MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

# Epoxy Composites with 10 and 50 wt % Micronanoiron: Strength, Microstructure, and Chemical and Thermal Resistance

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**Abstract**—The strength and resistance of epoxide (ED20 + polyethylenepolyamine)–micronanoiron (R10 or R20) composite systems, which are of interest for machine-building, instrument-making, and aerospace industry, were studied. Introduction of micronanoiron into the epoxy resin allows preparation of iron–epoxy composites without significant changes in the adhesion to steel and in the bending modulus, with only a slight (10–15%) decrease in the compression strength. Filling does not affect the heat resistance of the components (thermal gravimetric analysis) and enhances the flame resistance. The morphology of the composites is characterized by aggregative, relatively uniform distribution of iron particles in the resin. The compression strength increases after heating to 250°C (in contrast to the unfilled polymer). On the other hand, filling slightly weakens the resistance of iron–epoxy composites to aggressive media (with acetone–ethyl acetate mixture and 25% $HNO_3$ as examples). Surface modification of iron particles with acrylic varnish in some cases enhanced both the swelling resistance (with 10% modified R10 iron in contact with water and 25% $HNO_3$ as example) and the strength characteristics (with the bending modulus and compression strength after heating to 250°C as example).

Epoxy composites are used in many metal-demanding branches of industry (automobile-building, ship-building, aerospace, construction, repair industry). Therefore, interest in metal and metal-containing composites will hardly decrease. Micronanoiron is an interesting model filler. It can be expected that its introduction will improve many important properties owing to changes in the morphology and structure of the polymer composite and will give rise to magnetic sensitivity.

Data on composites of polyepoxides with iron and other dispersed metals (copper, aluminum) and their oxides have been reported [1–3]. Commercially efficient materials have been developed, such as, e.g., Cheddar, Moglice, Dichtol [2], Poxipol, and Aviasil. However, the effect of iron powders on polyepoxides is still poorly understood, and there is a broad field for new studies.

This study is a step to understanding changes that occur in the physicochemical and mechanical properties

and in the morphology an epoxy polymer composite after filling with micronanoiron.

## EXPERIMENTAL

The base of the working compound was a mixture of Epoxy-520 resin [Czechian analog of ED20 resin produced in the former Soviet Union, GOST (State Standard) 10587–84] and polyethylenepolyamine (PEPA) curing agent (also produced in Czechia) in 5 : 1 ratio. To check the data, we also used Eposir-740 resin produced in Italy (also an analog of ED20, but with an alkylepoxy diluent preventing from congealing at negative centigrade temperatures).

Micronanoiron of grades R10 and R20 (Yuzhmash, Dnipro, Ukraine) was used in the initial and modified forms. TM El'f acrylic varnish (El'f, Odessa, Ukraine, weight fraction of dry substance about 60 wt %) was used as a modifier; its choice was governed by relatively

**Table 1.** Assignment of some IR bands

| Band (and its analog in our spectra), cm$^{-1}$ | Assignment [2] |
| --- | --- |
| 554(560) | Epoxy polymer (matrix [2]), –CH$_2$– stretching vibrations |
| 574 (574) | Uncured epoxy oligomer, –CH$_2$– stretching vibrations |
| 828 (833) | Polymer, –NH– rocking vibrations |
| 1036 (1040) | Polymer, benzene ring vibrations and CN stretching vibrations |
| 1044 (1043) | Uncured, benzene ring vibrations |
| 1180 (1184) | Polymer, vibrations of amino groups |
| 1254 (1248) | Polymer, vibrations of OH and amino groups |
| 1260 (-) | Uncured, vibrations of epoxy CO groups |
| 1310 (1310) | Polymer vibrations of OH and amino groups |
| 1462 (1457) | Polymer, vibrations of benzene ring |
| 1510 (1514) | Polymer, vibrations of amino groups |
| 1608 (1608) | Polymer, vibrations of primary amino groups |
| 1610 (–) | Curing agent, –CH$_3$C– + –C–C– stretching vibrations |
| 1890 (1888) | Uncured epoxy oligomer, –CH– stretching vibrations |
| 2068 (2068) | Uncured, stretching vibrations of epoxy group |
| 2968 (2964) | Polymer, stretching vibrations of –CH$_2$–, –CH–, –OH, –CH$_3$C– groups |

weak effect that it exerts on the practically important radiotechnical properties of iron.

The composite based on Epoxy-520 resin was filled with micronanoiron of grade R10 (or R20) and was allowed to stand for 1–2 weeks (with intermittent manual stirring) for better wetting and distribution of the filler in the resin. After that, PEPA curing agent was added (1/5 of the resin weight), and the mixture was heated for 1–2 min and manually stirred for 5–10 min. After repeated heating for 1–2 min (to remove surface bubbles), the compound was cast into molds or spread over the surface of plates being glued. Vacuum treatment of the mixed compounds was not performed because of its low efficiency, especially for highly filled samples. After 2–3 days, the cured samples were taken off and heat-treated at 75°C for 2 h to complete the post effects (except the samples for swelling and chemical resistance tests).

To study the strength parameters, we performed tests for compression strength (GOST 4651–68, Shopper press, specimens in the form of cylinders 0.7 cm in diameter and 1.2–1.3 cm high), for break of adhesive joints with a mushroom-shaped steel item (GOST 14760–69, adhesive joint area 5 cm$^2$, UMM-10 machine, Armavir, Krasnodar krai, Russia), and for bending of composite plates (GOST 4648–71, plate size 1 × 5 × 0.2 cm).

In experiments on swelling in a physically aggressive organic medium, we used a 25% nitric acid solution (strongly acidic and oxidizing medium), a 1 : 1 mixture of acetone with ethyl acetate (a model solvent simulating, e.g., nail polish remover), and distilled water. Composite specimens in the form of lens-shaped pellets 7–8 mm in diameter with the height in the middle of 1–2 mm were placed in weighing bottles containing an aggressive liquid and kept there at room temperature (20 ± 2°C).

The IR reflection spectra of cured composite powders were recorded with a ThermoNicolett device without adding KBr.

As seen from the IR reflection spectra of the cured composites, filling leads to changes (enhancement) in the band intensities (Fig. 1). For example, a band at 573 cm$^{-1}$, characteristic of the uncured epoxy oligomer,
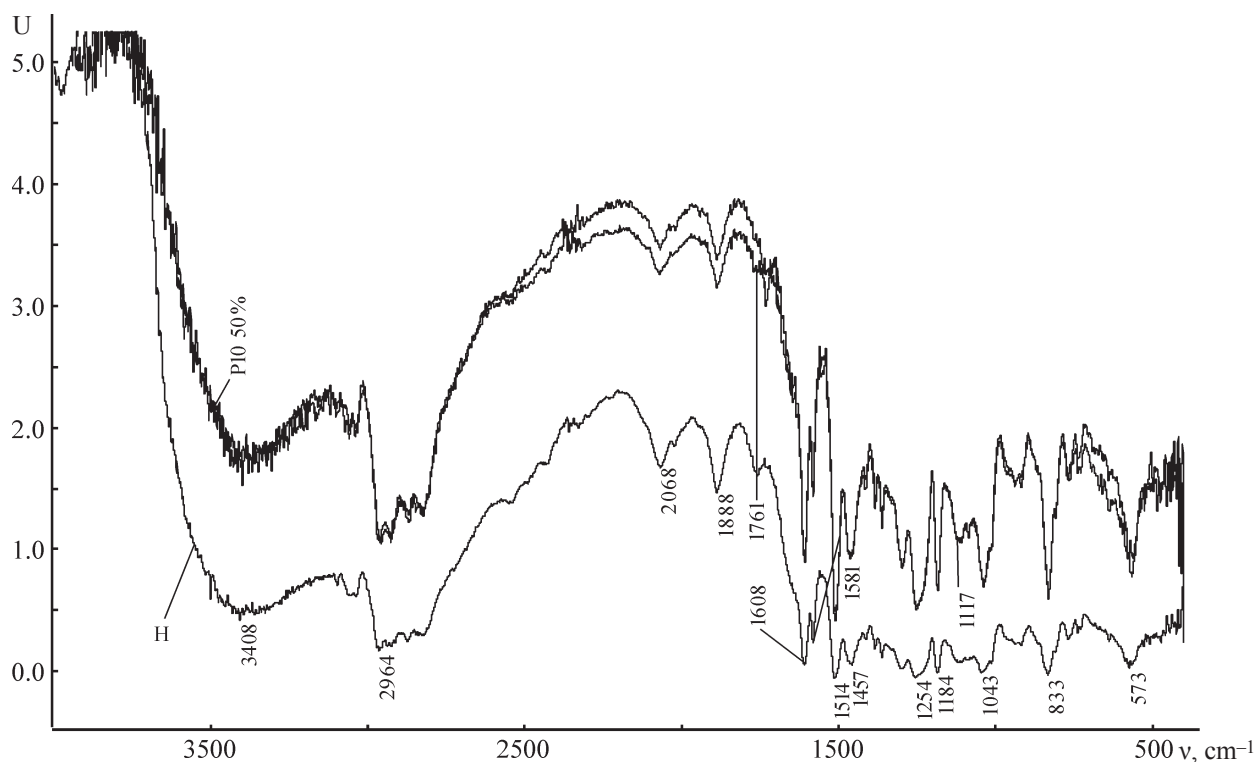
**Fig. 1.** IR reflectance spectrum of unfilled composite (U, lower spectrum) and superimposed spectra of composites with 50 wt % R10 and modified R10 (illustration of their identity). (A) reflectance and (ν) wavenumber.

is clearly seen in the spectrum of the unfilled composite (Table 1). In the spectrum of the iron-filled oligomer, a strong band at 560 cm$^{-1}$, assigned to the polymer, is observed instead. Similarly, the band at 1043 cm$^{-1}$ in the spectrum of the uncured unfilled oligomer is replaced by the band at 1040 cm$^{-1}$ in the spectrum of the polymer (Table 1). The band of the polymer at 833 cm$^{-1}$ becomes considerably stronger in the spectra of the filled composites. The bands of epoxy groups (844, 1260, 1362, 1384 cm$^{-1}$, etc.) are not manifested in the spectra, i.e., curing can be considered to be virtually complete. On the other hand, well-defined bands at 574 and 1888 cm$^{-1}$ and especially bands of epoxy groups at 2068 cm$^{-1}$ (and also weak bands at 2100–2812 cm$^{-1}$) suggest the presence of a noticeable amount of the uncured resin even in the composites, with its fraction decreasing with filling (Table 1).

All these facts show that the filled composite is cured better than the unfilled composite. Some of the bands in the spectrum remain unidentified, e.g., a weak but well-defined band at 1117 cm$^{-1}$, bands at 1761 and 3408 cm$^{-1}$, etc.

**Compression strength.** The compression, tensile, and bending strength values are the main reference characteristics of composites. However, for epoxy composites the tensile strength is poorly informative (because of high brittleness), but the remaining two characteristics furnish important information on the new composite. The compression strength of epoxides is largely conservative: Its 5–10% increase can be considered as appreciable, and 15–25% increase, as significant. A characteristic feature of this parameter is low data variance (3–5% in our case). It also noticeably depends on the specimen treatment conditions; i.e., it significantly changes (as a rule, decreases) after heat treatment at temperatures higher than 100–130°C or after keeping in an aggressive medium.

As seen from Table 2, the yield point somewhat decreases after filling: from 450 kgf for the unfilled composite (U) to 400 kgf for the composite 10% filled with the initial iron (R10, Table 1) and to 360–380 kgf at 50% filling (with R10 or R20). Modification of the iron surface leads to a certain increase in the yield point, to 400–420 kgf (the value decreases as the degree of filling is increased from 10 to 50 wt %, Table 1), but this value is still lower than before filling. That is, 10 and 50 wt % filling with microiron leads to a reproducible decrease in the failure load by 10–15%.

**Table 2.** Experimental strength characteristics of composites

| Filler, wt % | Yield point load, kgf, at compression of cylindrical composite specimens (area 0.38 cm$^2$). Superscipt: final failure limit (if recorded) | B, % relative to U |
|---|:---:|:---:|
| Unfilled | 450$^{450}$ Modulus $E = 8600$ kgf cm$^{-2}$) | 100 |
| R10 iron, 10 wt % | 390$^{530}$ | 87 |
| R10 iron, 50 wt % | 400$^{440}$ (Modulus $E = 7900$ kgf cm$^{-2}$) | 89 |
| R20 iron, 50 wt % | 370$^{430}$ | 82 |
| R10 modified with acrylate, 10 wt % | 400$^{550}$ | 89 |
| R10 modified with acrylate, 50 wt % | 400$^{470}$ | 89 |
|  | After heat treatment at 250°C for 1 h (estimated values) | |
| Unfilled | 420$^{420}$ | 100 |
| R20 iron, 10 wt % | 385$^{410}$ | 92 |
| R10 iron, 50 wt % | 420$^{570}$ | 100 |
| R20 iron, 50 wt % | 390$^{410}$ | 93 |
| R10 modified with acrylate, 10 wt % | 425$^{535}$ | 101 |
| R10 modified with acrylate, 50 wt % | 565$^{590}$ | 135 |
|  | Adhesion to steel (lap shear test), kgf (contact area 3 cm$^2$) | |
| Unfilled | 55 | 100 |
| R20 iron, 10 wt % | 65 | 118 |
| R10 iron, 50 wt % | 60 | 109 |
| R20 iron, 50 wt % | 45 | 82 |
| R10 modified with acrylate, 10 wt % | 55 | 100 |
| R10 modified with acrylate, 50 wt % | 50 | 91 |
|  | Adhesive detachment from steel, kgf (contact area 5 cm$^2$) | |
| Unfilled | 170 (taken as 100%) | |
| R20 iron, 50 wt % | 210 (124%) | |
| R10 modified with acrylate, 50 wt % | 120 (71%) | |
|  | Bending strength: average (maximum obtained) σ, kgf mm$^{-2}$ | Modulus $E_b \times 10^{-3}$ kgf cm$^{-2}$ |
| Unfilled | 7 (7.2) | 24 |
| R20 iron, 10 wt % | 7.1 (7.1) | 24 |
| R10 iron, 50 wt % | 7 (7.6) | 24 |
| R20 iron, 50 wt % | 7 (8.7) | 17 |
| R10 modified with acrylate, 10 wt % | – | 27 |
| R10 modified with acrylate, 50 wt % | 3.8 (4.2) | 30 |
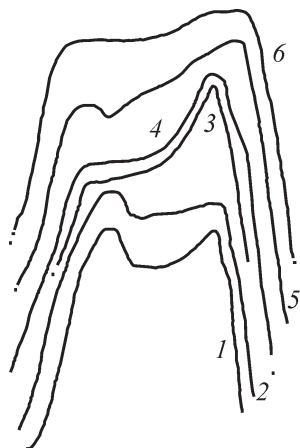
**Fig. 2.** Typical compression diagrams of (*1*, *2*) unfilled polymers and composites with (*3*, *4*) 10 wt % initial and modified R10 microiron, respectively, and (*5*, *6*) with 50 wt % R10 and R20 microiron, respectively.

However, another, and rather valuable, property appears after filling: The composite acquires resistance already after passing the yield point. The final failure limit for U is equal to, or lower than the yield point (Fig. 2), i.e., the polymer does not stand loads above the yield point. However, after filling with all the tested fillers, a well-defined peak of final failure limit appears in the diagram. In contrast to U, this peak is observed at a load considerably higher than the yield point (Table 2, Fig. 2). It is particularly high at 10 wt % filling with R10 iron or with its modified form. This fact means that

the composite after filling can stand considerably higher loads even after the yield point is exceeded. This is important for practice, namely, for the industry of highly loaded composite parts. For example, in automobile and aviation industry and service it is critically important that a part should continue to operate even after its primary deformation (e.g., when prompt repair is impossible). Composites with micronanoiron filler do acquire such property, although their yield point for them is slightly lower than that of the unfilled polymer.

It can also be seen that, after filling, the distribution of the parameters obtained is often more uniform than for U (which is seen from small difference between the maximal and average values of the yield point *F*), especially at high filling (50 wt %).

Figure 3 clearly shows that the composite prepared under common conditions (including heat treatment of the cured samples at 80°C) after 10 and 50 wt % filling with all the kinds of microiron (including modified powder) is characterized by reproducible small decrease in the compression strength. However, an interesting fact is observed: After heat treatment under severe conditions (250°C, limiting temperature for common epoxy items), the filled specimens, in contrast to the unfilled sample, become stronger (Fig. 3, Table 2). The unfilled specimen not only loses strength (Table 2), but even acquires dark color (which suggests partial degradation). The extent of strengthening at optimum iron modification and optimum filling percent can be
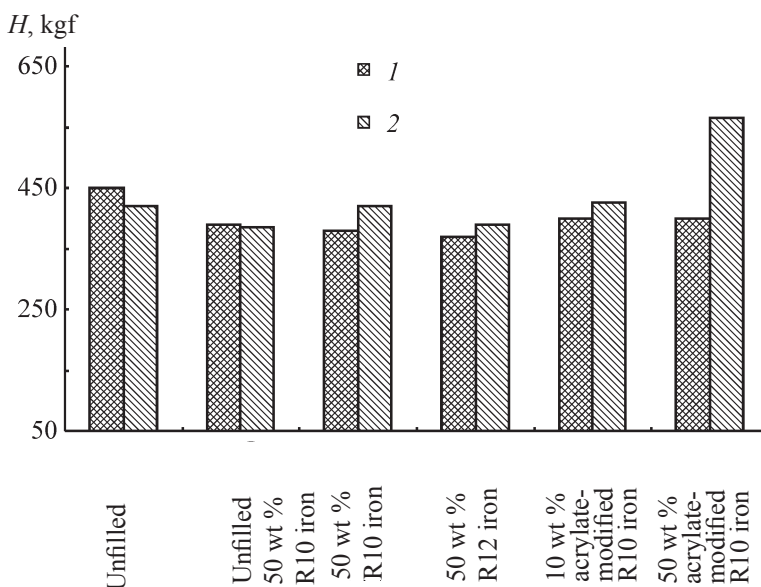


**Fig. 3.** Failure load *H* in compression of cylinders made of the composites. Compression (*1*) without heat treatment and (*2*) after heating at 250°C for 1 h.
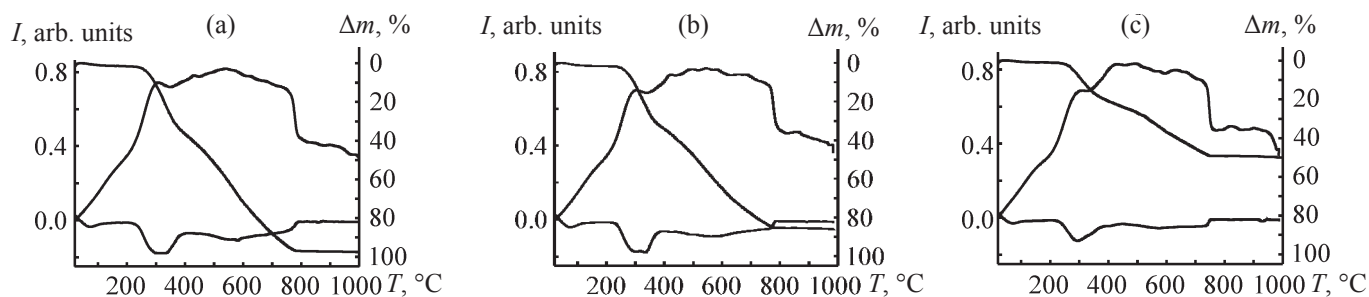
**Fig. 4.** Thermograms of samples: (a) unfilled, (b) with 10 wt % iron, and (c) with 50 wt % iron. (*I*) Intensity, ($\Delta m$) weight loss, and (*T*) temperature.

very high, which makes micronanofiller promising for composites subjected to thermal loads. For example, for the composite with 50 wt % modified R10 we observe a 50% increase relative to the initial filled polymer and more than 20% increase relative to the unfilled polymer. The strength of virtually all the filled samples increased, as seen from the increase in the compression load by 5–10% and sometimes to an even greater extent (for the composite with 50 wt % modified R10, by 30%). This fact shows that filling with micronanoiron is promising for making heat-resistant composites and adhesive joints.

**Adhesion to steel: detachment and shear tests.** As seen from Table 2, introduction of the initial R10 iron leads to an appreciable increase in the strength of detachment from steel and can somewhat increase (by 10–20% at 10 wt % filling) the lap-shear strength; i.e., iron particles somewhat improve (which seems quite natural) the compatibility of the resin with the steel surface. However, the adhesion decreases after modification of iron powder with acrylate. Probably, filler aggregates with a surface film preventing adhesive contact with the steel surface are formed in the resin.

**Thermograms:** The effect of iron is insignificant. Thermograms of samples without iron and with 10 wt %

R10 iron are virtually identical and differ only in the amount of the unburned residue (Fig. 4). For the 50% filled sample, the weight loss is almost 50%, because iron does not burn out at temperatures lower than 1000°C. Thus, the effect of iron on the general course of thermal oxidative degradation of the polyepoxide is insignificant.

**Flame resistance** is enhanced with filling. This trend itself is quite expected, but the magnitude of the effect is very large. The flame resistance increases by a factor of 1.5–2 and sometimes to an even greater extent (Table 3). With increasing filling, the flame resistance is enhanced, and self-extinction in the initial and middle steps of ignition is observed, which is an important property. That is, the initial micronanoiron shows promise as fire-retarding filler for epoxies. With iron subjected to surface modification, the final composite loses its self-extinction property (Table 3).

**Swelling.** The water absorption of composites under ambient conditions (at the temperature in the range $20 \pm 5$°C) is characterized by nonmonotonic growth (Fig. 5). Generally speaking, the composite with unmodified iron shows the dynamics similar to that of the unfilled composite. Modification allows the water absorption in the course of 1-month contact to be somewhat reduced.

**Table 3.** Flame resistance (seconds to ignition) and combustion character (self-propagation or self-extinction) of $1 \times 5 \times 0.2$ cm plates of composites (ignition with a lighter from the corner)

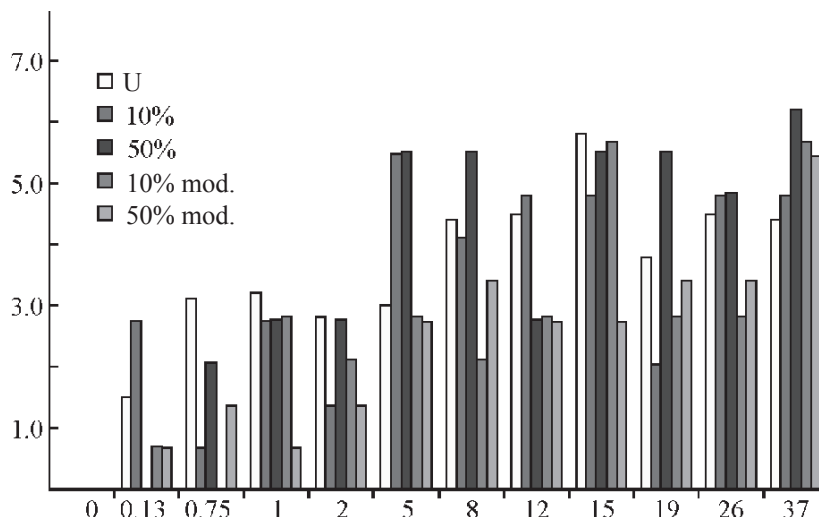| Parameter | Unfilled composite | 10 wt % R10 | 50 wt % R10 | 50 wt % R10 no. 2 | 50 wt % R20 | 10 wt % R10 modified | 50 wt % R10 modified |
|---|---|---|---|---|---|---|---|
| Ignition time, s | 2.5 | 3 | 4.5 | 4 | 3.5 | 3 | 4 |
| Combustion character | Self-propagation | Self-propagation | Self-extinction | Self-extinction | Self-extinction | Self-propagation | Self-propagation |
| Time to self-propagation, s | – | – | 5 | 4.5 | 4 | | |

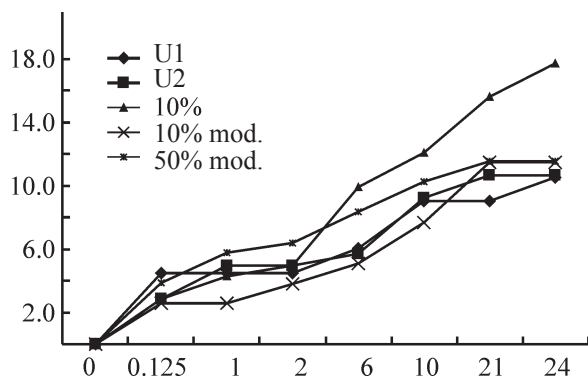**Fig. 5.** Histogram of swelling in water for samples with different content of R10 microiron.



**Fig. 6.** Plots of swelling in 25% HNO₃ for unfilled samples (U1, U2) and of samples with R10 micronanoiron.

As nitric acid readily reacts with microiron, the composite could be expected to have decreased resistance to nitric acid. However, this decrease was not always significant. Surface modification of iron can even temporarily decelerate the swelling at certain degrees of filling (e.g., with 10% modified R10, Fig. 6).

As seen from Table 4, introduction of dispersed iron, on the whole, does not enhance the resistance to swelling in a very aggressive acetone-containing organic solvent (major component of nail polish remover). Deceleration of swelling is observed only with 10 wt % initial R10 iron; in the other cases, swelling is accelerated. Iron filling also does not prolong the life of the composite in an acetone mixture: The life does not exceed 1 day (Table 4), after which the samples crack and disintegrate.

**Morphology of composites and microiron distribution.** The distribution of the initial dispersed iron in the compound is relatively uniform. The suspension contains a certain amount of agglomerates of up to 0.2 mm size and rare air bubbles (surrounded by microparticles). Both the distribution density and the size of

**Table 4.** Swelling dynamics of samples with R10 iron in an acetone–ethyl acetate mixture

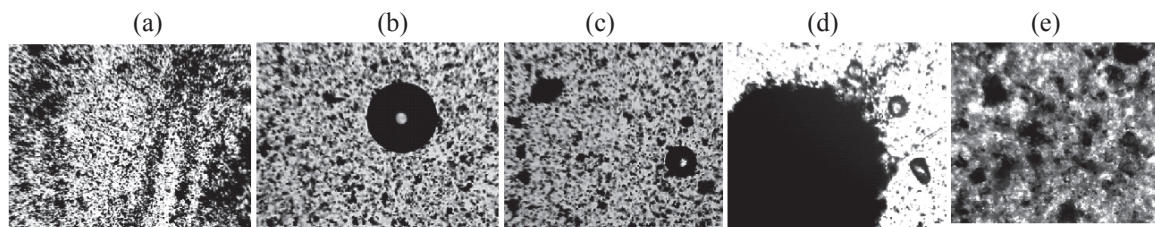| Time, days | Swelling, % | | | | |
|---|---|---|---|---|---|
| | unfilled composite | 10 wt % R10 | 50 wt % R10 | 10 wt % modified R10 | 50 wt % modified R10 |
| 0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 0.04 | 6.6 | 6.8 | 2.8 | 7.5 | 1.8 |
| 0.17 | 13.2 | 8.7 | 10.2 | 10.8 | 10.9 |
| 1 | 15.7 | 12.6 | 17.6 | 16.7 | – |
| Drying for 2 days | 7.4 | 6.8 | 7.4 | 9.2 | – |

**Fig. 7.** Photomicrographs of compounds before curing (magnification 50–100): (a–c) with unmodified and (d, e) with modified R10.
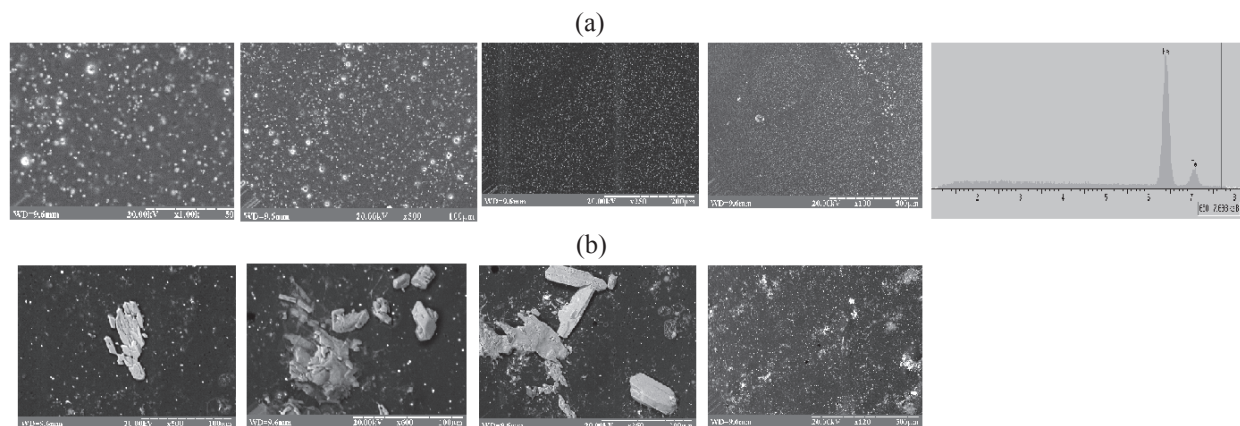


**Fig. 8.** SEM images and X-ray spectrum of samples of epoxy polymer with iron. (a) Epoxy polymer with 50 wt % unmodified R10 micronanoiron (right image: X-ray spectrum of the filler) and (b) epoxy polymer with 50 wt % R10 micronanoiron modified with 7 wt % water-thinnable acrylic varnish.

heterogeneous regions increase with increasing concentration (Fig. 7).

After iron modification, separate dense regions (aggregates, Figs. 7d, 7e) in the suspension become noticeable. They can reach large size; i.e., after the modification the tendency of particles to self-agglutination is enhanced, and the particle aggregation changes. On the other hand, the particle distribution in the compound is also relatively homogeneous.

Differences in the structure of the composites are clearly seen in Fig. 8. Unmodified iron gives approximately uniform distribution. Aggregates are also present (micrographs were taken with a step of 500 μm) and are apparently concentrated at the boundaries of polymer domains. Only the signals of pure iron are seen in the spectrum. For the epoxy polymer with modified iron, ordered formations weakly bonded with the structure can be seen (Fig. 8). The spectrum of this composite reveals the presence of potassium ions, i.e., the formations may correspond to crystals of a potassium salt (apparently, an additive to the acrylic varnish). The same structures are probably responsible for changes (in particular, decrease) in some characteristics of the polymer after modification.

## CONCLUSIONS

(1) Introduction of micronanoiron can be efficient for preparing specialty composites (with magnetic or electrical properties) without serious deterioration of such important parameters as strength and chemical resistance.

(2) The compression strength of the composites decreases by 10–15% after filling. However, epoxy–iron composites have an important property: After heat treatment under severe conditions (250°C), the strength increases, in contrast to the unfilled composite (for which it decreases). At optimum modification of the iron surface, it can increase by approximately 25% relative to the unfilled composite. That is, micronanoiron shows promise for making heat-resistant coatings.

(3) The adhesion to steel (at lap shear and detachment) and the thermal degradation pattern of the composite do not change significantly relative to the unfilled polymer.

(4) The water and acid (with 25% $HNO_3$ as example) resistance change insignificantly after filling. Optimum modification of iron allows the water absorption to be somewhat decreased and the dynamics of swelling

in acid to be somewhat decelerated. Introduction of dispersed iron, on the whole, does not enhance the resistance to swelling in an acetone-containing solvent.

(5) Introduction of micronanoiron enhances the flame resistance of the composite, especially when unmodified R10 iron is introduced in an amount of 50 wt % (when the composite acquires the ability for self-extinction). SEM examination shows that the iron distribution is approximately uniform, but agglomerates of up to 1 μm size (and, more seldom, of 2–3 μm size) are also seen.

## ACKNOWLEDGMENTS

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