure gas pipelines, based on epoxy compositions (ECs) are widely used. The use of coupling joints formed from epoxy polymers (EPs), having shape memory effect, attracts special attention. It is known that during plastic deformation of a polymer, a nonequilibrium stress state can be realized, which, when heated to certain temperatures, relaxes with the restoration of the original shape of the product (polymer sample) [1].

This property is called the thermal shrinkage. It has been satisfactorily studied for the films and fibers made of thermoplastic polymers and only partially studied for the case of EPs [2]. Thermal expansion and shrinkage of polymers is manifested by a change in the volume of a polymer with a constant chemical structure when the temperature changes, including by radiation heating for products from thermoplastics [3]. This property is of great practical importance, because it determines the dimensional stability of the resulting products and the internal stresses that occur when the deformation of the polymer is limited.

The effect of thermal shrinkage of polymeric materials was considered in detail in a number of works [4,5]. Analysis of the results reported in these works shows that it is necessary to create favorable conditions for the orientation of interstitial fragments in EPs in order to obtain tubular products based on EPs with shape memory effect. These EPs should have a relatively low effective crosslinking density and be a mixture of densely-frequent and rare-mesh components with rigid peripheral and flexible internal interstitial chains.

Moreover, a different degree of change in the shape of these EPs during their deformation is associated with unequal density of their networks and mobility of inter-nodal chains. When the cross-

linked polymers are heated to a temperature exceeding the glass transition temperature, their elastic modulus decreases sharply [2]. Therefore, under these conditions, the polymers are deformed at a relatively low pressure (1–5 MPa). This contributes to the formation of products of various profiles by forming cross-linked polymers in a highly elastic state by plunger extrusion [6].

It is very important to stabilize and improve the operational characteristics of the final coupling joints in order to ensure the durability of molded repair products. This can be achieved, for example, by carrying out chemical and physical modification of liquid ECs during the manufacture of these compounds. Regulating of structure formation at the phase boundary, in particular, by incorporation of short fibrous fillers into liquid EC [7] (an example of chemical modification) is one of the ways to improve the operational characteristics of EPs.

The strengthening effect of fillers of a fibrous structure (such as glass fiber) is significantly higher than that of dispersed fillers (such as talc, graphite, molybdate, disulfate, aluminum powder, titanium dioxide, etc.). However, the incorporation of a continuous fibrous filler (e.g. fiberglass) prevents thermal shrinkage of the couplings. Therefore, it is advisable to incorporate precisely short fibrous fillers of various geometric shapes.

As for physical modification, the use of low-frequency ultrasonic (US) treatment of liquid EC before it is mixed with the hardener is one of the effective methods. Moreover, this is valid in the manufacture of both unfilled ECs [8] and fibrous polymer composite materials (PCMs) based on an epoxy matrix [9]. In many cases, US treatment enhances the production efficiency of the PCMs [10], in particular, intensifies the process of capillary impregnation of fiber fillers with liquid ECs [11] as well as improves the operational properties of hardened reinforced EPs [12].

The variety of US treatment modes involves the use of increased static pressure to reduce the duration of sonication of liquid ECs [13]. Thus, it can be assumed that the combined physicochemical modification of liquid ECs could be very efficient when forming heat-shrinkable products from EPs by optimizing the content of short fibrous fillers and the parameters of US treatment of liquid ECs together with these fillers. Indeed, this opens up new possibilities for the directed control of the operational characteristics of functional PCMs with the shape memory effect [14].

Experimental

The composition of the investigated filled and unfilled ECs during their chemical modification was selected so that the glass transition temperature of the hardened EPs based on them was in the range of 50 to 100^{0}C. This temperature range is due to the requirement that the formed coupling should resist involuntary shrinkage during the hot summer.

The manufacture of heat-shrinkable couplings was carried out using ECs which contained rigid and elastic components [2]. An aromatic complex of diglycidyl ether in the form of epoxy resin (ER) of the ED-20 and UP-640 brands was used as a rigid component of ECs, whereas a block oligomer of an aliphatic ER and an acid oligoester in the form of a modified ER of the UP-599 brand was used as an elastic component. The weight ratio between the rigid and elastic components was 3:2, respectively.

A mixture of isomethyltetrahydrophthalic anhydride with an accelerator UP-606/2, taken in stoichiometric relation to the resin part served as a hardener for all compositions. ECs were prepared by combining all the ingredients at a temperature of 60–70^{0}C. The ECs hardening regime was as follows: 70^{0}C/8 hour+100^{0}C/4 hours+120^{0}C/2 hours.

The above-mentioned components of ECs were chosen because they ensure the most successful combination of the contribution of chemical and physical networks. The polymers obtained by hardening of such compositions have a glass transition temperature that is convenient for operation and high deformability in the glassy and highly elastic states.

In addition, the preparation of these ECs is extremely simple and consists in the mixing of components. It should be added here that the above ratio of the ingredients provides an acceptable combination of tensile strength and relative elongation of EPs.

Chopped fiberglass RBN-10-2570-78 was used as a short fibrous filler, its average length of segments and diameter being $(1-2)\cdot10^{-3}$ m and 10^{-5} m, respectively.

The manufacture of couplings from EPs based on liquid ECs (both filled and unfilled) was performed as a sequence of the following operations:

1) A short fiber glass filler was added to the mixture of the rigid and elastic components of the EC in a soluble state. Then, the filled composition was subjected to the influence of low-frequency US for 20–35 minutes at high static pressure.

2) The sonicated components of ER with a short fiber glass filler were mixed with a mixture of accelerator and hardener to obtain the initial liquid filling EC.

3) Tubular billets were made by pouring the

obtained liquid EC into specially prepared metal molds followed by the solidification of the EC according to the above step temperature-time regime. This operation ensured formation of an extremely hardened structure with a 95–97% sol-fraction content.

4) Finished tubular billets were transferred to a highly elastic state by heating to a temperature of 100°C. Then, they were placed on the mandrel, which provides a necessary increase in the inner diameter of the billets (flaring deformation, Fig. 1,a).

5) After deformation of the billet along the inner diameter to a predetermined size, it was cooled to a temperature lower than the glass transition temperature T_g=78–82°C, which will allow reaching an almost 100% degree of thermal shrinkage of the coupling (Fig. 1,b).

6) After exposure at the indicated temperature, the billets were removed from the mandrel (Fig. 1,c) and their visual inspection was carried out. After this control, the billets weree considered ready for use as a heat-shrinkable coupling.

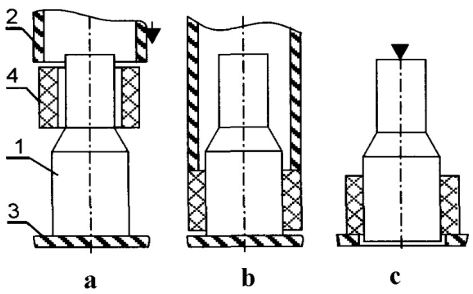


Fig. 1. Scheme of the preparation of heat-shrinkable products from filled and unfilled EPs: 1 – mandrel; 2 – coupling; 3 – base plate; 4 – EP billet

The following physical-mechanical and operational properties of the hardened EPs were studied: tensile strength σ_t, elastic modulus E, failure deformation ε_f, and flaring deformation ε_{fl} of the inner diameter of the EP billet. The flaring deformation ε_{fl} of the polymer billet was determined as the ratio of the difference between the inner diameters of the polymer billet before and after its deformation to the inner diameter of the polymer billet after its deformation. EP couplings had an inner diameter of 19.8 mm and an outer diameter of 30.1 mm.

The physical-mechanical properties in the glassy state (at temperature T=20±2°C) and highly elastic state (T=100°C) were studied in tensile tests of standard hardened samples of unfilled and filled EPs. The tests were carried out using a machine of the ZP-10190 type (10 t) at a gripping speed of 10 mm min^{-1}. To prevent destruction in the grips of the machine, special pads were made. To eliminate slippage of the samples and improve adhesion between the liners of the grippers, double-sided fine-grained sanding paper was used. The number of test samples per variable parameter was 10.

A 0.4 kW ultrasonic disperser was used as a source of low-frequency ultrasound. The frequency (f), amplitude (A), intensity (I) and temperature (T) were controlled. Excessive static pressure during US treatment with liquid EC was P=0.4 MPa.

Results and discussion

Effect of the inner diameter of the epoxy polymers billets on their flaring deformation

The study of the relationship between the internal diameter of EP billets and their flaring deformation is very important, because it determines the range of use of specific type sizes of heat-shrinkable couplings.

It was found that the magnitude of the flaring deformation ε_{fl} correlates with the values of the internal d_o and external d_o^i diameters of the coupling: the higher the d_o and d_o^i, the smaller the flaring deformation is. Therefore, the value of the inner diameter d_o of the coupling gives quite definite information about the possible values (or the range of values) of the flaring deformation.

Thus, the limiting value of the flaring deformation for the selected epoxy-anhydride composition and for couplings with an inner diameter of d_o≈20 mm was ε_{fl}≈17% in the basic method [6]. However, experiments showed that the values of the flaring deformation, achieved without breaking the billet, was decreased with an increase in the inner diameter of the billet.

For example, for a billet with an inner diameter of d_o≈60 mm, it was not possible to achieve high values of the flaring deformation. The flaring deformation of the billets was 12%, 15% and 17%, which led to their destruction. Only couplings with ε_{fl}=3%–5% showed acceptable heat-shrinkable parameters in terms of ease of repairing.

A negative outcome in terms of flaring deformation (ε_{fl}=4% and 6%) was obtained for d_o≈110 mm. Couplings of acceptable quality (without physical damage and cavities) were manufactured if the values of flaring deformation ε_{fl}=1.5–2.5%.

Thus, the operational characteristics of heat-shrinkable couplings from EPs are determined not only by the composition of the selected EC, but also by the absolute value of the inner diameter of the resulting coupling. The above results indicate that when forming couplings from EPs, the

geometrical dimensions of the couplings should be taken into account.

Optimization of the content of short-fiber filler in liquid ECs

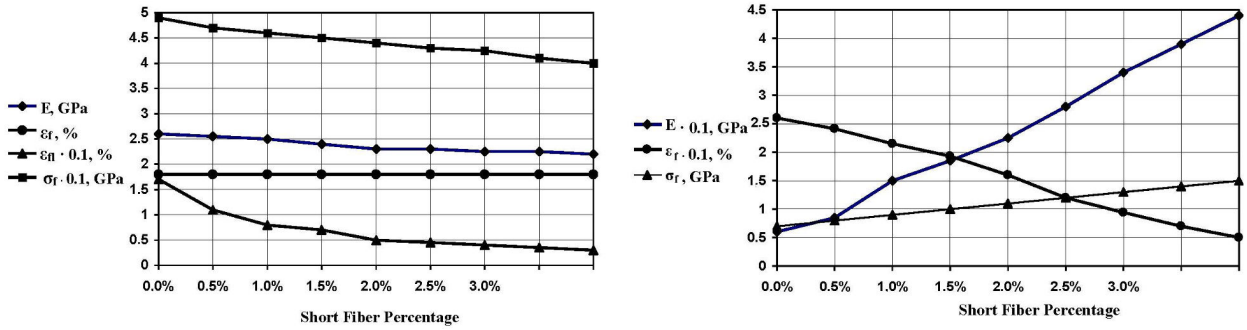
It is known that during incorporation of finely chopped fiberglass it is necessary to evenly distribute it in liquid EC and ensure acceptable adhesion and wettability of its surface towards a soluble polymer medium. As a rule, 0.5 wt.% to 30 wt.% of glass fiber are incorporated into the EC composition, depending on the functional purpose of the molded polymer [7]. This is due to the fact that glass-filled polymers exhibit improved physical-mechanical and electrical properties, high heat and deformation resistance, and, as a rule, have low shrinkage as compared with the unfilled EPs. However, the optimal values of the filler content should be found experimentally for each composition, depending on its functionality.

When conducting these studies, the range of variation of the short-fiber glass filler was significantly narrowed: the degree of filling varied within (0.5–5.0) wt.% (with respect of EC weight). At the same time, at a maximum degree of filling (5 wt.% with respect of EC weight), the composition in a soluble state becomes technologically unacceptable, which is consistent with results described elsewhere [6]. Thus, the viscosity of these compositions increases so much that it is not possible to obtain hardened EP samples with a smooth surface and without cavities in the structure.

An analysis of the mechanical properties of these materials in a glassy state (Fig. 2,a) in comparison with the initial polymer [6] indicates that the incorporation of a certain amount of fillers 5 wt.% does not significantly affect ductility (ε_f) in a glassy state. In this case, the elastic modulus E and the tensile strength σ_t decrease. This allows us to make an assumption about the negative effect of the short-fiber glass filler on the heat-shrinkable properties of tubular products.

The ultimate flaring deformation for a coupling with a 5% glass filler content decreases from 17% to 3% as compared with the initial composition (Fig. 2,a).

Thus, the concentration of short fibrous glass filler in ECs of 1–2% allows getting the most acceptable physical-mechanical and service



a b

Fig. 2. Effect of the content of short-fiber glass filler on the physical-mechanical properties of heat-shrinkable EPs in the glassy (a) and highly elastic (b) states

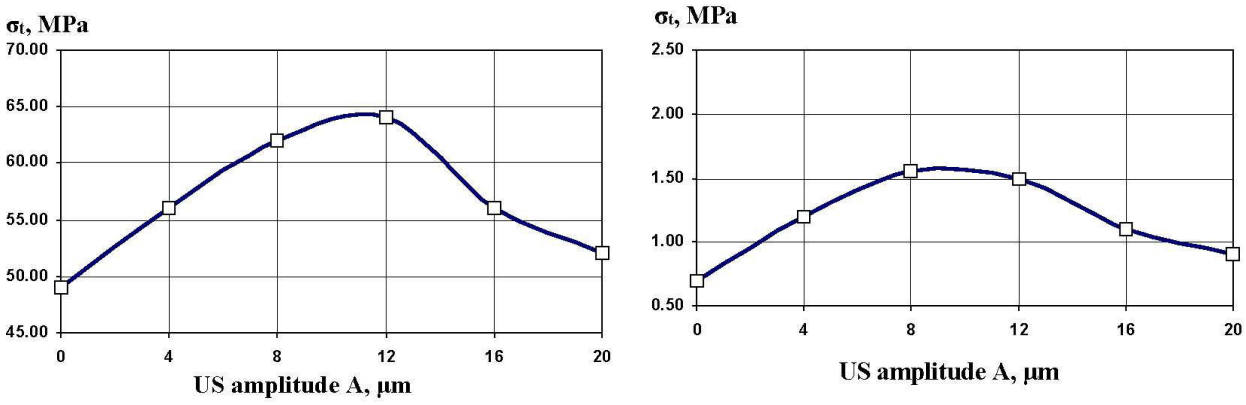


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Fig. 3. Dependence of the tensile strength on the amplitude of the US treatment for EP filled with dispersed fiberglass filler under the combined action of low-frequency US and overpressure in glassy (a) and highly elastic (b) states

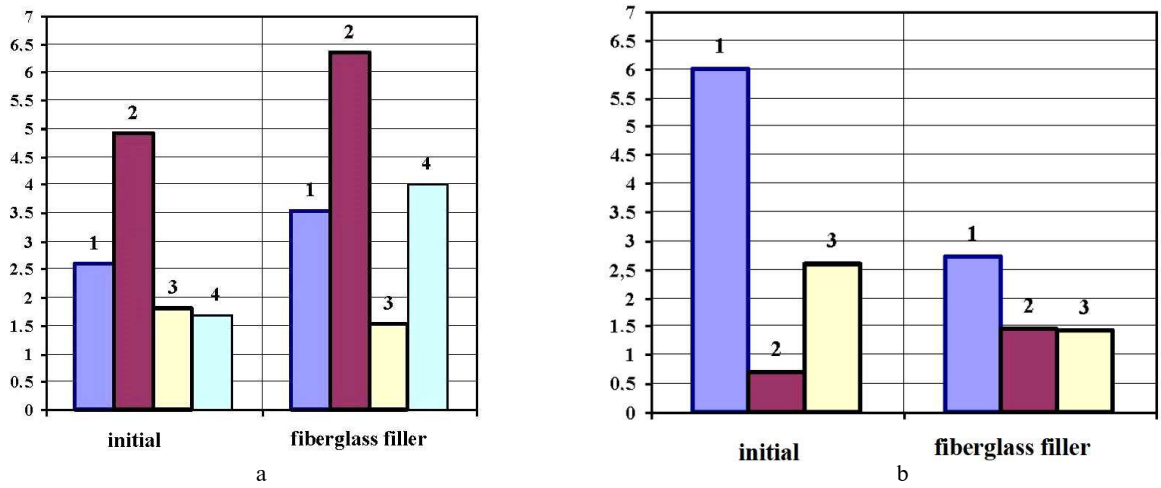

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Fig. 4. Effect of US treatment at excessive static pressure on the average values of the mechanical properties of a filled heat-shrinkable EP in comparison with the initial EP for the glassy (a) and highly elastic (b) states: 1 – 0.1·E, GPa; 2 – 0.1·σ_t, MPa; 3 – ε_f, % (a) or 0.1·ε_f, % (b); 4 – ε_{fl}, %

properties of the hardened EPs. It can be seen from Fig. 2,a that, the mechanical characteristics of a filled EP in a glassy state practically do not differ from those of the initial unfilled EP when the degree of filling with fiberglass is 1–2%.

At the same time, the stiffness (E) increases more than 3.5–4 times and the tensile strength σ_t increases (1.3 – 1.6) times in the highly elastic state (Fig. 2,b); this confirms the efficiency of chemical modification with short-fiber glass fillers in the above amount.

Ultrasonic treatment of a liquid filled epoxy composition

It was found that the use of US treatment towards a mixture of a part of a rigid (UP-640) and elastic (UP-599) resin components filled with short fiber glass fillers leads to some positive effects. Under the influence of US energy, the viscosity of the composition decreases 2–3 times in a short time, resulted from the heating of these resin components filled with short-fiber glass fillers. This contributes to both degassing and a more complete, faster and uniform mixing of short-fiber glass fillers in ER.

In addition, there is a more uniform distribution of the glass filler in the ER, which leads to an increase in the stability of the properties of hardened filled EPs. Therefore, a decrease in the strength characteristics of EPs was observed when the amplitude of the US vibrations deviated from its optimal values (6–12 μm) both in glassy and in highly elastic states (Fig. 3).

It was established that the dependence of the strength of the filled EPs on the duration of sonication exhibits a maximum at τ=25 min. The most intense strengthening of the filled EPs was observed at the sonication at the frequency of 18 kHz, the amplitude of 12 mm, the intensity of 10 W cm^{-2} and the temperature of 70°C.

Fig. 4 shows the effects of combined US treatment with overpressure on the mechanical properties of heat-shrinkable EPs filled with short glass fibers as compared with the initial EP in the glassy and highly elastic states measured by the method described in ref. [6].

The highest strengthening of the filled EPs under the combined action of US and overpressure on the resin part of EC was 40–50% and 50% in the glassy state and in the highly elastic state, respectively. The resulting value of flaring deformation was 4% for couplings of filled heat-shrinkable EPs with the inner diameter of 19 mm and the outer diameter of 30.1 mm. This value of flaring deformation is quite acceptable from a technological point of view for the above coupling diameters.

At the same time, the above experiments showed that the value of the flaring deformation ε_{fl}, achieved without destroying the billet, decreases with an increase in the inner diameter of the billet.

Another positive aspect of the application of US treatment of the resin part of EC for the heat-shrinkable couplings is a decrease in the solidification time of the sonicated thermosetting binder by at least 30–40%.

Conclusions

It was shown that the use of a combined physicochemical modification of liquid ECs (low-frequency ultrasound together with optimal filling with short-fiber glass fillers) is an efficient way to produce heat-shrinkable EPs. It stabilizes and increases the operational characteristics of the

obtained coupling joints.

Obtained EPs have a high strength and crack resistance in the glassy state as well as high rigidity in a highly elastic state while maintaining acceptable working values of the deformation of the flare formed products. The maximum hardening of the filled EPs was 40–50% and 50% in the glassy state and in the highly elastic state, respectively. This was achieved by sonication at a frequency of 18 kHz, amplitude of 12 μm, intensity of 10 W cm^{-2}, temperature of 70^0C, excessive static pressure of 0.4 MPa and a filling value of 1.5–2%.

REFERENCES

1. *Van Krevelen D.W., Te Nijenhuis K.* Properties of polymers: their correlation with chemical structure; their numerical estimation and prediction from additive group contributions. – Amsterdam: Elsevier, 2009. – 1030 p.

2. *Beloshenko V.A., Voznyak Y.V., Yakovleva R.A.* Shape memory effect and electrical resistance of a composite made from epoxy polymer and heat-expanded graphite // Int. Polym. Sci. Technol. – 2007. – Vol.34. – No. 1. – P.7-10.

3. *Engineering* approach to the determination of the radiation field of a polyethyleneterephthalate (PET) medium under radiant heating / Sidorov D.E., Kolosov A.E., Pogorelyi O.V., Gur'eva A.A. // J. Eng. Phys. Thermophys. – 2015. – Vol.88. – No. 6. – P.1409-1415.

4. *Shape-memory* polymers / Mazurek-Budzynska M., Razzaq M.Y., Behl M., Lendlein A. // Functional polymers. Polymers and polymeric composites: a reference series. – 2019. – P.605-663.

5. *Chemical* shrinkage characterization techniques for thermoset resins and associated composites / Nawab Y., Shahid S., Boyard N., Jacquemin F. // J. Mater. Sci. – 2013. – Vol.48. – No. 16. – P.5387-5409.

6. *Beloshenko V.A., Beygelzimer Ya.E., Varyukhin V.N.* Thermal shrinkage of polymer mixtures obtained by solid-state extrusion // Polymer. – 2000. – Vol.41. – No. 10. – P.3837-3840.

7. *Determination* and modelling of the cure shrinkage of epoxy vinylester resin and associated composites by considering thermal gradients / Nawab Y., Tardif X., Boyard N., Sobotka V., Casari P., Jacquemin F. // Compos. Sci. Technol. – 2012. – Vol.73. – P.81-87.

8. *Kolosov A.E.* Low-frequency ultrasonic treatment as an effective method for modifying liquid reactoplastic media // Chem. Petrol. Eng. – 2014. – Vol.50. – No. 1-2. – P.79-83.

9. *Substantiation* of the efficiency of using ultrasonic modification as a basis of a production cycle for preparing reinforced objects of epoxy polymer composition / Kolosov A.E., Sakharov A. S., Sivetskii V.I., Sidorov D.E., Sokolskii A.L. // Chem. Petrol. Eng. – 2012. – Vol.48. – No. 5-6. – P. 391-397.

10. Kolosov A.E. Prerequisites for using ultrasonic treatment for intensifying production of polymer composite materials // Chem. Petrol. Eng. – 2014. – Vol.50. – No. 1-2. – P.11-17.

11. Kolosov A.E. Impregnation of fibrous fillers with polymer binders. 1. Kinetic equations of longitudinal and transverse impregnation // Mech. Compos. Mater. – 1988. – Vol.23. – No. 5. – P.625-633.

12. Kolosov A.E. Effect of low-frequency ultrasonic treatment regimes on reactoplastic polymer composite material operating properties // Chem. Petrol. Eng. – 2014. – Vol.50. – No. 3-4. – P.150-155.

13. Kolosov A.E. Low-frequency ultrasonic treatment of liquid reactoplastic media with pressure variation // Chem. Petrol. Eng. –. 2014. – Vol.50. – No. 5-6. – P.339-342.

14. Karger-Kocsis J., Keki S. Review of progress in shape memory epoxies and their composites // Polymers. – 2018. – Vol.10. – Article No. 34.

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ФІЗИКО-ХІМІЧНА МОДИФІКАЦІЯ ЕПОКСИДНИХ ПОЛІМЕРІВ, ЩО ТЕРМОУСАДЖУЮТЬСЯ

О.Є. Колосов, О.В. Гондлях, В.І. Сівецький, Д.Е. Сідоров, О.П. Колосова, В.В. Ванін, С.І. Антонюк

Розглянуто підхід до здійснення фізико-хімічної модифікації епоксидно-діанових полімерів, що термоусаджуються, які знаходять застосування як муфти для ремонту полімерних трубопроводів різного функціонального призначення. Метою модифікації є стабілізація та підвищення експлуатаційних характеристик кінцевих муфтових з'єднань, що термоусаджуються. Проаналізована перспективність одержання виробів різного профілю шляхом формування сітчастих полімерів, що знаходяться у високоеластичному стані, методом плунжерної екструзії за рахунок створення сприятливих умов для орієнтації міжвузлових фрагментів в епоксидно-діанових полімерах. До складу вихідної епоксидної композиції входили жорсткий і еластичний компоненти. Полімери, що одержуються при твердінні таких композицій, мають зручну для роботи температуру склування і високу деформованість у склоподібному й високоеластичному станах. Досліджували межу міцності при розриві, модуль пружності при розриві, деформацію щодо розтягання, а також деформацію роздачі внутрішнього діаметра заготовки епоксидно-діанових полімерів. Фізичну модифікацію рідкої наповненої епоксидної композиції до її змішування з твердником здійснювали шляхом використання низькочастотного ультразвукового оброблення. Проаналізовано результати впливу комбінованого ультразвукового оброблення на фізико-механічні та експлуатаційні властивості наповненого короткими скловолокнами епоксидно-діанового полімеру, що термоусаджується.

Ключові слова: фізико-хімічна модифікація, ультразвук, наповнення, скловолокно, епоксидно-діановий полімер, термоусадка.

PHYSICOCHEMICAL MODIFICATION OF HEAT-SHRINKABLE EPOXY POLYMERS

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REFERENCES

1. Van Krevelen DW, Te Nijenhuis K. *Properties of polymers: their correlation with chemical structure; their numerical estimation and prediction from additive group contributions.* Amsterdam: Elsevier; 2009. 1030 p.

2. Beloshenko VA, Voznyak YV, Yakovleva RA. Shape memory effect and electrical resistance of a composite made from epoxy polymer and heat-expanded graphite. *Int Polym Sci Technol.* 2007; 34(1): 7-10. doi: 10.1177/0307174X0703400102.

3. Sidorov DE, Kolosov AE, Pogorelyi OV, Gur'eva AA. Engineering approach to the determination of the radiation field of a polyethyleneterephthalate (PET) medium under radiant heating. *J Eng Phys Thermophys.* 2015; 88: 1409-1415. doi: 10.1007/s10891-015-1325-0.

4. Mazurek-Budzynska M, Razzaq MY, Behl M, Lendlein A. Shape-memory polymers. In: Jafar Mazumder M, Sheardown H, Al-Ahmed A, editors. *Functional polymers. Polymers and polymeric composites: a reference series.* Springer Cham; 2019. p. 605-663. doi: 10.1007/978-3-319-95987-0_18.

5. Nawab Y, Shahid S, Boyard N, Jacquemin F. Chemical shrinkage characterization techniques for thermoset resins and associated composites. *J Mater Sci.* 2013; 48: 5387-5409. doi: 10.1007/s10853-013-7333-6.

6. Beloshenko VA, Beygelzimer YE, Varyukhin VN. Thermal shrinkage of polymer mixtures obtained by solid-state extrusion. *Polymer.* 2000; 41: 3837-3840. doi: 10.1016/S0032-3861(99)00553-4.

7. Nawab Y, Tardif X, Boyard N, Sobotka V, Casari P, Jacquemin F. Determination and modelling of the cure shrinkage of epoxy vinylester resin and associated composites by considering thermal gradients. *Compos Sci Technol.* 2012; 73: 81-87. doi: 10.1016/j.compscitech.2012.09.018.

8. Kolosov AE. Low-frequency ultrasonic treatment as an effective method for modifying liquid reactoplastic media. *Chem Petrol Eng.* 2014; 50: 79-83. doi: 10.1007/s10556-014-9859-0.

9. Kolosov AE, Sakharov AS, Sivetskii VI, Sidorov DE, Sokolskii AL. Substantiation of the efficiency of using ultrasonic modification as a basis of a production cycle for preparing reinforced objects of epoxy polymer composition. *Chem Petrol Eng.* 2012; 48: 391-397. doi: 10.1007/s10556-012-9629-9.

10. Kolosov AE. Prerequisites for using ultrasonic treatment for intensifying production of polymer composite materials. *Chem Petrol Eng.* 2014; 50: 11-17. doi: 10.1007/s10556-014-9846-5.

11. Kolosov AE. Impregnation of fibrous fillers with polymer binders. 1. Kinetic equations of longitudinal and transverse impregnation. *Mech Compos Mater.* 1988; 23: 625-633. doi: 10.1007/BF00605688.

12. Kolosov AE. Effect of low-frequency ultrasonic treatment regimes on reactoplastic polymer composite material operating properties. *Chem Petrol Eng.* 2014; 50: 150-155. doi: 10.1007/s10556-014-9871-4.

13. Kolosov AE. Low-frequency ultrasonic treatment of liquid reactoplastic media with pressure variation. *Chem Petrol Eng.* 2014; 50: 339-342. doi: 10.1007/s10556-014-9904-z.

14. Karger-Kocsis J, Keki S. Review of progress in shape memory epoxies and their composites. *Polymers.* 2018; 10(1): 34. doi: 10.3390/polym10010034.