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Preparation of a New Material Based on Epoxy Oligomers for Forming Corrosion-Protective Coatings

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Abstract—New adhesive materials based on a single-part hot-cured epoxy adhesive for forming corrosion-protective coatings were obtained. Perfluoropentanoic acid N-methylpiperazide and polyethylenepolyamine were used as curing catalysts. The adhesive compounds in the cured state were characterized by the degree of swelling, gel fraction content, Vickers hardness, elastic modulus, and creep strain; their corrosion-protective properties with respect to low-carbon steel (St. 3) and aluminum–magnesium alloy (AMg-6) were determined. The chemical structure of the organic solvent and amine curing agent largely determines the operation characteristics of the coatings obtained.

Keywords: corrosion-protective epoxy coatings, hardness, elastic modulus, creep behavior

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High reactivity of epoxy groups in glycidyl derivatives of OH acids not only ensures their use as a base of adhesive materials for high-performance adhesives, sealants, and paint-and-varnish coatings [1, 2], but also opens the possibility of simple chemical modification of commercial epoxy resins to improve or cardinally change the characteristics of the final product [3, 4]. However, such pathway of preparing new materials based on diglycidyl esters has a significant limitation, because it requires targeted synthesis of epoxy oligomers [1, 5, 6], which ultimately reduces the commercial availability of the adhesive base. The strategy of modifying the properties of the most widely used large-tonnage epoxy products by filling with inorganic [7, 8] and organic [3, 9] compounds ensures slight improvement of the mechanical and operation properties to a limit after which further increase in the amount of the components does not lead to cardinal changes in the properties. To change the properties of a material significantly, it is necessary to increase the content of special components [10, 11], which increases the cost of the material and restricts its practical use.

For curing of the epoxy resin of any type, it is necessary to use a curing agent or a cocuring system [1–5]; therefore, an efficient method for preparing new materials based on diglycidyl esters involves preparation of polyfunctional components and their addition to the adhesive base. Indeed, polyamido amines [2, 12], polyamino siloxanes [3, 10], aniline–formaldehyde resins [13], and polythiols [4] largely determine the mechanical properties of the new materials. Introduction of functionalized polyethylenimine increases the electrical conductivity [14], and introduction of alkoxysilane derivatives enhances the heat resistance [3, 9]. Introduction of organophosphorus compounds into the adhesive base makes the material flame-resistant [15]. Introduction of OH acids increases the adhesion of the material [16, 17], and its modification with fluorinated organic compounds makes it more hydrophobic [18] and ensures corrosion-protective properties [19].

Highly efficient curing of epoxy resins is ensured when using titanium(IV) alkoxides [20, 21]; it leads to high-quality gluing of inorganic materials and enhances the heat and vacuum resistance.

In view of prospects for enhancing the functionality of curing agents by modification, this study was aimed at preparing a corrosion-protective coating based on commercial ED-20 epoxy resin cured with titanium(IV) alkoxide.

EXPERIMENTAL

In our study, we used ED-20 epoxy–4,4'-isopropylidenediphenol resin produced by Sverdlov Plant (Dzerzhinsk, Nizhny Novgorod oblast, Russia) with the epoxy number of 21.1%, ETP adhesive [20, 22], and polyethylenimine (branched, Aldrich, mean molecular mass 25 kDa). Chemically pure grade ethyl cellosolve and tetrahydrofuran were distilled and thoroughly dried before use. 1-Methyl-4-(2,2,3,3,4,4,5,5,5-nonafluoropentanoyl)piperazine was prepared as described previously in [23].

Adhesive compounds were prepared and cured by methods developed previously [19–21]. Their composition was characterized with a PE 2400 automatic elemental analyzer (Perkin Elmer) and a Spectrum One Fourier IR spectrometer (Perkin Elmer). The content of the soluble fraction in the cured compounds was determined by exhaustive hot extraction with acetone [20].

The mechanical properties of the coatings were studied by instrumental indentation using a FISCHERSCOPE HM2000 XYm automated system for microhardness measurement in accordance with ISO 14577. The indentation was performed on the surface of a coating that had not been subjected to mechanical actions, so as to exclude the effect of additional treatment on the results. The tests were performed at 22 ± 2°C using a tetragonal pyramidal Vickers indenter with the angle between the faces of 136°. The following characteristic quantities were considered: hardness (*HV*), contact elastic modulus (*E**), contribution of the work of plastic strain to the total work of indentation (n_{plast}), and creep index (C_{IT}), which was calculated as a relative increase in the indentation depth, observed at a constant load of 1 N during 60 s.

The rate of uniform corrosion of metal electrodes coated with the cured adhesive compounds was studied at room temperature by the method of polarization resistance with an Ekspert-004 corrosion meter and a two-electrode measuring sensor in 10% HCl solution for St. 3 steel and a 3.5% sea salt solution for AMg-6 alloy.

RESULTS AND DISCUSSION

The one-part epoxy adhesive containing titanium(IV) alkoxide showed high performance not only as an adhesive [19, 20] but also as a material for coating metals [19, 21]. To make the latter application more efficient, the ready ETP adhesive was diluted with ethyl cellosolve with the aim of reducing the viscosity to obtain a thin uniform coating. This alteration made it necessary to additionally use an amine curing cocatalyst, polyethylenepolyamine (the standard curing agent for epoxy resins) and 1-methyl-4-(2,2,3,3,4,4,5,5,5-nonafluoropentanoyl)piperazine (MNP), an amide of a fluorinated carboxylic acid, which showed catalytic properties in resin curing with simultaneous enhancement of corrosion-protective properties [19].

The IR spectra of the cured compounds contain an absorption band at 910 cm^{-1} of varied intensity, suggesting the presence of unchanged oxirane groups. Determination of the soluble fraction content (Table 1) clearly demonstrates different extent of network formation in the cured compounds depending on the kind of the amine curing agent, its amount, and solvent. The cured compounds do not swell in water and in aqueous HCl and NaCl solutions.

The coating quality does not depend directly on the conversion of epoxy groups in the course of curing (Table 1), as it is observed when using adhesive materials as adhesives [19, 21]. On the contrary, the cured fraction of the epoxy resin actually acts as filler in the uncured or weakly cured fraction of the resin, reinforcing it in accordance with the known relationships [5–7, 24, 25]. Indeed, when straight ETP adhesive is used for preparing an 0.32–0.35 mm thick coating (see table, compound nos. 1 and 6), the hardness and elastic modulus of the coating are low compared to the same adhesive cured with polyethylenepolyamine (compound nos. 2 and 7). Dilution of ETP adhesive with ethyl cellosolve in the presence of a catalytic amount of polyethylenepolyamine made the coating still stronger (compound nos. 3 and 8), despite lower thickness (0.03–0.04 mm). The conversion of epoxy groups decreases in the same series of compounds, as judged from an increase in the relative content of the soluble fraction in the cured compound, which contradicts the observed relationship of enhancement of the gluing performance with an increase in the gel fraction content. The use of tetrahydrofuran instead of ethyl cellosolve (Table 1, compound no. 4) when

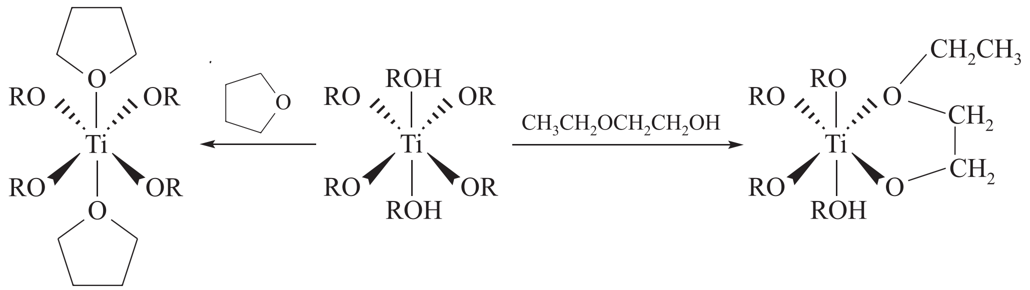
Table 1. Characteristics of mechanical properties of cured compounds based on ETP adhesive

Compd. no.	Amine curing coagent	Solvent	Soluble fraction content, %	Vickers hardness, MPa	Contact elastic modulus, GPa	Contribution of work of plastic strain, %	Creep index, %
Coating of St. 3 steel							
1	–	–	55	260 ± 3	3.83 ± 0.05	54.2 ± 0.2	6.03 ± 0.02
2	Polyethylenepolyamine	–	68	330 ± 3	5.25 ± 0.05	59.3 ± 0.2	7.77 ± 0.02
3	Polyethylenepolyamine	Ethyl cellosolve	76	450 ± 3	23.32 ± 0.05	84.9 ± 0.2	6.97 ± 0.02
4	Polyethylenepolyamine	Tetrahydrofuran	62	300 ± 3	5.09 ± 0.05	59.3 ± 0.2	7.21 ± 0.02
5	1-Methyl-4-(2,2,3,3,4,4,5,5,5-nonafluoropentanoyl) piperazine	Ethyl cellosolve	83	200 ± 3	27.84 ± 0.05	99.2 ± 0.2	23.41 ± 0.02
Coating of AMg-6 aluminum alloy							
6	–	–	55	275 ± 3	3.87 ± 0.05	52.3 ± 0.2	5.69 ± 0.02
7	Polyethylenepolyamine	–	68	380 ± 3	5.38 ± 0.05	80.7 ± 0.2	7.03 ± 0.02
8	Polyethylenepolyamine	Ethyl cellosolve	76	430 ± 3	16.02 ± 0.05	77.3 ± 0.2	7.49 ± 0.02
9	1-Methyl-4-(2,2,3,3,4,4,5,5,5-nonafluoropentanoyl) piperazine	Ethyl cellosolve	83	280 ± 3	5.70 ± 0.05	71.8 ± 0.2	7.19 ± 0.02

preparing the coating is virtually equivalent to the cold curing of ETP adhesive (compound no. 2), suggesting participation of titanium(IV) alkoxide in the formation of the set of mechanical properties of the final material. Ethyl cellosolve is a chelating alcohol exhibiting higher donor power compared to tetrahydrofuran, which is a monodentate ether. With ethyl cellosolve, compared to tetrahydrofuran, the metal coordination sphere is saturated more efficiently with the formation of stronger coordination compounds (Scheme 1) [26].

As a consequence, the Lewis acidity of the titanium(IV) atom and its activity in resin curing decrease, and the solvent is removed from the coating in the drying step incompletely, remaining in the form of a new coordination compound. This complex can act as resin filler, enhancing its mechanical strength, and as plasticizer, as indicated by increased contribution of the work of plastic strain to the total work of indentation (Table 1, compound no. 3). Thus, the choice of the solvent for changing the type of the adhesive compound containing titanium(IV) alkoxide from an adhesive to a varnish allows performing simple chemical modification of the curing agent in situ, expanding the operation potential of the compound.

Scheme 1. Interaction of titanium(IV) alkoxide with tetrahydrofuran and ethyl cellosolve.



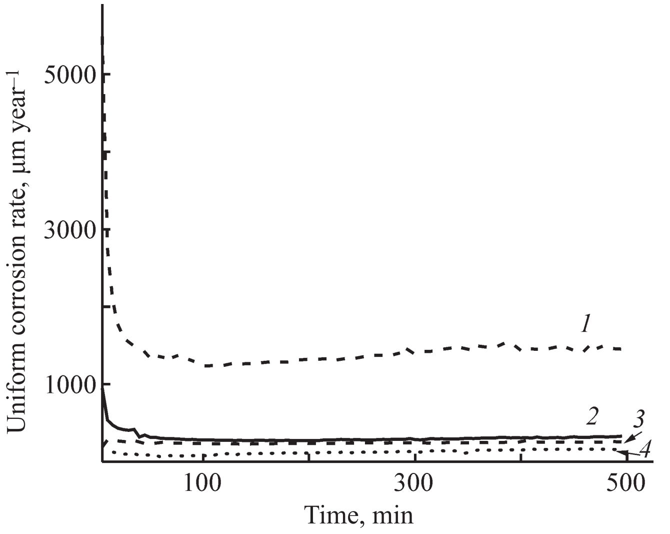


Fig. 1. Uniform corrosion rate in 10% HCl solution as a function of time for electrodes made of St. 3 steel and coated with cured adhesive compounds. (*1*) Blank experiment (uncoated electrodes), (*2*) coating with the polyethylenepolyamine-cured varnish, (*3*) coating with the MNP-cured varnish, and (*4*) coating with ETP adhesive.

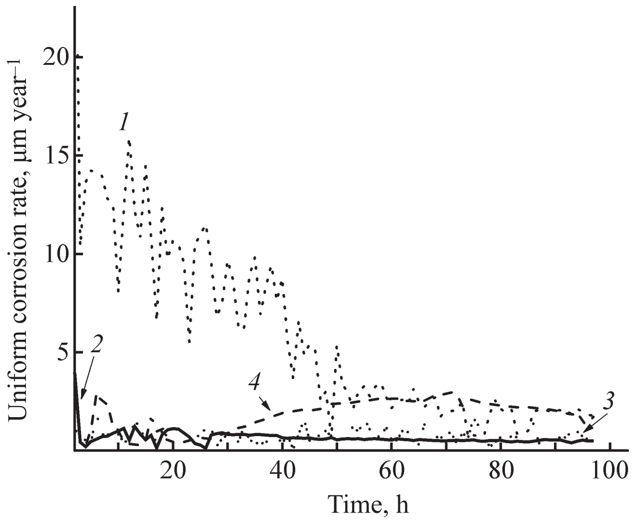


Fig. 2. Uniform corrosion rate in a 3.5% sea salt solution for electrodes made of AMg-6 alloy and coated with cured adhesive compounds. (*1*) Blank experiment (uncoated electrodes), (*2*) coating with the polyethylenepolyamine-cured varnish, (*3*) coating with the MNP-cured varnish, and (*4*) coating with ETP adhesive.

On replacement of polyethylenepolyamine as an amine curing coagent by the previously studied fluorinated carboxamide MNP, we obtained a material (see table, compound nos. 5 and 9) with the properties strongly depending also on the kind of the support. High content of the soluble fraction in the cured compound suggests low degree of network formation, which is due to the deactivating effect of ethyl cellosolve on the Lewis acid sites and to the lower reactivity of the amide compared to polyethylenepolyamine [19]. Low hardness and the contradicting high value of n_{plast} demonstrate high plasticization of the cured polymer, with the plasticizing effect exerted by the uncured oligomers, titanium(IV) alkoxides, and fluorinated carboxamide.

It is known that partially fluorinated compounds enhance the moisture resistance and increase the glass transition point of materials based on epoxy resins [27, 28]. Specifically the presence of MNP in the compound strongly differentiates the coating properties depending on the kind of the metal being coated. In the other cases, the mechanical properties of coatings on different supports do not differ significantly. The creep index (C_{IT}), which was calculated as the relative increase in the indentation depth at a constant load, is a comparative characteristic for evaluating the ability of materials to stand mechanical loads for a long time. Low value of C_{IT}, obtained for all the compounds except compound no. 5 (see table), demonstrates high performance of the coatings.

Estimation of the uniform corrosion rate (K_{n}) for electrodes made of St. 3 steel and AMg-6 alloy and coated with the adhesive compounds shows that the corrosion-protective properties do not become worse in going from the adhesive to the varnish based on it.

The degree of protection (Z), calculated using the equation

$$Z = \frac{K_{\mathrm{n}1} - K_{\mathrm{n}2}}{K_{\mathrm{n}1}} \times 100\%,$$

where $K_{\mathrm{n}1}$ and $K_{\mathrm{n}2}$ are the rates of the uniform hydrochloric acid corrosion of uncoated and coated St. 3 electrodes, respectively (Fig. 1), is 79% for the varnish cured with polyethylenepolyamine, 83% for the varnish cured with MNP, and 87% for the straight ETP adhesive.

The coating made of the varnish cured with polyethylenepolyamine ensured the most stable corrosion protection of AMg-6 electrodes in a salt solution (Fig. 2). The degree of protection was 77%. Coatings with MNP curing agent and ETP adhesive showed unstable results with the degree of protection in the range 73–97 and 28–97%, respectively, as indicated by the saw-shaped profiles of the uniform corrosion rate (Fig. 2). Such behavior of the latter two coatings may be caused by their nonuniform thickness due to certain loss of the adhesion of the materials to AMg-6 alloys compared to St. 3 steel, leading not only to progressive removal of the metal from the electrode surface, but also to acceleration of the local corrosion (pitting). Practically the adhesive compounds are equally suitable for inhibiting the corrosion of aluminum–magnesium alloys under the conditions of seawater corrosion.

Thus, the formed coatings based on ETP adhesive exhibit high adhesion to steel and aluminum alloy and can ensure additional protection of the adhesive joint or coated metal from corrosion under the conditions of mechanical action.

CONCLUSIONS

The procedure for preparing adhesive compounds by chemical modification of the curing agents in situ in the compound allows preparation of new materials based on hot-cured one-part epoxy adhesive containing titanium(IV) alkoxide. The mechanical properties of the coatings, such as the hardness, elastic modulus, and creep strain, are determined by relatively extent of the network formation and by the kind of the solvent and amine curing coagent. The use of the new adhesive compounds as coatings for metal surfaces ensures also their efficient corrosion protection in various media.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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