

PAPER • OPEN ACCESS

Investigation of adhesive-strength characteristics of fire-retardant epoxy polymers modified with metal-containing additives

To cite this article: O Hryhorenko *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **907** 012060

View the [article online](#) for updates and enhancements.

Investigation of adhesive-strength characteristics of fire-retardant epoxy polymers modified with metal-containing additives

O Hryhorenko¹, Ye Zolkina¹, N Saienko², Y Popov², R Bikov²

¹Department fire and technogenic safety of facilities and technologies, National University of Civil Defense of Ukraine, Chernishevskaya Street 94, 61023, Kharkiv, Ukraine,

²Department of General Chemistry, Kharkiv National University of Civil Engineering and Architecture, Sumska Street 40, 61000, Kharkiv, Ukraine

hryhorenko81@gmail.com

Abstract. Composite materials based on epoxy oligomers due to their unique properties are widely used in various fields of construction and mechanical engineering, including fire retardant coatings. The introduction of flame retardants and dispersed inert fillers as a rule, affects the structure of epoxy polymers. When addressing issues related to the creation of flame-retardant, composite materials, there is insufficient data on the impact of dispersed mineral fillers on their performance properties. Attention is mainly paid to the indicators of flammability, toxicity of combustion products and thermophysical properties of the coating. Therefore, the aim of this work is to conduct experimental studies of changes in the adhesive and strength characteristics of fire-retardant epoxy polymer from the content of metal-containing additives. As a result of experimental studies, it was found of that changing the component composition of the composition can vary widely the adhesive strength characteristics of fire-retardant epoxy polymers. The obtained data must be taken into account when developing epoxyamine coatings for fire protection of building structures and technological communications.

1. Introduction

Composite materials based on epoxy oligomers due to their unique properties are widely used in various fields of construction and mechanical engineering. The main disadvantage of epoxy composite materials is their flammability. This problem is solved by the introduction of various fillers and flame retardants. The tendency of epoxy resins to carbonization allows to obtain on their basis fire-retardant coatings of intumescent type. However, the filling of the composition leads to a change in their properties, including operational.

It is known that the performance characteristics of epoxy polymers are largely determined by the technological properties of the polymeric binder, structuring processes, adhesive interactions at the interface between polymer-solid, intermolecular interactions and other factors [1-8].

The introduction of fillers, as a rule, significantly affects the structuring processes, chemical and water resistance, adhesive strength, rheological properties and structure of epoxy polymers. However, in addressing issues related to the creation of non-combustible, composite materials, there is insufficient data on the impact of dispersed mineral fillers on their performance properties. Attention is



mainly paid to the indicators of flammability, swelling rate, smoke formation, toxicity of combustion products and thermophysical properties of the coating [1, 9-13].

Previous studies [10] allowed us to obtain results that reflect the influence of the nature and content of metal-containing additives on the swelling rate and the value of the coke residue of fire-retardant epoxyamine coatings of low flammability.

The dependence of the swelling epoxy polymer content on the additive content was investigated experimentally and the resistance of the polymer to the action of a celite rod heated to 950 ° C was studied.

The change of thermomechanical properties [14] of epoxy polymers modified with metal-containing additives has been studied. It is shown that the rate of gas evolution in the temperature range after the transition of the system to the viscous state until the phase transition from the plastic state to curing, determines the multiplicity of swelling of the intumescent composition.

In [15-19] the results of research of thermal and thermo-oxidative destruction of epoxy polymers are given. However, no less important are the studies of their mechanical properties [20-23].

2. Unresolved issues

These studies give an idea of the mechanisms of formation of a swollen oblique layer on the surface of the epoxy polymer, as well as the effect of metal-containing additives on the processes of thermal and thermo-oxidative destruction, thermomechanical properties of the polymer and others. However, no less important characteristics of fire-retardant coatings are also their performance properties.

The adhesive strength of a polymeric binder with a substrate is a decisive factor in obtaining compositions intended for the protection of building structures. Given that fire-retardant epoxyamine compositions are complex highly filled systems, it is of interest to study the effect of metal-containing additives on their adhesive strength, impact viscosity and destructive bending stress.

The purpose of this work is to conduct experimental studies of changes in the adhesive strength characteristics of fire-retardant epoxy polymer from the content of metal-containing additives.

3. Main part

An epoxy oligomer-based composition was used as the base flame retardant epoxy polymer ED-20, and monocyanethylenediethylenetriamine was used as a hardener [1, 10, 11] Monoammonium phosphate (MAP) ($\text{NH}_4\text{H}_2\text{PO}_4$) and activated basalt husk (ABS) ($\text{SiO}_2 - 30.2$; $\text{FeO} + \text{Fe}_2\text{O}_3 - 16.1$; $\text{TiO}_2 - 1.6$; $\text{Al}_2\text{O}_3 - 14.0$; $\text{CaO} - 9.6$; $\text{MgO} - 4.1$) were used to reduce flammability.

Copper oxide (II), zinc oxide (II), vanadium oxide (V) and bentonite [10, 13] were used as metal-containing additives (clay-based material with a percentage by weight: $\text{SiO}_2 - 72.5$; $\text{TiO}_2 - 0.27$; $\text{Al}_2\text{O}_3 - 14.45$; $\text{Fe}_2\text{O}_3 - 1.23$; $\text{CuO} - 1.5$; $\text{MgO} - 2.8$; $\text{K}_2\text{O} - 0.29$; $\text{Na}_2\text{O} - 1.55$). Additives were introduced into the composition of epoxy polymers in an amount of from 5 to 20 mass parts (m.p.).

The adhesive strength was determined experimentally by the method of uniform separation from each other of two metal washers with a base diameter of 25 mm, made of steel grade St3. The essence of the method is to determine the magnitude of the destructive load P_{dest} , when stretching two washers, the bases of which are pre-glued with the investigated epoxy polymers, forces perpendicular to the bonding plane. The nature of the destruction can be both adhesive or cohesive, and mixed [6, 24]. The studies were conducted on a series of 10 samples. The largest and smallest value of the destructive load P_{dest} from the series were not taken into account in further calculations. The remaining 8 values of the destructive load P_{dest} used to determine the average value of the destructive load P_{dest} .

Tensile strength $\sigma_{t.st.}$ was determined based on the average value of the destructive load P_{dest} and the cross-sectional area of the washer base F [20]:

$$\sigma_{t.st.} = \frac{P_{destr.a.}}{F} \quad (1)$$

Figure 1 shows the results of experimental studies of the effect of metal-containing additives on the tensile strength $\sigma_{t.st.}$ fire-retardant epoxy polymers for steel grade St3.

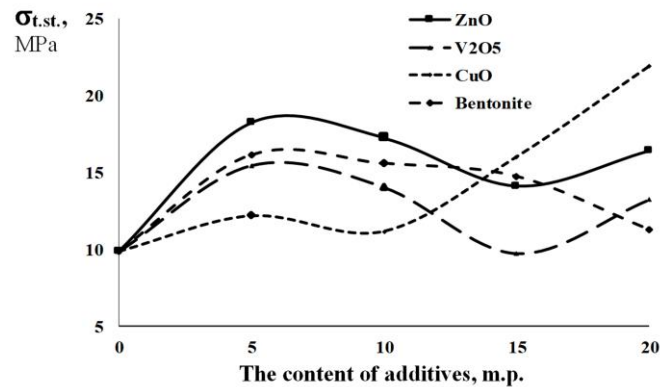


Figure 1. The dependence of the tensile strength $\sigma_{t.st.}$ fire-retardant epoxy polymers for steel St3 from the content of metal-containing additives: ZnO, V₂O₅, CuO and bentonite.

From the presented data it is seen that all metal-containing additives increase the adhesive strength of the fire-resistant epoxy polymer to varying degrees. The introduction of a small number of additives up to 5 m.p. leads to a sharp increase in adhesive strength: ZnO 1.8 times, V₂O₅ and bentonite – 1.6 times, CuO – 1.2 times. Further increase in the content of additives from 5 to 15 m.p. leads to a decrease in adhesive strength (except CuO). Filling the polymer matrix with metal-containing additives (except bentonite) from 15 to 20 m.p. also leads to an increase in adhesive strength by 1.3 to 2.1 times compared with fire-retardant epoxy polymer without additives. Introduction 20 m.p. bentonite has almost no effect on the adhesive strength of the flame retardant epoxy polymer.

The effect of metal-containing additives on the change in impact strength without notch according to ISO 179 and destructive bending stress was also studied σ_{dbS} according to ISO 1209 of the investigated fire-retardant epoxy polymer from the content of additives.

The essence of the method of testing the impact strength without incision is the effect of pendulum dill on the test sample, which is placed on two supports. The impact energy spent on the destruction of the sample is recorded as the difference between the initial stock of potential energy of the pendulum and the energy remaining in the pendulum after the destruction of the test sample [21, 24].

Studies of the impact strength were performed on samples without incision type 1/179-1 with dimensions of 80×10×4 mm, ten samples were used in each series of tests. The distance between the supports on which the sample is 62 mm. The pendulum hit was carried out on a sample placed "flat".

The results of studies of the effect of metal-containing additives on the change in impact strength are presented in Figure 2.

From the presented data (Figure 2) it is seen that metal-containing additives affect the impact strength of the fire-resistant epoxy polymer is not the same. The addition of bentonite in small amounts (up to 10 m.p. by weight) leads to a 1.5-fold increase in impact strength, but a further increase in the additive content gradually reduces this index. Introduction to the composition of the fire-retardant epoxy polymer additives of oxides of metals of transition valence V₂O₅, CuO in amounts up to 5 m.p. leads to a decrease in the impact viscosity of the samples. The largest decrease is observed for epoxy polymer with the addition of V₂O₅ – 1.5 times, for CuO – 1.1 times. For ZnO there is a slight increase of 1.05 times. A further increase in the content of ZnO and CuO additives leads to a sharp increase in impact strength by 1.8 and 1.6 times, respectively. Increasing the content of V₂O₅ to 10 m.p. does not significantly change the impact viscosity compared to filled with 5 wt.h. epoxy polymer. Increasing the content of additives to 15 m.p. leads to a decrease in impact viscosity in all cases except epoxy polymer with the addition of V₂O₅. The most significant decrease is observed for

epoxy polymer with the addition of ZnO. For epoxy polymer with V₂O₅ there is an increase in impact strength by 1.2 times compared to fire-retardant epoxy polymer without additives. Further increase the content of additives to 20 m.p. leads to a gradual decrease in impact viscosity in all cases.

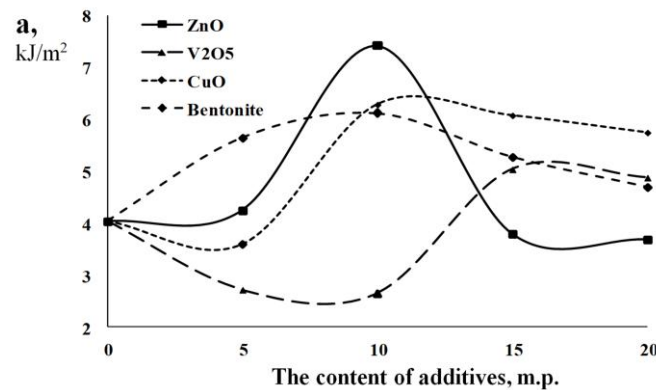


Figure 2. Dependence of the impact strength of fire-retardant epoxy polymers on the content of metal-containing additives: ZnO, V₂O₅, CuO and bentonite.

The essence of the test method to determine the destructive stress during bending σ_{dbs} is the effect on the sample, which is scattered on the two supports, short-term load applied in the middle between the supports [21, 23].

Investigation of the index of destructive stress during bending σ_{dbs} were performed on samples with dimensions of 80×10×4 mm according to the method described in [21, 23].

The results of studies of the effect of metal-containing additives on the change in the destructive stress during bending σ_{dbs} presented in Figure 3.

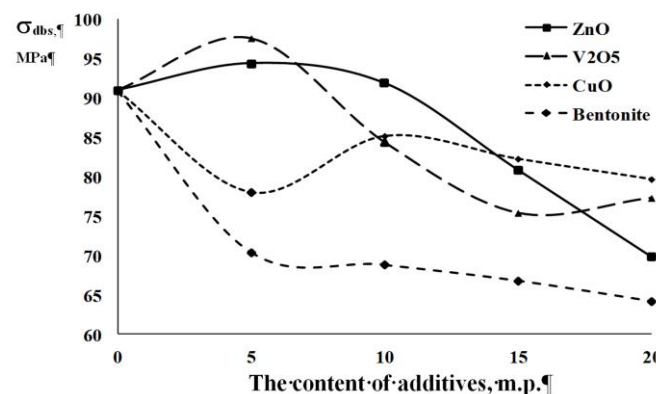


Figure 3. Dependence of destructive stress during bending σ_{dbs} fire-retardant epoxy polymers from the content of metal-containing additives: ZnO, V₂O₅, CuO and bentonite.

As can be seen from the graphs in Figure 3 increase in the content of metal-containing additives with 5 до 20 m.p. leads to a gradual decrease in the destructive stress during bending σ_{dbs} fire-retardant epoxy polymers 1.23, 1.15, 1.12 and 1.29 times for additives ZnO, V₂O₅, CuO and bentonite, respectively. Introduction of small amounts to 5 m.p additives ZnO and V₂O₅ has almost no effect on the destructive stress, the growth is slightly – 1.04 and 1.07 times, respectively. Add to 5 m.p. CuO

and bentonite, on the other hand, reduce this Figure by 1.14 and 1.23 times. A further increase in the content of additives leads to a deterioration of the destructive stress during bending σ_{dbs} .

From the obtained results it is seen that by changing the component composition of the composition it is possible to vary the adhesion-strength characteristics of fire-retardant epoxy polymers.

4 Conclusion

The paper presents the results of studies of the effect of metal-containing additives – ZnO, V₂O₅, CuO and bentonite – on the adhesive strength, impact viscosity and destructive stress in bending of fire-retardant epoxy polymer based on oligomer ED-20.

As a result of experimental studies, it was found that metal-containing additives on the adhesive and strength characteristics of fire-retardant epoxy polymers do not affect equally. The adhesive strength of the studied samples, mainly, increases, achieving the best performance when filling to 5 m.p., except for samples with the addition of CuO, for which the best performance is observed when filling to 20 m.p. The results of studies of the effect of metal-containing additives on the change in impact strength indicate the possibility of adjusting this characteristic in a wide range. The best values were achieved during the introduction 10 m.p. ZnO, receiving an increase in impact strength of 1.8 times. The introduction of flame retardant epoxy polymers of metal-containing additives leads to a gradual decrease in the destructive stress during bending.

From the conducted experimental researches it is visible that changing component structure of a composition it is possible to vary in wide limits adhesive-strength characteristics of fire-retardant epoxy polymers. The obtained data must be taken into account in the development of epoxyamine coatings for fire protection of building structures and technological communications.

References

- [1] Saienko N, Bykov R and Muratov U 2016 *Problems of Fire Safety* **40** 174-178 http://nbuv.gov.ua/UJRN/Ppb_2016_40_31
- [2] Su L, Zeng X, He H, Tao Q and Komarneni S 2017 *J. App. Clay Sci.* **148** 103-108
- [3] Danchenko Yu M, Obizhenko T M, Umanska T I and Barabash E S 2018 *Scientific Bulletin of Civil Engineering* **94** (4) 160-170 https://vestnik-construction.com.ua/images/pdf/4_94_2018/28.pdf
- [4] Andronov V A, Danchenko I M and Bukhman O M 2012 *Problems of Fire Safety* **31** 10-18 <http://repositsc.nuczu.edu.ua/bitstream/123456789/3690/1/29.pdf>
- [5] Danchenko Yu, Kachomanova and Barabash E *Chemistry and Chemical Technology* **12** (2) 188-195 <http://ena.lp.edu.ua/handle/ntb/45161>
- [6] Fedoseev M S, Derzhavinskaya L F and Tsvetkov R V 2014 *Perspective materials* **4** 30-36 https://elibrary.ru/download/elibrary_21350149_49885537.pdf
- [7] Starokadomsky D L and Pahlov E M 2015 *Composites and nanostructures* **7** (7) 41-51 <http://www.issp.ac.ru/journal/composites/2015/Starokadomskii.pdf>
- [8] Danchenko Yu M 2017 *Polymer materials and technologies* **3** (2) 56-63
- [9] Kovalov A, Otrosh Y, Vedula S, Danilin O and Kovalevska T 2019 *Nauk.Visn. Nats. Hirn. Univ.* **3** 46-533
- [10] Hryhorenko O and Zolkina Y 2018 *Problems of Fire Safety* **43** 31-37 <https://nuczu.edu.ua/sciencearchive/ProblemsOfFireSafety/vol44/Hryhorenko.pdf>
- [11] Spirina-Smilka E, Jakovleva R, Saienko N, Dovbish A and Ribka Je 2011 *Problems of Fire Safety* **30** 247-252
- [12] Berezovskiy A 2014 *Visnyk Cherkaskogo derzhavnogo tehnologichnogo universitetu* **4** 66-71 http://nbuv.gov.ua/UJRN/Vchdtu_2014_4_14
- [13] Eremina T Yu, Rob M V and Dmitrieva Yu N 2012 *Fire and Explosion Safety* **21** (7) 52-56
- [14] Hryhorenko O, Mikhailuk A and Zolkina Y 2018 *Fire Safety* **44** 15-19 <http://repositsc.nuczu.edu.ua/handle/123456789/8761>

- [15] Berezovsky A, Maladyka I, Popov Yu, Sayenko N (2012) *Fire safety* **20** 27-31 <https://journal.ldubgd.edu.ua/index.php/PB/article/view/683>
- [16] Buketov A, Maruschak P, Sapronov O, Brailo M, Leshchenko O, Bencheikh L and Menou A 2016 *Mol. Cryst. and Liq. Cryst.* **628** 167-179
- [17] Mostovoi A, Bunenkov P and Panova L 2016 *Inorg. Mater. Appl. Res.* **7** 768-772
- [18] Mostovoi A, Nurtazina A, Kadykova Y and Bekeshev A 2019 *Inorg. Mater. Appl. Res.* **10** 1135-1139 <https://doi.org/10.1134/S2075113319050228>
- [19] Shen J, Huang W, Wu L, Hu Y and Ye M 2007 *Compos. Part A: Appl. Sci. and Manuf.* **38** 1331-1336
- [20] Skrypnyk O and Zolotov S 2011 *Mun. Econ. of Cities* **101** 41-46 <https://eprints.kname.edu.ua/23338/1/41-46%20%D0%A1%D0%BA%D1%80%D0%B8%D0%BF%D0%BD%D0%B8%D0%BA%20%D0%95%D0%A1.pdf>
- [21] Buketov A and Skyrdenko V 2015 *Phys.-Chem. Mech. of Mater.* **51** 43-49 <http://dspace.nbu.gov.ua/handle/123456789/134330>
- [22] Huang P, Zheng S, Huang J, Guo Q and Zhu W 1997 *Polym.* **38** 5565-5571
- [23] Jakovleva R, Popov Yu, Saienko N, Shevtsova K 2007 *Advances in Chemistry and Chemical Technology* **21** 6 (74) 23-28 <https://cyberleninka.ru/article/n/ognebiostoykie-epoksidnye-kompozitsii-dlya-zaschity-drevesiny>
- [24] Danchenko Y, Andronov V, Barabash E, Obigenko T, Rybka E, Meleshchenko R and Romin A 2017 Research of the intramolecular interactions and structure in epoxyamine composites with dispersed oxides *Eastern-European Journal of Enterprise Technologies* **6** (12) 4 <http://journals.uran.ua/eejet/article/view/120998>