



Semnan University

Mechanics of Advanced Composite Structures

journal homepage: <http://MACS.journals.semnan.ac.ir>

Effect of the Nature of Oxide Nanofillers on Changes in the Mechanical Properties of Epoxy Coatings under Thermal Cycling

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KEYWORDS

Coatings;
Epoxy resin;
Mechanical properties;
Thermal properties.

ABSTRACT

The paper demonstrates the applicability of micro indentation as a sensitive method for detecting the effect of the nature of oxides as fillers on the properties of epoxy coatings in comparison with conventional physicochemical methods of infrared spectroscopy (IR) and thermogravimetry (TGA). This applicability was discovered when studying the surface mechanical properties (hardness, elastic modulus, and creep) of epoxy coatings filled with nanoscale oxides TiO₂, SiO₂, and ZnO. The behavior of the mechanical characteristics of the materials under thermal cycling at temperatures ranging from –40 to +60 °C was evaluated by instrumented indentation with the use of a Fischerscope HM system after 5 and 10 cycles. It is shown that the 10% addition of TiO₂ oxide increases the values of hardness and the elastic modulus by 5 and 15%, respectively, while the addition of SiO₂ and ZnO decreases them by 7 and 5%. The micromechanical properties of the studied materials depend on the time of the increase in mechanical loading. All the compositions exhibit viscous properties consisting of hardness decrease with the decreasing rate of loading. Thermal cycling decreases the hardness and elastic modulus of the unfilled epoxy coating and those containing SiO₂ and ZnO by 12 and 18%, respectively, and it ensures the self-restoration of the hardness of the TiO₂-filled coating. All the additives decrease the creep index. Thermal cycling increases the creep index for all the materials under study.

1. Introduction

Organic materials based on epoxy resins are currently key structural materials, and they are widely used in various industries, for example, as a base for polymer coatings [1–3]. However, this type of material is rarely used in a one-component form; most often, different modifying additives improving mechanical, physical, thermal, electrical, and other properties are introduced [3–10]. At the same time, the end-use properties of obtained heterogeneous materials depend on several factors, namely the nature and mass concentration of the additive, the size and distribution of the filler particles in the polymer matrix, the nature of the relationship between the

matrix material and the filler [6–14]. Besides, it is necessary to take into account the effect of the introduced additives on the performance characteristics of the material. Besides mechanical properties, the current trends in material science require the formation of a smart material, which, among other things, is capable of self-healing during operation [7, 15]. This is achieved by encapsulating the active component into an inorganic shell [11, 14–16] or an organic one [15, 17–19], as well as by using organic adhesives capable of a retro-Diels–Alder reaction [20–21].

The self-healing ability of organic structural materials is revealed when characterizing the mechanical properties of modified polymers,

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which are determined on samples subjected to standard tensile, compressive, and bending testing. However, such tests are technically difficult to apply to the determination of the mechanical properties of coatings. In connection with the development of test equipment, coatings have been actively studied in recent years, with the determination of local properties by the indentation method [22–23]. It can be successfully applied not only for testing the mechanical properties of the final material in order to estimate the mechanical properties (elastic modulus, hardness, and creep) of the formed coatings exhibiting, among other things, self-healing ability [24–26] but also for studying organic polymer-based coatings properly. This allows one to reveal the relationship between the structure of the coating material and its performance [27–30]. However, the use of indentation for detecting the phenomenon of material structure self-restoration has yet to be discussed in the literature.

Taking into account the fact that the characteristics of coatings, including protective ones, change under operating conditions (e.g. temperature, strong acids, and bases, mechanical factors, etc.) [31–32], this paper studies the influence of the chemical nature of nanosized TiO₂, SiO₂, and ZnO oxides as fillers on the elastic modulus, microhardness, and creep of the epoxy coating after multiple temperature changes. Due to the difference between the coefficient of linear thermal expansion of the substrate and that of the coating material, the system will experience variable internal stresses; this may eventually change the structure and, as a result, mechanical properties. In case the modifying components are introduced into the polymer material, the different linear thermal expansion coefficients of the additives and the polymer base, as well as specific processes of the molecular interaction of the constituents, can contribute to a change in the properties of the coating under study. At the same time, delicate changes in the interactions of the organic polymer and oxides as fillers cannot be detected using standard physicochemical methods such as infrared spectroscopy (IR), thermogravimetry (TGA), DSC, and XPS analysis. However, the use of the micro indentation method makes it possible not only to characterize the mechanical properties of the coating but also to reveal specific interactions of its constituents and changes in the structure of the material during operation.

2. Materials and Experimental Methods

2.1. Preparation and Characterization of the Epoxy Coatings

Epoxy resin (bisphenol A diglycidyl ether) with 21.1% epoxy groups was purchased from the Sverdlov Plant, FSE, Russia; branched polyethylenimine with an average molecular weight of 25 kDa was purchased from Alfa Aesar, USA; TiO₂, SiO₂, and ZnO nanoparticles were purchased from Sigma-Aldrich, Germany (Table 1).

Specimens made of an AlMg6 aluminum-magnesium alloy plate with a roughness Ra of 0.35 μm were used as the substrate [33].

The adhesive compositions were prepared as follows: the epoxy resin was dissolved in tetrahydrofuran. The corresponding oxide was added to this solution in an amount of 10 wt% in relation to epoxy resin, and the mixture was processed in a ball mill at 25 °C for 4 h. Then, polyethylenimine was added to the composition; the resulting mixture was smeared on the substrate and kept at 25 °C for 24 h. For the specimen with an unfilled epoxy coating, the coating thickness was 123 μm; for the compositions containing oxides, the values are given in Table 1.

Infrared (IR) spectra were recorded on a Nicolet 6700 FT-IR spectrometer (Thermo Scientific) equipped with an attenuated total reflectance (ATR) accessory with a diamond crystal in a range of 4000 to 450 cm⁻¹. Thermogravimetric studies with simultaneous differential thermal analysis were carried out using a TGA/DSC 1 thermal analyzer (Mettler Toledo) with a heating rate of 1 °C · min⁻¹ in argon (60 mL · min⁻¹). The soluble fraction in the cured compositions was determined using hot extraction with acetone [27].

Table 1. Characteristics of the oxides and the coating thickness obtained after their introduction

Modifiers	Purity, %	Particle size, nm	Coating thickness, μm
Titanium oxide (IV), TiO ₂	99.5	21	112
Silicon oxide (IV), SiO ₂	99.5	10-20	216
Zinc oxide (II), ZnO	99.5	<100	98

2.2. Microindentation

Microhardness was determined by instrumented indentation [34] with the use of a Fischerscope HM 2000 XYm automated system for microhardness measurements (Germany). A Vickers tetrahedral diamond pyramid was used as an indenter. Martens hardness HM which takes into account plastic and elastic strains and is applicable to a wide range of materials was studied. Martens hardness [33] is determined as the ratio of the instantaneous value of the test load F to the indenter cross-section area AS at a

distance h (indentation depth) from the apex and calculated by the formula

$$HM = \frac{F}{A_s(h)} = \frac{F}{26.43h^2} \quad (1)$$

The reduced (contact) normal elastic modulus measured by the instrumented indentation method was calculated by the slope of a tangent to the unloading curve according to ISO 14577 1:2002. The elastic modulus of the coating material was calculated by the formula

$$E_{IT} = \frac{1 - (\nu_s)^2}{\frac{1}{E_r} - \frac{1 - (\nu_i)^2}{E_i}} \quad (2)$$

where ν_i is the Poisson's ratio of the tip material (0.07 for diamond); E_i is the elastic modulus of the tip ($1.14 \cdot 10^6$ N/mm for diamond), ν_s is the Poisson's ratio of the test specimen material (the value is supposed to be known). According to our earlier studies [35], composite epoxy materials can be viewed as amorphous and considered to be an isotropic homogeneous viscoelastic medium having experimentally determined mechanical properties. This phenomenological approach enables us to avoid difficulties associated with studying the mechanisms of phase interaction and to describe fairly simply the main features in the behavior of rheological media affected by specified loads. Poisson's ratio can be calculated by the rule of mixtures [36, 37]. According to the resin manufacturer's specifications, the Poisson's ratio ranges between 0.33 and 0.35 for a fully cured resin [38], 0.17 for SiO₂ [39], 0.27 for TiO₂ [40], and 0.358 for ZnO [41]. The calculations made by the rule of mixtures yield that Poisson's ratio ranges between 0.332 and 0.351. This variation is insignificant in processing experimental data of real materials, for which the scatter of properties can be much greater. Therefore, for the PCMs under study, it was assumed that $\nu = 0.35$.

The value of the relative change in the indentation depth was used as a characteristic of the creep of the coating material with a given time of holding and a constant test load,

$$C_{IT} = \frac{h_2 - h_1}{h_1} 100\%, \quad (3)$$

where h_1 is the indentation depth when the test load is reached, which is kept constant from the moment t_1 , mm; h_2 is the indentation depth at the moment t_2 after holding under the load, mm, Figure 1(a).

Two loading conditions were used during indentation, namely triangular and trapezoidal, Figure 1(b), (c). The triangular loading condition (Figure 1(b)) implies a linear growth of loading and unloading with a specified constant time. The trapezoidal loading condition (Figure 1(c)) is

characterized by different holding times t_h under load in combination with constant loading time t_l and unloading time t_u .

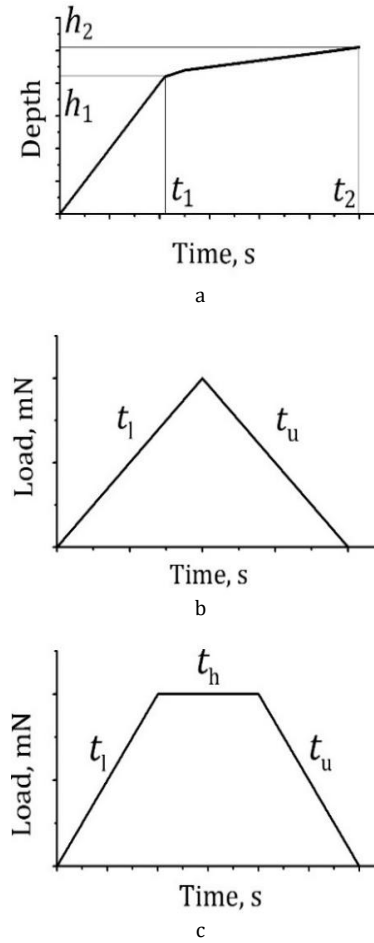


Fig. 1. Loading diagram (a) and loading conditions: triangular (b) and trapezoidal (c)

Hardness was tested under the triangular loading condition, with an unloading time of 20 s; creep was tested under the trapezoidal loading condition.

Indentation was performed at a temperature of 22 ± 2 °C and a humidity of 40%.

In statistics, the standard deviation S responsible for data scattering around the mean value \bar{x} is among the main numerical measurement characteristics. The standard deviation is determined by the formula

$$S = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n}}, \quad (4)$$

where x_i denotes experimentally obtained values and n is the number of observations.

2.3. Thermal Cycling

Thermal cycling testing is performed in order to determine the ability of a product to withstand ambient temperature cycling and to keep its parameters within the prescribed limits

thereafter. In this study, thermal cycling was performed according to GOST 7037 [42]. The cycle used in the study is shown graphically in Figure 2. The specimens were put into a hot chamber, where the temperature was previously brought up to $60 \pm 2 \text{ }^\circ\text{C}$ and held at this temperature for 1 h. Thereafter, they were transferred into a cold chamber, and the time of transfer from one chamber to another was at most 2 min. The specimens were held at a temperature of $-40 \pm 2 \text{ }^\circ\text{C}$ for 1 h. At the end of the cycle, they were taken out of the chamber and held at $20 \pm 5 \text{ }^\circ\text{C}$ for 15 min. The cycle was then repeated. In this paper, specimens after 5 and 10 cycles are studied.

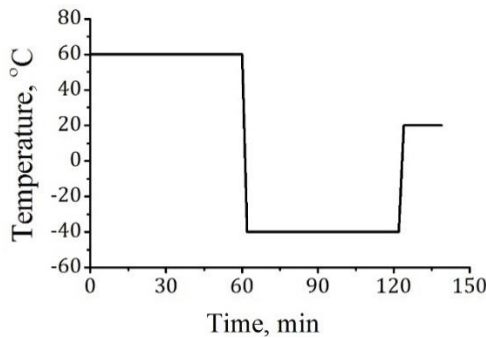


Fig. 2. The behavior of temperature in thermal cycling tests

3. Results and Discussion

3.1. The Hardness of the Coatings in the Initial State

Initially in this study, we methodologically selected the loading parameters at which the obtained experimental data are independent of the indentation conditions. The value of the maximum load was selected in accordance with previous studies [35], and it was 1 N; therefore, only the effect of loading time on hardness was studied. Loading times of 5, 20, 40, 60, 80, and 100 s were considered, with 8 tests being performed for each of them. Figure 3 shows the obtained HM values as dependent on the loading time for specimens with different fillers.

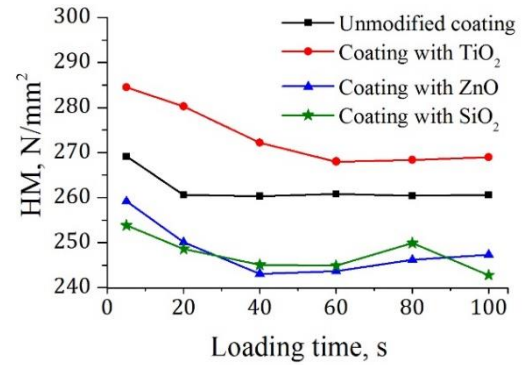


Fig. 3. The effect of loading time on HM values for the modified coatings

With an increase in the loading time to 40 s, a decrease in hardness is observed for all the specimens; namely, HM decreases by 10 N/mm^2 for the unmodified epoxy coating, by 16 N/mm^2 for the coating with TiO_2 , by 12 N/mm^2 for the coating with ZnO , and by 9 N/mm^2 for the coating with SiO_2 . In other words, the coatings exhibit viscous properties. A further increase in the loading time over 40 s has no significant effect on the values of hardness for all the specimens, and HM is within the instrument error. A loading time of 40 s was used in the further study of the coatings.

The values of HM and the normal elastic modulus for the coatings under study are presented in Table 2; Parenthesized values are the standard deviation values obtained by (4).

The introduction of modifying additives changes the hardness of the coatings as follows: the hardness increases for the TiO_2 modifier, and it decreases for the ZnO and SiO_2 additives as compared to the unmodified coating. The situation is a little different for the elastic modulus, i.e., it significantly increases with the TiO_2 additive (15%), remains practically unchanged with the ZnO one (the difference is 1.5%), and slightly decreases with SiO_2 (5.5%). In [43], the effect of these modifiers on an epoxy coating unaffected by temperature was studied more completely.

Table 2. Geometrical characteristics of the specimens

Parameter	Unmodified coating	Coating with TiO_2	Coating with ZnO	Coating with SiO_2
<u>In the initial state</u>				
HM, N/mm^2	260 (1.4)	275 (2.3)	242 (2.6)	245 (2.6)
E_{IT} , GPa	7.3 (0.05)	8.4 (0.07)	7.4 (0.07)	6.9 (0.1)
<u>After 5 thermal cycles</u>				
HM, N/mm^2	235 (3.6)	220 (4.4)	230 (4.2)	230 (3.1)
E_{IT} , GPa	7.2 (0.14)	6 (0.09)	7.1 (0.13)	6 (0.06)
<u>After 10 thermal cycles</u>				
HM, N/mm^2	227 (4.9)	260 (5.4)	230 (5.1)	235 (3.8)
E_{IT} , GPa	6.9 (0.13)	7.9 (0.16)	6.4 (0.15)	6.1 (0.05)

Parenthesized values are standard deviation

From the observed dependence of the coating properties on the composition of the introduced oxide, it is evident that the oxide in the epoxy resin reveals itself not as an indifferent filler changing the material strength properties according to the classical theory of polymer adsorption [44], but as a reactive component forming a certain set of molecular interactions, including covalent interaction [27, 45–46].

3.2. Creep of the Coatings in the Initial State

When studying creep, we evaluated the piece of the indentation curve corresponding to holding under load and recorded changes in the indentation depth. The study was performed with a load of 1 N and a loading time of 40 s. According to previous evaluative research [35], times of holding under loads of 0, 20, 40, and 60 s were considered. Figure 4 presents the average values of C_{IT} for the coatings considered in the paper. In [43], the holding time dependence of the creep index for an epoxy coating with oxide was evaluated in detail.

For the filled epoxy coating, the values of C_{IT} were shown to decrease on average by 15%. The creep of the coatings under load is mostly caused by the polymer base. Presumably due to the low content of oxides in the coating, the modifiers have no significant effect on the creep properties of the polymer.

3.3. Effect of Thermal Cycling on the Coatings

In the third stage of the research, the values of hardness, the reduced elastic modulus, and the creep index were obtained for the specimens after 5 and 10 thermal cycles at temperatures ranging from -40 to $+60$ °C. Table 2 shows the obtained values of HM and E_{IT} as dependent on the number of cycles. The obtained hardness and

elastic modulus values as dependent on the number of thermal cycles were briefly presented in [46]. This study presents a complex analysis of the obtained data and attempts to explain the results.

The hardness values for the unmodified coating after 5 and 10 thermal cycles decrease by 9,6% and 12,7%, respectively, as compared to the HM value for the initial material. A similar situation is observed for the reduced elastic modulus; namely, E_{IT} decreases by 1,4% and 5,5% after 5 and 10 cycles, respectively.

The hardness values for the ZnO- and SiO₂-modified coatings in the initial state are practically identical (differ by 1,2%). After 5 cycles, the values decrease and become identical, 230 N/mm². After the tenth thermal cycle, the HM of the lacquer with ZnO remains unchanged. In turn, after 10 cycles, the HM of the SiO₂-doped coating increases slightly and amounts to 235 N/mm².

The elastic modulus for lacquer with SiO₂ is initially the lowest, it decreases by 13% after 5 cycles and increases only very slightly (by 1%) after 10 cycles. The values of E_{IT} for the unmodified lacquer and the ZnO-doped lacquer in the initial state are practically the same (they are 1% lower for the unmodified coating), they decrease insignificantly after 5 cycles but remain practically equal. After 10 cycles, the elastic modulus continues to decrease, the reduced elastic modulus of the ZnO-doped coating decreases more intensively, and the difference between the E_{IT} values for these materials is 7%.

Thermal cycling significantly affects the coating modified with TiO₂. In the initial state, this coating has the highest hardness of 270 N/mm²; however, after 5 thermal cycles, it is this coating that demonstrates the greatest decrease in hardness, namely by 20%.

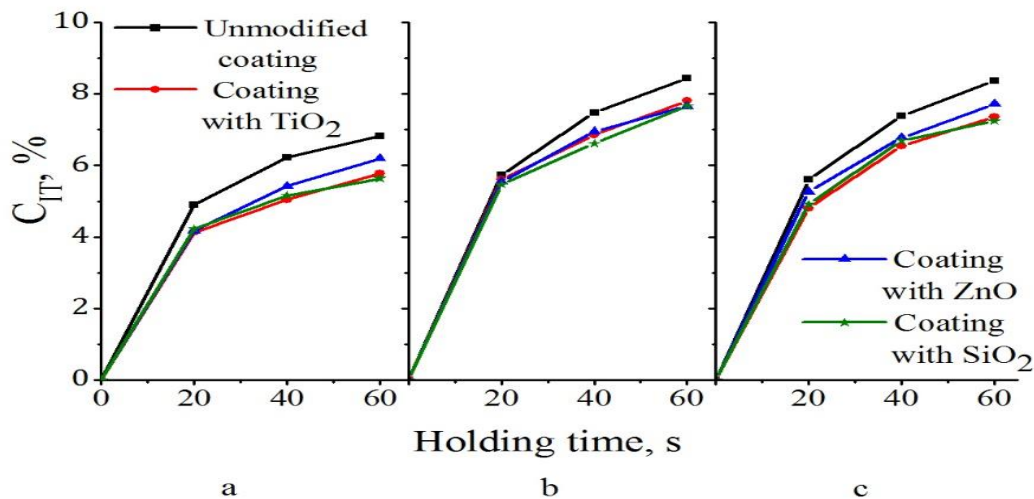


Fig. 4. The values of the creep index for the modified coatings after 0 (a), 5 (b), and 10 (c) thermal cycles

After 10 cycles, the hardness increases to 260 N/mm² and becomes only 5,5% lower than that of the thermally unaffected coating. The situation is the same for the reduced elastic modulus. After 5 thermal cycles, E_{IT} decreases by 28,6%; it increases after 10 cycles to become only 6% lower than that of the initial material, not subjected to thermal cycling. This behavior clearly shows material structuring due to the post-polymerization of epoxy groups and the orientation of macromolecules during their adsorption/desorption on the filler particles under thermal cycling [9, 12, 29, 45]. Taking into account that titanium (IV) is a stronger Lewis acid than silicon (IV) and zinc (II), it can be supposed that, under thermal cycling, titanium oxide actively functions as a structural modifier [46].

The use of FT-IR spectroscopy and thermogravimetry to characterize the structure of coatings does not allow for revealing the specificity of the interaction of epoxy resin with TiO₂ as a filler. It follows from the FT-IR spectroscopy data (Figure 1S) that in the spectra of all the coating specimens there is an absorption band at 915 cm⁻¹, which is indicative of the presence of unreacted epoxy groups. We have failed to determine their amount and to see whether it changes under thermal cycling. According to thermogravimetry (Figure 2S), the presence of an inorganic oxide does not affect the type of decay curves and the heat resistance of the coating.

Experimental determination of the content of the gel fraction, which demonstrates a change in the degree of curing of the coating during thermal cycling, was a production method that confirmed the specificity of the interaction of epoxy resin with TiO₂ as compared to SiO₂ and ZnO. The evaluation of the gel fraction content in the hardened coatings has shown (Table 3) that, in the presence of oxide, the polymerization of the epoxy groups of the resin is almost half as good. However, it is only in the case of TiO₂ that post-polymerization takes place under thermal cycling; it manifests itself as the increasing density of the polymer network and results in the recovery of the coating hardness (Table 2).

Apparently, only TiO₂ can react with epoxy groups to form in situ titanium (IV) alkoxides in the hardened material [47–51], which are effective curing agents for epoxy resins [27, 29, 45]. During thermal cycling, titanium (IV) alkoxides formed on the surface of TiO₂ nanoparticles (Scheme 1, structure 1) promote the reaction of post-polymerization of unreacted epoxy groups (Scheme 1, structure 2), thus increasing the gel fraction content and restoring the coating hardness.

Table 3. Gel fraction content in the hardened coatings as dependent on the number of thermal cycles

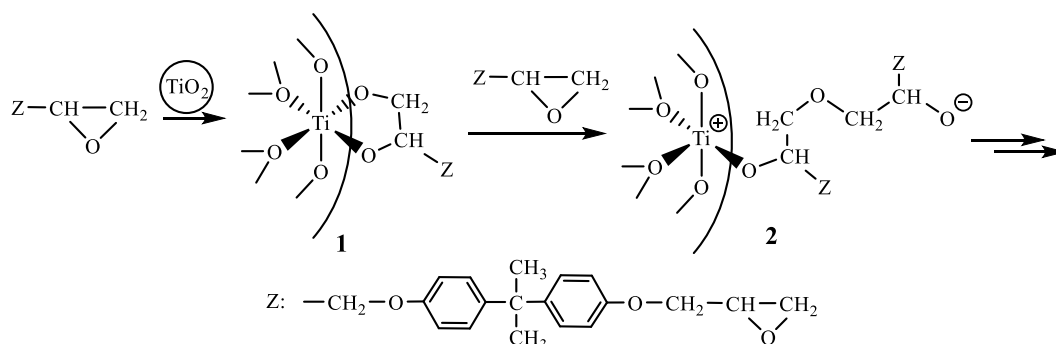
Coating	Gel fraction content, %		
	0 cycles	5 cycles	10 cycles
Unfilled	76.7	77.6	77.1
With 10% TiO ₂	44.7	53.2	58.6
With 10% SiO ₂	48.5	47.8	47.1
With 10% ZnO	46.9	47.8	45.3

The curves showing the behavior of C_{IT} as a function of holding time have a qualitatively identical form for all the specimens after 5 and 10 cycles, Figure 4(b) and (c). This again testifies that the creep of the loaded coatings is mostly caused by the polymer base. At the same time, the numerical values change.

After 5 thermal cycles, the creep values of the unmodified coating and the coatings with ZnO and SiO₂ increase practically for all the holding times by approximately 20%, 26%, and 27%, respectively. After 10 thermal cycles, the values remain unchanged.

A different behavior is observed for TiO₂; namely, creep increases on average by 35% after 5 thermal cycles. After 10 thermal cycles, C_{IT} further decreases by 7% from that of the coating after 5 cycles.

Thus, the obtained experimental data allow us to characterize TiO₂, as compared to SiO₂ and ZnO, as a latent reactive component (rather than an indifferent filler), which, under certain conditions, provides self-recovery of the supramolecular structure and hence of the material properties.



Scheme 1. A possible mechanism of interaction of epoxy resin with the surface of TiO₂ nanoparticles during thermal cycling

The conducted research is an example of the interdisciplinary approach to the preparation and analysis of the properties of filled epoxy polymers. It has demonstrated the effectiveness of micro indentation as compared to standard physical and chemical analysis techniques for identifying the structural features of an organic material and, as a consequence, determining the dependence of its mechanical properties on the composition and structure of the constituents. The standard phenomenological approach to the analysis of the mechanical properties of structural materials ignores both their composition and changes in the chemical structure of molecules under mechanical loads. This significantly limits the ability to understand the influence of the molecular and supramolecular structure of a material on its properties and restricts the possibility of creating new advanced materials.

The application of an integrated approach to testing organic materials, including a simultaneous analysis of the supramolecular structure and operational characteristics, allows one to discover new specific structural and operational effects in systems with known commercial components. This study has exemplified the implementation of this approach and found that TiO₂, as compared to SiO₂ and ZnO, is an active rather than indifferent filler of epoxy resin, which, under certain conditions, provides the effect of self-restoration of the supramolecular structure and hence of the material properties.

The discovered phenomenon in the “nanosized TiO₂ – epoxy resin” system launches a new approach to creating self-healable organic materials based on epoxy resins. In comparison with the methodologies being developed lately, which imply encapsulation of active components, including curing agents, the proposed approach based on specific component interaction preserves simple methods for obtaining organic materials, thus preventing their prices from rising, but expanding the application of their functional potential.

4. Conclusions

Experiments on the thermal cycling of epoxy coatings modified with ZnO, SiO₂, and TiO₂ have revealed that, as distinct from the other modifiers, which cause a continuous decrease in the mechanical properties of the coatings as the number of thermal cycles grows, using TiO₂ significantly restores the hardness and contact elastic modulus of the coating material during micro indentation after 10 thermal cycles.

The analysis of the obtained results, together with the data on the increased content of the gel

fraction, has shown that the restoration of the mechanical properties may be caused by the process of post-polymerization of epoxy groups and orientation of macromolecules during the cycles of their adsorption/desorption on the filler particles under thermal cycling. This is due to the fact that titanium (IV) is a stronger Lewis acid than silicon (IV) and zinc (II). During thermal cycling, titanium (IV) alkoxides formed on the surface of TiO₂ nanoparticles promote the reaction of polymerization of unreacted epoxy groups (scheme 1, structure 2), thereby increasing the gel fraction content and restoring coating hardness and elasticity.

In contrast to the latter properties, coating creep is a property less sensitive to the material structure since the creep curves for all the modified coatings are identical. This must be due to the fact that, despite the decrease in the creep rate with the introduction of oxide fillers, creep is predominantly governed by the polymer base.

The application of a complex approach to testing organic materials, which includes simultaneous analysis of the supramolecular structure and micromechanical properties, reveals new specific structural and operational effects in systems with known commercial constituents; these effects may sometimes fail to be detected by standard methods of physical and chemical analyses.

The established fact of the restoration of the mechanical properties of a TiO₂-containing epoxy coating after thermal cycling testing testifies that the new approach to creating epoxy-based self-healing organic materials, which is based on using the effect of specific interaction of constituents, can be fairly promising.

Acknowledgments

The experimental techniques for studying polymer coatings have been developed according to the research plan of the IES UB RAS, theme AAAA-A18-118020790145-0, and the IOS UB RAS, theme AAAA-A19-119012290116-9. The experiments were performed by means of the equipment of the Plastometriya Shared Research Facilities at the IES UB RAS, Ekaterinburg, and the SAOS Shared Research Facilities at the IOS UB RAS, Ekaterinburg.

Conflicts of Interest

The author declares that there is no conflict of interest regarding the publication of this manuscript. In addition, the authors have entirely observed the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy.

Appendixes

Supplementary information to the manuscript:

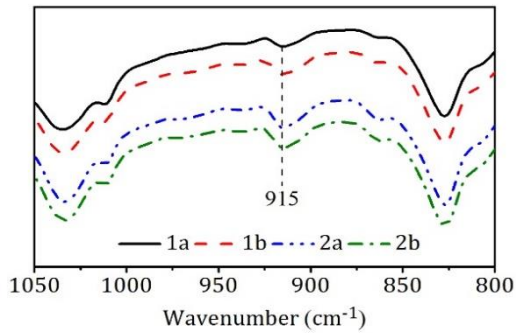


Fig. 1S. The FT-IR spectra fragment of hardened unfilled coating (1) and coating with 10% TiO₂ (2) before thermal cycling (a) and after 10 thermal cycles (b)

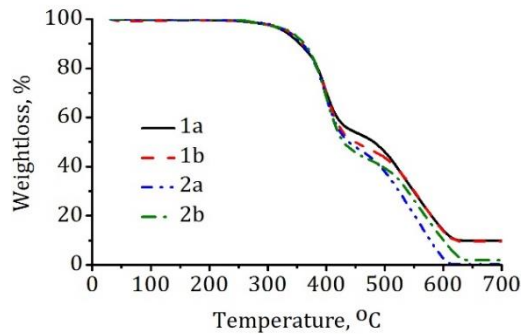


Fig. 2S. Thermogravimetric curves of hardened unfilled coating (1) and coating with 10% TiO₂ (2) before thermal cycling (a) and after 10 thermal cycles (b)

References

- [1] Peerzada, M., Abbasi, S., Lau, K. T. and Hameed, N., 2020. Additive Manufacturing of Epoxy Resins: Materials, Methods, and Latest Trends. *Industrial & Engineering Chemistry Research*, 59, pp.6375–6390.
- [2] Roudsari, G. M., Mohanty, A. K. and Misra, M., 2017. Green Approaches To Engineer Tough Biobased Epoxies: A Review. *ACS Sustainable Chemistry & Engineering*, 5, pp.9528–9541.
- [3] Mousavi, S. R., Estaji, S., Paydayesh, A., Arjmand, M., Jafari, S. H., Nouranian, S., Khonakdar, H. A., 2022. A review of recent progress in improving the fracture toughness of epoxy-based composites using carbonaceous nanofillers. *Polymer Composites*, 43, pp.1871-1886.
- [4] Chen, Q., Chasiotis, I., Chen, C. and Roy, A., 2008. Nanoscale and effective mechanical behavior and fracture of silica nanocomposites. *Composites Science and Technology*, 68, pp.3137–3144.
- [5] Song, K., Polak, R., Zhang, S., Rubner, M. F., Cohen, R. E. and Askar, K. A., 2019. Reversible Self-Healing for Preserving Optical Transparency and Repairing Mechanical Damage in Composites. *ACS Applied Materials & Interfaces*, 11, pp.12797–12807.
- [6] Wichmann, M., Cascione, M., Fiedler, B., Quaresimin, M. and Schulte, K., 2006. Influence of surface treatment on mechanical behaviour of fumed silica/epoxy resin nanocomposites. *Composite Interfaces*, 13, pp.699–715.
- [7] Mousavi, S.R., Estaji, S., Raouf Javidi, M., Paydayesh, A., Khonakdar, H. A., Arjmand, M., Rostami, E., Jafari, S. H., 2021. Toughening of epoxy resin systems using core-shell rubber particles: a literature review. *Journal of Materials Science*, 56, pp.18345–18367.
- [8] Allahverdi, A., Ehsani, M., Janpour, H. and Ahmadi, S., 2012. The effect of nanosilica on mechanical, thermal and morphological properties of epoxy coating. *Progress in Organic Coatings*, 5, pp.543– 548.
- [9] Pinto, D., Bernardo, L., Amaro, A. and Lopes, S., 2015. Mechanical properties of epoxy nanocomposites using titanium dioxide as reinforcement - A review. *Construction and Building Materials*, 95, pp.506–524.
- [10] Keykha, A., 2018. Experimental investigation of the strength of glass fiber-reinforced concrete exposed to high temperature. *Mechanics Of Advanced Composite Structures*, 5(2), pp. 103-113.
- [11] Starkova, O., Buschhorn, S.T., Mannov, E., Schulte, K. and Aniskevich, A., 2012. Creep and recovery of epoxy/MWCNT nanocomposites. *Composites: Part A*, 43, pp.1212–1218.
- [12] Atta, A. M., Al-Lohedan, H. A., El-saeed, A. M., Al-Shafey, H. I. and Wahby, M. H., 2017. Epoxy embedded with TiO₂ nanogel composites as promising self-healing organic coatings of steel. *Progress in Organic Coatings*, 105, pp.291-302.
- [13] Jia, Y., Peng K., Gong, X. and Zhang Z., 2011. Creep and recovery of polypropylene/carbon nanotube composites. *International Journal of Plasticity*, 27, pp.1239–1251.
- [14] Sh., H. Aboubakr, Kandil, U.F. and Taha, M.R., 2014. Creep of epoxy-clay nanocomposite adhesive at the FRP interface: A multi-scale investigation. *International Journal of Adhesion&Adhesives*, 54, pp.1–12.
- [15] Turkenburg, D. H. and Fischer, H. R., 2018. Reversible crosslinking in composite binders - In-situ repair options and recyclability. *Advanced Materials Letters*, 9, pp.861-866.
- [16] Wen, J., Lei, J., Chen, J., Liu, L., Zhang, X. and Li, L., 2020. Polyethylenimine wrapped mesoporous silica loaded benzotriazole with

- high pH-sensitivity for assembling self-healing anti-corrosive coatings. *Materials Chemistry and Physics*, 253, p.123425.
- [17] Danaee, I., Darmiani, E., Rashed, G.R. and Zaarei, D., 2014. Self-healing and anticorrosive properties of Ce(III)/Ce(IV) in nanoclay-epoxy coatings. *Iranian Polymer Journal*, 23, pp.891-898.
- [18] Fadil, M., Chauhan, D.S. and Quraishi, M.A., 2018. Smart Coating Based on Urea-Formaldehyde Microcapsules Loaded with Benzotriazole for Corrosion Protection of Mild Steel in 3.5 % NaCl. *Russian Journal of Applied Chemistry*, 91, pp.1721-1728.
- [19] Mousavi, S.R., Amraei, I. A., 2016. Influence of nanosilica and methyl methacrylate-butadiene-styrene core-shell rubber particles on the physical-mechanical properties and cure kinetics of diglycidyl ether of bisphenol-A-based epoxy resin. *High Performance Polymers*, 28, pp. 809-819.
- [20] Cao, Y., Zhang, J., Zhang, D., Lv, Y., Li, J., Xu, Y., He, K., Chen, G., Yuan, C., Zeng, B. and Dai, L., 2020. A novel shape memory-assisted and thermo-induced self-healing boron nitride/epoxy composites based on Diels-Alder reaction. *Journal of Materials Science*, 55, pp.11325-11338.
- [21] Fang, L., Chen, J., Zou, Y., Xu, Z. and Lu, C., 2017. Thermally-induced self-healing behaviors and properties of four epoxy coatings with different network architectures. *Polymers*, 9, p.333.
- [22] Díez-Pascual, A.M., Gómez-Fatou, M.A., Ania, F. and Flores, A., 2015. Nanoindentation in polymer nanocomposites. *Progress in Materials Science*, 67, pp.1-94.
- [23] Oliveira, G. L., Costa, C. A., Teixeira, S. C. S. and Costa, M. F., 2014. The use of nano- and micro-instrumented indentation tests to evaluate viscoelastic behavior of poly (vinylidene fluoride) (PVDF). *Polymer Testing*, 34, pp.10-16.
- [24] Wang, X. F., Han, R., Han, T. L., Han, N. X. and Xing, F., 2018. Determination of elastic properties of urea-formaldehyde microcapsules through nanoindentation based on the contact model and the shell deformation theory. *Materials Chemistry and Physics*, 215, pp.346-354.
- [25] Vidinejevs, S. and Aniskevich, A., 2017. The system of carbon fibre-reinforced plastics micro-tubes for self-healing of glass fibre-reinforced plastics laminates. *Journal of Composite Materials*, 51, pp.1717-1727.
- [26] Lee, J., Zhang, M., Bhattacharyya, D., Yuan, Y. Ch., Jayaraman, K. and Mai, Y. W., 2012. Micromechanical behavior of self-healing epoxy and hardener-loaded microcapsules by nanoindentation. *Materials Letters*, 76, pp.62-65.
- [27] Pestov, A.V., Osipova, V.A., Koryakova, O.V., Gorbunova, T.I., Smirnov, S.V. and Veretennikova I.A., 2020. Preparation of a New Material Based on Epoxy Oligomers for Forming Corrosion-Protective Coatings. *Russian Journal of Applied Chemistry*, 93, pp.391-396.
- [28] Smirnov, S. V., Veretennikova, I. A. and Konovalov, D. A., 2020. Effect of nanosized oxide fillers on the adhesive strength of epoxy lacquer under scratching. *IOP Conference Series Materials Science and Engineering*, 709, p.044007.
- [29] Pestov, A.V., Kuznetsov, V.A., Mekhaev, A.V., Gorbunova, T.I., Saloutin, V.I., Smirnov, S.V., Vichuzhanin, D.I. and Matafonov, P.P., 2015. Designing new adhesive materials based on epoxy oligomers filled with organic compounds. *Polymer Science, Series D*, 8, pp.149-152.
- [30] Pestov, A.V., Puzyrev, I.S., Mekhaev, A.V., Gorbunova, T.I., Saloutin, V.I., Smirnov, S.V., Vichuzhanin, D.I. and Matafonov, P.P., 2014. Modification of adhesive materials based on epoxy oligomers with fluorinated organic compounds. *Russian Journal of Applied Chemistry*, 87, pp.474-479.
- [31] Wang, X., Li Y., Qian, Y., Qi, H., Li, J. and Sun, J., 2018. Mechanically robust atomic oxygen-resistant coatings capable of autonomously healing damage in low earth orbit space environment. *Advanced Materials*, 30, p.1803854.
- [32] Sousa, J.M., Correia, J.R., Firmo, J.P., Cabral-Fonseca, S. and Gonilha, J., 2018. Effects of thermal cycles on adhesively bonded joints between pultruded GFRP adherends. *Composite Structures*, 202, pp.518-529.
- [33] Smirnova, E.O., Veretennikova, I.A., Smirnov, S.V., Pestov, A.V. and Konovalov, D.A., 2018. Adhesive characteristics of epoxy glue in relation to the microgeometry of the substrate surface. *AIP Conference Proceedings*, 2053, p.030066.
- [34] ISO 14577-1, 2015: *Metallic materials — Instrumented indentation test for hardness and materials parameters — Part 1: Test method. 07.*
- [35] Smirnov, S.V., Veretennikova, I.A., Fomin, V.M., Filippov, A.A. and Brusentseva, T.A., 2019. Studying the viscoelastic properties of an epoxy resin strengthened with silicon dioxide nanoparticles by instrumented microindentation. *Mechanics of Composite Materials*, 55, pp.337-348.
- [36] Fudzii, T. and Dzako, M., 1982. Fracture Mechanics of Composite Materials [in Russian], M., Mir.

- [37] Arefi, M., Bidgoli, E. M.-R., Dimitri, R. and Tornabene, F., 2018. Free vibrations of functionally graded polymer composite nanoplates reinforced with graphene nanoplatelets. *Aerosp. Sci. Technol.*, 81, pp. 108-117
- [38] Saseendran, S., Wysocki, M. and Varna, J., 2017. Cure-state dependent viscoelastic Poisson's ratio of LY5052 epoxy resin, *Advanced Manufacturing: Polymer & Composites Science*, 3:3, p.92.
- [39] Kim, M.T., 1996. Influence of substrates on the elastic reaction of film for the microindentation tests. *Thin Solid Films*, 283, p.15.
- [40] Borgese, Laura & Gelfi, Marcello & Bontempi, Elza & Goudeau, Philippe & Geandier, Guillaume & Thiaudière, Dominique & Depero, Laura E., 2012. 15. Young modulus and Poisson ratio measurements of TiO₂ thin films deposited with Atomic Layer Deposition. *Surface and Coatings Technology*, Volume 206, Issues 8–9, 15 January 2012, pp. 2459-2463.
- [41] Soomro, M.Y, Hussain, I, Bano, N., Broitman, E., Nur, O. and Willander, M., 2012. Nanoscale elastic modulus of single horizontal ZnO nanorod using nanoindentation experiment. *Nanoscale Res Lett.*; 7(1), 146, pp. 2-5.
- [42] GOST 27037, 1986. *Paint materials. Method of determination of stability to temperature changes.*
- [43] Smirnov, S.V., Veretennikova, I.A., Smirnova, E.O and Pestov A.V., 2017. Effect of fillers in epoxy coatings based on the ED-20 resin on the mechanical properties determined by instrumented microindentation. *AIP Conference Proceedings*, 1915, p. 020008.
- [44] Tadros, T. (ed.), 2013. *Encyclopedia of Colloid and Interface Science*. Springer, Berlin, Heidelberg.
- [45] Suvorov A.L., Dul'tseva, L.D., Ovchinnikova, G.I., Khrustaleva, E.A., Ostanina, N.Yu. and Abramova V.I., 2003. Preparation and properties of polymers derived from epoxy resins and oligochelatotitanophenylsiloxanes. *Russian Journal of Applied Chemistry*, 76, pp.1844-1849.
- [46] Hoebbel, D., Nacken, M. and Schidt, H., 2001. On the influence of metal alkoxides on the epoxide ring-opening and condensation reactions of 3-glycidoxypropyltrimethoxysilane. *Journal of Sol-Gel Science and Technology*, 21, pp.177-187.
- [47] Smirnov, S.V., Konovalov, D.A., Veretennikova, I.A., Pestov, A.V. and Smirnova, E.O., 2020. Effect of modifying dopes on the mechanical properties of epoxy coatings affected by thermocycling. *Procedia Structural Integrity*, 25, pp.209–213.
- [48] Zhu, Z., Al-Ajlouni, A.M. and Espenson, J.H., 1996. Convenient Synthesis of Bis(alkoxy) rhenium(VII) Complexes. *Inorganic Chemistry*, 35, pp.1408-1409.
- [49] Simon-Manso, E. and Kubiak, C. P., 2005. A trihydroxy tin group that resists oligomerization in the trinuclear nickel cluster [Ni₃(μ-P,P'-PPh₂CH₂PPh₂)₃(μ₃-L)(μ₃-Sn(OH)₃)], *Angewandte Chemie, International Edition*, 44, pp.1125-1128.
- [50] Dahham, O.S. and Zulkepli N.N., 2020. Robust interface on ENR-50/TiO₂ nanohybrid material based sol-gel technique: Insights into synthesis, characterization and applications in optical. *Arabian Journal of Chemistry*, 13, pp.6568-6579.
- [51] Ochi, M., Wakao, K. and Koujima, K., 2004. Dielectric properties of epoxy/titania hybrid systems. *Journal of The Adhesion Society of Japan*, 40, pp.417-423.