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Designing New Adhesive Materials Based on Epoxy Oligomers Filled with Organic Compounds

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Abstract—Adhesive compositions based on epoxy resin containing titanium(IV) alkoxide have been developed. It has been shown that the obtained compositions can serve as highly efficient adhesive materials for diverse metals and alloys. The proposed compositions, which exhibit good adhesion and provide efficient corrosion protection, can be also used as coatings of metal surfaces.

Keywords: epoxy resin, titanium(IV) alkoxides, oxiranes, amine curing agents

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INTRODUCTION

Epoxy or urethane polymers are used as an efficient adhesive base for adhesive, sealing, and paint-and-varnish compositions for metal articles. However, their industrial production is encountering many difficulties in Russia; therefore, the present work aims at design of adhesive, sealing, and paint-and-varnish materials based on filled epoxy resins, which exhibit good adhesive and corrosion protective properties to extend the field of their application and make the market for these materials import-independent. To improve the working properties of adhesive and paint-and-varnish compositions based on epoxy resins, new oxirane-containing monomers are obtained [1–3] or commercially available epoxy oligomers are modified with inorganic [4–9] or organic [10–15] compounds, including Lewis acids [16–20]. The latter approach is preferable to the former, because it employs commercially available substances and does not require synthesizing complex organic compounds.

Earlier-developed epoxy compositions containing titanium organic compounds showed high and stable operating and processing properties [20, 21]. However, the literature data provide evidence that aluminum(III), tin(IV), and tantalum(V) alkoxides are active catalysts for polymerization of oxiranes [22]. Nevertheless, among the investigated titanium(IV), aluminum(III), and zirconium(IV) alkoxides used for filling of the commercial ED-20 epoxy resin, the best properties have been established with an adhesive composition based on titanium(IV) [23]. The present work is devoted to further development of the methodology of filling epoxy resins with organic compounds—in particular, titanium(IV) alkoxides—for obtaining new highly efficient adhesive and paint-and-varnish materials.

OBJECTS AND METHODS OF RESEARCH

In the present study, an ED-20 epoxy–diane resin (FKP Zavod imeni Sverdlova) with an epoxy value of 21.1% and commercial branched polyethylene imine (PEI) (Aldrich) with a mean molecular weight of 25000 were used. Adhesive compositions were prepared and cured according to earlier-designed techniques [20, 21]. Their composition was analyzed on a PE 2400 automatic elemental analyzer (PerkinElmer) and a Spectrum ONE Fourier IR spectrometer (PerkinElmer). A thermogravimetry analysis was performed on a derivatograph (METLER TOLLEDO). The ultimate shear strength of adhesive joints was determined according to *GOST* (State Standard) *14759* on an INSTRON 8801 universal servohydraulic testing machine with recording of load diagrams. Energy release rate G upon exfoliation of the coating was determined using the Bourne–Rickbery technique described in [24], a Zwick Z2.5 testing machine (the indenter was a hard-alloy cone with an apex angle of 90°) was employed in scratching experiments. A hardness, a contact modulus of elasticity, and a ratio

Strength properties of adhesive joints bonded using the investigated adhesive compositions

Curing agent	Curing agent content, wt %	Shear strength of the adhesive joints of metals, MPa			
		St3	D16AT aluminum alloy	Cu	M1 copper alloy
PEI	10	5.5 ± 0.6	3.3 ± 0.4	2.0 ± 0.6	5.2 ± 0.5
Titanium(IV) alkoxide	15	21.5 ± 0.5	20.5 ± 1.2	6.0 ± 0.5	13.4 ± 0.9
	7.5	16.0 ± 0.4	15.4 ± 0.8	4.1 ± 0.4	
	3	16.4 ± 0.4	15.2 ± 0.6	3.4 ± 0.4	

between the work of elastic and plastic deformation were investigated on a FISHERSCOPE 200xym system for measuring microhardness according to ISO 14577 using the Oliver–Pharr technique [25]. During testing, a Vickers pyramidal diamond indenter with an interfacial angle of 136° was employed.

Investigation of the uniform corrosion rate of coated metal electrodes was carried out in a 1 M HCl solution for St3 steel at room temperature by the technique of polarization resistance using an Ekspert-004 corrosimeter and a two-electrode measuring sensor according to techniques described in [26, 27].

RESULTS AND THEIR DISCUSSION

Application of Lewis acids in curing of epoxy resins substantially improves working properties of the materials [16–21]. Nevertheless, titanium(IV) alkoxides, which are medium-strength Lewis acids [28], display high activity in polymerization of oxiranes, providing a high degree of linkage in cured epoxy compositions

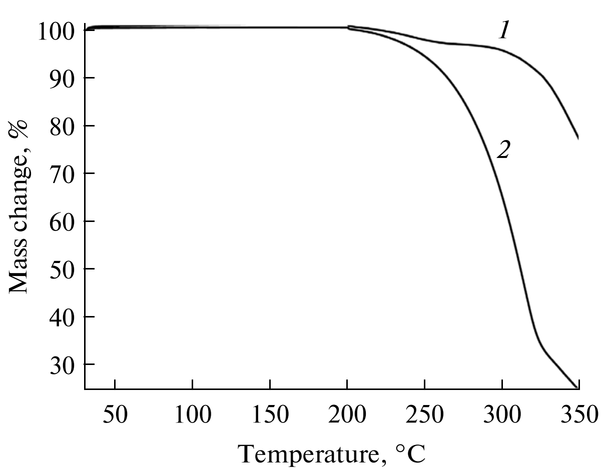

Fig. 1. Thermoanalytical curves for the ED-20 epoxy resin containing (*1*) titanium(IV) alkoxide and (*2*) no titanium(IV) alkoxide.

[20, 21]. In fact, from the obtained data (table), it follows that the composition containing titanium(IV) alkoxide exhibits high adhesive properties relative to both steel and aluminum and copper alloys compared to the composition cured with an amine curing agent.

Decreasing the amount of a curing agent (table) lowers the composition's adhesive ability, which is evidence that participation of a metal site is needed in polymerization of substituted oxiranes. Increasing the curing agent content over 20 wt % yields a considerable growth in a composition viscosity due to an augmented intermolecular interaction [20], which rules out its technological applicability. However, the dependence of the composition adhesive ability on the curing agent content seems to possess a nonlinear behavior owing to the features of cuing of epoxy resins [29, 30].

The cured compositions do not swell in water, hydrochloric-acid and water-salt solutions; they exhibit comparable temperature stability irrespective of the amount of the titanium(IV) alkoxide contained in them. The temperature of a 5% loss in mass is 306°C (Fig. 1). The composition containing no alkoxide is thermally stable up to only 264°C (Fig. 1). Therefore, the presence of a metal provides not only Lewis-acid catalysis of the curing of adhesive composition, i.e., bonding strength, but also a higher thermal stability of the resulting cured material.

Uncured compositions are inherently fluid; hence, they can be used as both adhesives and varnishes. At 18°C, a coating has a hardness of 288 ± 7 MPa, a contact modulus of elasticity of 3.56 ± 0.04 GPa, and a fraction of the work of elastic deformation in the total work of deformation of 54.0 ± 2.5%. The results were obtained at a rate of loading of 0.05 N/s up to a maximal value of 0.1 N, and the indentation depth was 14.7 ± 0.1 μm. The adhesion of a coating to the substrate was so strong that it was impossible to exfoliate it in scratching experiments, while the indenter penetrated through the thickness of the coating and embedded in a base causing no violation to the conti-

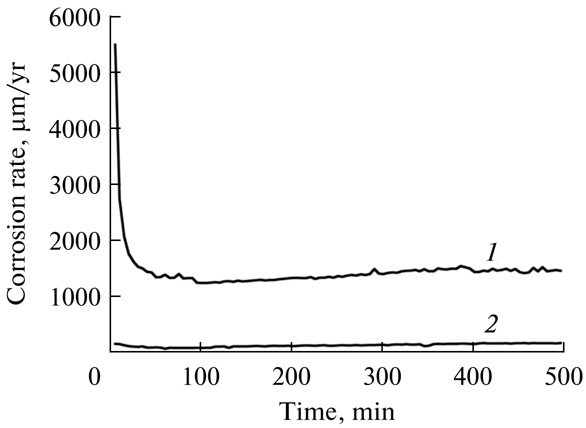

Fig. 2. Dependence of the uniform corrosion rate for samples of St3 steel (*1*) uncoated and (*2*) coated with the composition on the duration of holding in a 1 M hydrochloric acid solution.

nuity of a joint. On the basis of processing of the experimental results, it was thus established that the energy release rate upon exfoliation of a 350-μm coating was 4.9 kJ. Therefore, the formed coating has a high adhesion to a D16AT aluminum alloy and provides protection of a coated metal against corrosion under mechanical action. In fact, as it follows from the obtained data (Fig. 2), the rate of uniform corrosion of a coated St3 steel sample in a hydrochloric-acid medium is about 12 times slower than that of an uncoated metal surface.

CONCLUSIONS

(1) One-pot compositions based on epoxy resin containing titanium(IV) alkoxides are highly efficient adhesive materials for various metals and alloys.

(2) The proposed compositions can be used as coatings with a high adhesion to metal surfaces, providing efficient anticorrosion protection.

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REFERENCES

1. K. P. Unnikrishnan and E. T. Thachil, Designed Monomers Polym. **9** (2), 129–152 (2006).
2. Yu. S. Kochergin, V. V. Shologon, T. I. Grigorenko, et al., “Properties of composites based on epoxy-modified derivatives of 2-Vinyloxyethoxymethyloxirane,” Polym. Sci. Ser. D **1** (4), 277–285 (2008).
3. M. S. Fedoseev, L. F. Derzhavinskaya, V. I. Karmanov, et al., Zh. Prikl. Khim. (St. Petersburg) **83** (4), 671–675 (2010).
4. S. Sprenger, J. Appl. Polym. Sci. **130** (3), 1421–1428 (2013).
5. V. A. Beloshenko, M. K. Pakter, and L. E. Chuikova, Plast. Massy, No. 7, 36–38 (2007).
6. P. A. Sitnikov, A. G. Belykh, M. S. Fedoseev, et al., Zh. Prikl. Khim. (St. Petersburg) **81** (5), 789–792 (2008).
7. V. M. Mikhal’chuk, V. A. Beloshenko, and T. E. Konstantinova, Zh. Prikl. Khim. (St. Petersburg) **81** (5), 783–788 (2008).
8. A. I. Barabanova, P. L. Shevnin, T. A. Pryakhina, et al., Vysokomol. Soedin., Ser. A. **50** (7), 1242–1254 (2008).
9. Yu. A. Gorbatkina and V. G. Ivanova-Mumzhieva, “Adhesive ability of soot-filled epoxides,” Polym. Sci. Ser. D **2** (2), 78–81 (2009).
10. Yu. S. Kochergin, M. A. Grigorenko, T. I. Grigorenko, and D. P. Loiko, “The influence of preliminary thioetherification reaction on properties of epoxy adhesives modified by liquid thiocol,” Polym. Sci. Ser. D **5** (2), 67–72 (2012).
11. Sh. F. Sadygov, N. Ya. Ishchenko, Kh. G. Nazaraliev, and S. A. Ageeva, Plast. Massy, No. 4, 24–26 (2011).
12. M. S. Fedoseev, L. F. Derzhavinskaya, and E. V. Fomina, “Study of the epoxyline resin ED-20 hardening by modified oligoaminoamide dimerizated fatty-acid derivates,” Polym. Sci. Ser. D **2** (2) 75–77 (2009).
13. A. A. Efremov, A. I. Zagidullin, M. V. Kolpakova, et al., “Use of organosilicon compounds as modifiers of epoxy compositions,” Polym. Sci. Ser. D **1** (4), 244–249 (2008).
14. A. I. Zagidullin, P. M. Garipov, M. V. Kolpakova, and O. V. Stoyanov, “Structure and properties of epoxy composites cured with new organosilicon amines,” Polym. Sci. Ser. D **1** (3), 158–163 (2008).
15. P. M. Garipov, M. V. Kolpakova, A. I. Zagidullin, et al., Lakokras. Mater. Ikh Primen., Nos. 7-8, 33–36 (2007).
16. E. G. Zinov’eva, V. A. Efimov, and N. I. Kol’tsov, Plast. Massy, No. 7, 3–5 (2011).
17. E. N. Shved, M. A. Sinel’nikova, Yu. N. Bespel’ko, and N. M. Oleinik, Zh. Prikl. Khim. (St. Petersburg) **85** (10), 1709– 1712 (2012).
18. A. A. Androshchuk, M. A. Lenskii, and A. M. Belousov, Plast. Massy, No. 10, 22–25 (2009).
19. A. A. Lugovaya, V. M. Mikhal’chuk, V. A. Beloshenko, and D. V. Gurtovoi, Zh. Prikl. Khim. (St. Petersburg) **81** (11), 1887– 1892 (2008).
20. A. L. Suvorov, L. D. Dul’tseva, G. I. Ovchinnikova, et al., Zh. Prikl. Khim. (St. Petersburg) **76** (11), 1895–1900 (2003).
21. N. Yu. Ostanina, L. D. Dul’tseva, A. L. Suvorov, and O. N. Chupakhin, Zh. Prikl. Khim. (St. Petersburg) **75** (5), 832–835 (2002).

22. D. Hoebbel, M. Nacken, and H. Schidt, J. Sol-Gel Sci. Technol. **21** (3), 178–187 (2001).

23. A. V. Pestov, I. S. Puzyrev, A. V. Mekhaev, et al., Butlerov. Soobshch. **35** (9), 125–128 (2013).

24. A. A. Volinsky, N. R. Moody, and W. W. Gerberich, Acta Materia, No. 50, 441–466 (2002).

25. W. C. Oliver and G. M. Pharr, Mater. Res. **7** (6), 1564–1583 (1992).

26. T. I. Gorbunova, D. N. Bazhin, A. Ya. Zapevalov, and V. I. Saloutin, Zh. Prikl. Khim. (St. Petersburg) **84** (6), 948–950 (2011).

27. T. I. Gorbunova, D. N. Bazhin, A. Ya. Zapevalov, and V. I. Saloutin, Zh. Prikl. Khim. (St. Petersburg) **86** (7), 1059–1063 (2013).

28. Yu. G. Yatluk, A. L. Suvorov, E. A. Khrustaleva, and S. V. Chernyak, Zh. Org. Khim. **40** (6), 810–813 (2004).

29. E. S. Zhavoronok, I. N. Senchikhin, E. F. Kolesnikova, et al., Vysokomol. Soedin., Ser. B. **52** (4), 706–714 (2010).

30. M. Arasa, X. Ramis, J. M. Salla, et al., Polymer **50** (10), 2228–2236 (2009).

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