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Investigation of superhigh-frequency treatment influence on structuring of epoxy composites by infrared- and electron paramagnetic resonance spectroscopy analyses

P.D.Stukhlyak, O.S.Holotenko, R.Z.Zolotyi, A.G Mykytyshyn

Department of Computer - Integrated Technologies, Ternopil I.Puluj National Technical University, 56 Ruska Str., 46001 Ternopil, Ukraine

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The regularities of the rate of physical-chemical processes during the formation of epoxy binder are determined. Infrared (IR) and electron paramagnetic resonance spectral analyses of epoxy composites filled with dispersed particles and modified by superhigh-frequency electromagnetic field were carried out. The mechanism of interaction of the matrix with filler particles of different dispersion and nature has been substantiated.

Keywords: epoxy composite, interaction mechanism, IR spectral analysis, structure, disperse filler, polyethylene polyamine.

Дослідження впливу НВЧ-обробки на структурування епоксикомпозитів аналізом ІЧ- та ЕПР-спектроскопії. *П.Д.Стухляк, О.С.Голотенко, Р.З.Золотий, А.Г.Микитишин*

Встановлено закономірності перебігу фізико-хімічних процесів при формуванні епоксидного зв'язувача. Проведено ІЧ- та ЕПР-спектральний аналіз епоксидних композитів, наповнених дисперсними частками і модифікованих надвисокочастотним електромагнітним полем. Обгрунтовано механізм взаємодії матриці та часток наповнювача різної дисперсності та природи.

Установлены закономерности течения физико-химических процессов при формировании эпоксидного связующего. Проведено ИК- и ЭПР-спектральный анализ эпоксидных композитов наполненных дисперсными частицами и модифицированных сверхвысокочастотным электромагнитным полем. Обоснован механизм взаимодействия матрицы и частиц наполнителя различной дисперсности и природы.

1. Introduction

At the current stage of industry development, the problem of creating new metal- and energy-saving materials for improving the operational characteristics of machinery and machines is an important task of modern material science. The development and application of composite materials (CM) based on epoxy resins possessing a complex of valuable properties is perspective in this direction. It is known that CMs in most cases are used in filled form [1–3]. The use of fillers and plasticizers makes it possible to change the technological and operational properties of the material. At the same time, electrophysical methods of processing materials to obtain products with the introduction of fillers are being intensively studied. It is quite effective to use the energy of superhigh-frequency (SHF) electromagnetic oscillations [4, 5].

The main purpose of the investigation is to establish the basic regularities of the effect of SHF electromagnetic field on the processes of structure formation of polymer-composite materials filled with particles of different nature.

2. Experimental

Epoxy diane oligomer ED-20 was chosen as the main component for the binder in the formation of CM. Materials based on ED-20 are characterized by high specific physical-mechanical characteristics, insignificant shrinkage, high adhesion and cohesive strength, processability while applied to long-dimensional surfaces of a complex profile, a developed raw material base in Ukraine. For cross-linking epoxy compositions, polyethylene polyamine hardener is used which ensures the formation of materials at room temperature. Different stages of cross-linking are modeled and investigated by introducing the hardener into the composition at the content of 8–12 weight part per 100 weight part of ED-20. The technology of CM formation consists of the following steps: dosing of components; hydrodynamic combination of plasticizer and epoxy diane resin ED-20 to obtain the homogeneous mixture; heat treatment of the mixture during the time $\tau = 4.0 \pm 0.1$ h at the temperature $T = 393 \pm 2$ K; cooling to the temperature $T = 393 \pm 2$ K; introduction of the hardener; solidification of the composition. The CM is consolidated according to the experimentally established mode: the formation of specimens and their exposure for 2 h at a temperature of 293±2 K; heating to a temperature of 393±2 K at a rate of $V =$ 3 deg/min; an exposure for $\tau = 2.0 \pm 0.05$ h; slow cooling to a temperature of 293±2 K. For stabilization of the structural processes in the matrix, the samples are kept for 60 h in the air at a temperature of 293±2 K, followed by experimental testing. Silicon carbides (SiC) and boron (B_4C) and red mud (RM) are used as fillers for experimental investigations. Selected fillers with the particle size of 60–65 μm (SiC, B_4C) and 10 μm (RM) are characterized by high strength, hardness and modulus of elasticity. The optimum content of the filler is $q = 30$ parts by weight [6].

SHF irradiation is carried out at the preliminary stage of the material formation (before the introduction of the hardener), providing more intense physicochemical processes at the interphase boundary during the formation of CM [6, 11]. The SHF treatment of epoxy compositions is carried out using a developed SHF emitter with a power of 600 W in a multimode mode with a frequency of $f = 2450$ MHz, at a wavelength of 0.1225 m, an operating voltage of 220 V, and a current of 50 Hz. The duration of irradiation of the compositions (ithout introducing the hardener) is $t = 0–60$ s with an interval of 5 s. The mass of the irradiated compositions is $m = 200 \pm 10$ g. A thin layer of the composition with a thickness of $h = 25...30$ mm is irradiated. The layer thickness was chosen experimentally. An increase in the thickness of the irradiated layer over 30 mm leads to uncontrolled heating of the composition, which results in destructive processes in the binder: the destruction of the main chain of the macromolecule was confirmed by IR spectral analysis.

The analysis of IR spectra is carried out in accordance with the Lambert-Baire law, taking into account the value of the transmittance (T, %) and the half-width (b) and the area (S) of the absorption bands in the spectrum. The interpretation of the IR spectra was carried out according to the methods [7, 8]. The IR-spectra are recorded using a spectrophotometer "IRAffinity-1" (Japan) in the range of wave numbers $\nu = 400...4000$ cm^{-1} by a single-beam method in reflected light. Spectrum scanning in the range of selected wave numbers $\lambda - 1 = \nu$ is carried out on a diagram in the range of 225 mm. Wave numbers, transmittance, half width and bandwidth were determined using the IRsolution program. The error in determining the wave number is $\nu = \pm 0.01$ cm^{-1}; the accuracy of determining the position of the peak is $\nu = 0.125$ cm^{-1}. The photometric accuracy is ±0.2 % with software slot control and integration time $t = 10$ s. The integration step is $\Delta\lambda = 4$ cm^{-1}. We carried out the IR-spectral analysis of composites with different contents of particles. The material was pre-crushed, dried at a temperature of $T = 373 \pm 2$ K for $t =$ 20 min, mixed in an agate mortar with KBr powder; then, on a hydraulic press with the load $\sigma = 20$ MPa, the samples were formed in the ratio: the test material — 1 mg, KBr — 300 mg. EPR-spectra of the materials are investigated according to the method described in [10].

3. Results and discussion

The IR-spectral analysis of the filled CM made it possible to determine the change of the following parameters: transmittance intensity (T, %), half width (b, cm^{-1}) and area (S, %) of the absorption bands characterizing different degrees of crosslinking in the binder. This is due to the peculiarities

of the interaction of filler active centres with macromolecules and segments of the epoxy oligomer.

At the first stage, the regularities of physical-chemical processes during the formation of epoxy matrices were determined (Fig. 1). The IR-spectral analysis make it possible to establish the fact, that the absorption bands in the range of wave numbers $\nu = 420.48...474.49$ cm^{-1} correspond to oscillations of -CH_2-groups. The absorption band at a wave number of $\nu = 829.39$ cm^{-1} corresponds to the pendulum -NH-, -CH-, valence -C–C- oscillations, primary CH_2–NH_2, CH–NH_2 amino groups and epoxycycles. At the same time, the minimum transmittance intensity, which is $T = 18.7$ %, with a half width of $b = 21.9$ cm^{-1}, characterizes the matrix modified by SHF electromagnetic treatment with a processing time of 30 seconds, which indicates an increased degree of crosslinking. Also, an increase in the indicators of physical, mechanical and thermophysical properties of the material was determined [4, 6]. Absorption bands at $\nu = 729.09$ cm^{-1} and $\nu = 767.67$ cm^{-1} found in all investigated matrices, correspond to the pendulum oscillations of -CH-, -NH-groups and a primary amino group -NH_2. An absorption band was also found at $\nu = 1246.02$ cm^{-1} (Fig. 1), indicating deformation oscillations of -OH-groups, valence oscillations of -C–O-, -C–N, the presence of epoxy groups and secondary -NH–R and tertiary -N–R2 amino groups. An absorption band at $\nu = 1732.08$ cm^{-1} corresponds to double bonds of -C=C-, -C=N- and -CO-groups. At the same time, the smallest transmittance intensity $T = 13.3$ % with a half width of $b = 38.9$ cm^{-1} is characteristic for the matrix modified by SHF electromagnetic field for 30 s (Fig. 1, spectra 3–4). An increase in the indicators of physical, mechanical and thermophysical properties is expected. In addition, the presence of absorption bands in the frequency range of $\nu = 3552.88...2870.08$ cm^{-1} indicates the presence of -CH- and hydrogen -OH-groups, the maximum number of which is detected for a matrix modified by SHF electromagnetic field for 30 seconds (Fig. 1, spectrum 3).

The next step was to use the method of IR spectral analysis to determine the regularities of the physicochemical processes of structure formation of epoxy composites filled with dispersed particles after SHF treatment. Preliminarily, IR-spectral analysis was carried out for composites filled with dispersed particles of red mud with a dispersion of 5...10 μm in a content of $q = 30$ parts by weight. The lowest intensity and half-width of the absorption band (Fig. 2, spectra *2* and *3*) was observed at $\nu = 829.39$ cm^{-1}, that is characteristic for -CH_2- and alkenes C=CH_2-groups. At the same time, the lowest intensity and half-width of the absorption band (with respect to the matrix modified by SHF field for 30 s), with the wave number $\nu = 829.39$ cm^{-1}, is characteristic for a composite modified by SHF for 30 s. The high degree of crosslinking of the modified material compared to the original improves the physical-mechanical properties of CM [6, 12]. It should also be noted that the intensity of absorption bands and their half-width in the IR spectrum of CM (relative to modified matrices, Fig. 1) decreases in the frequency range $\nu = 2363.83...1890.24$ cm^{-1}. This is typical for triple bonds of -C≡N-. The lowest transmittance intensity is characteristic for CM filled with RM previously modified by SHF electromagnetic field for 30 s. The obtained results indicate an improvement in the interaction of the binder components with filler particles during crosslinking and, as a consequence, an increase in the adhesion and physical-mechanical properties of CM, in particular, adhesion strength, residual stresses, destructive bending stress, flexural modulus, impact strength [6, 12].

Significant transformations are found in the frequency range $\nu = 3745.76...2870.08$ cm^{-1}. Displacement of absorption bands relative to the matrix (valence oscillations -CH-, methyl -CH_3–C and methylene -CH_2-groups) towards larger wave numbers ($\nu = 2931.80$ cm^{-1}) by $\Delta\nu = 3.86$ cm^{-1} was revealed. At the same time, the lowest transmittance $T = 7.8$ %, with the half width $b = 14.9$ cm^{-1} is characteristic for CM filled with RM and previously treated by SHF electromagnetic field for 30 seconds (Fig. 2, spectrum *2*).

It has been proven that the increased degree of crosslinking of the filled CM is the result of structural transformations due to SHF treatment. When comparing the IR-spectra of the filled CM with matrix spectra, the displacement and reduction of absorption bands in the range of wave numbers $\nu = 3552.88...3414.00$ cm^{-1} characteristic for -OH- and -NH groups is revealed. This indicates the increased degree of crosslinking in the investigated CM relative to the matrices.

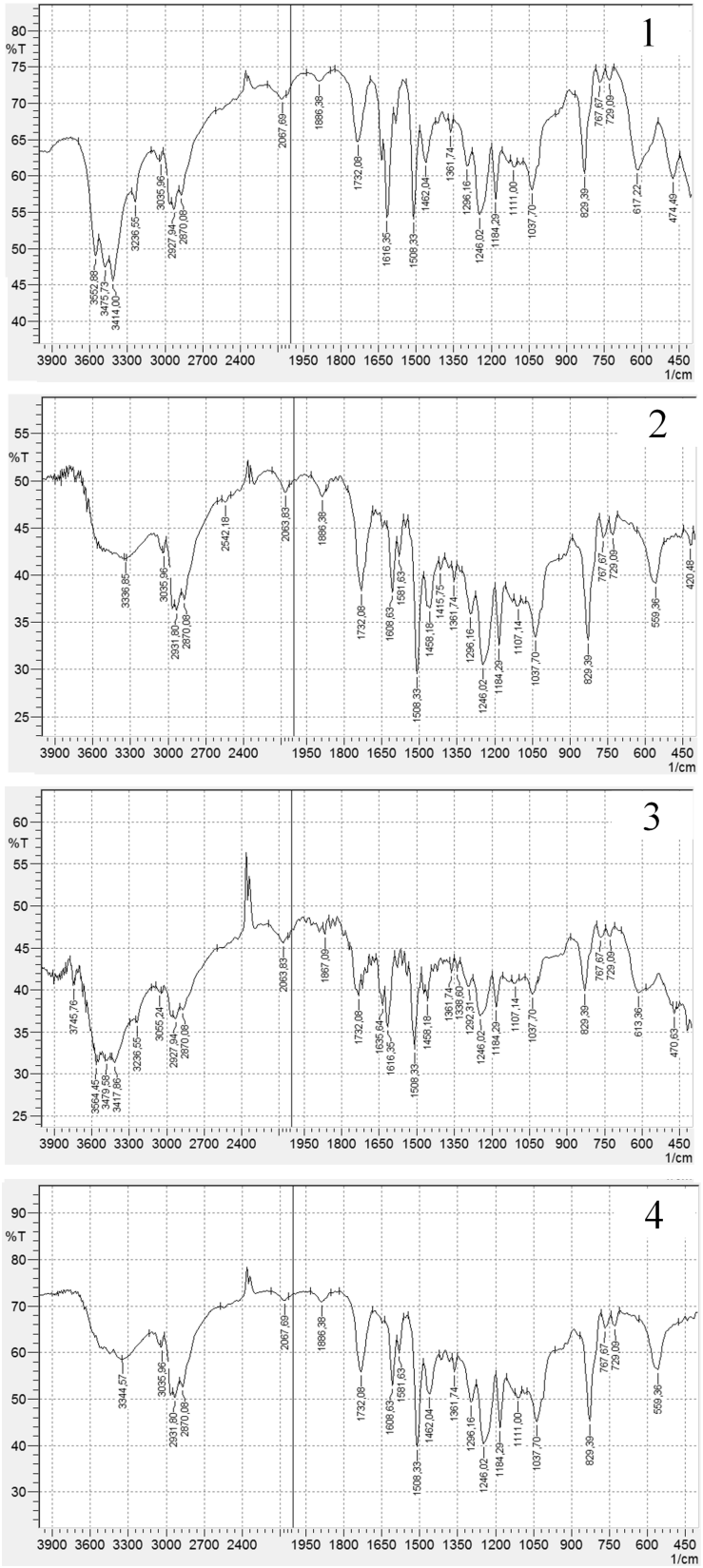

Fig. 1. Infrared spectra of initial and modified epoxy matrices: *1* — matrix (control sample); *2* — matrix without treatment; *3* — matrix treated by SHF electromagnetic field (30 s); *4* — matrix treated by SHF electromagnetic field (60 s).

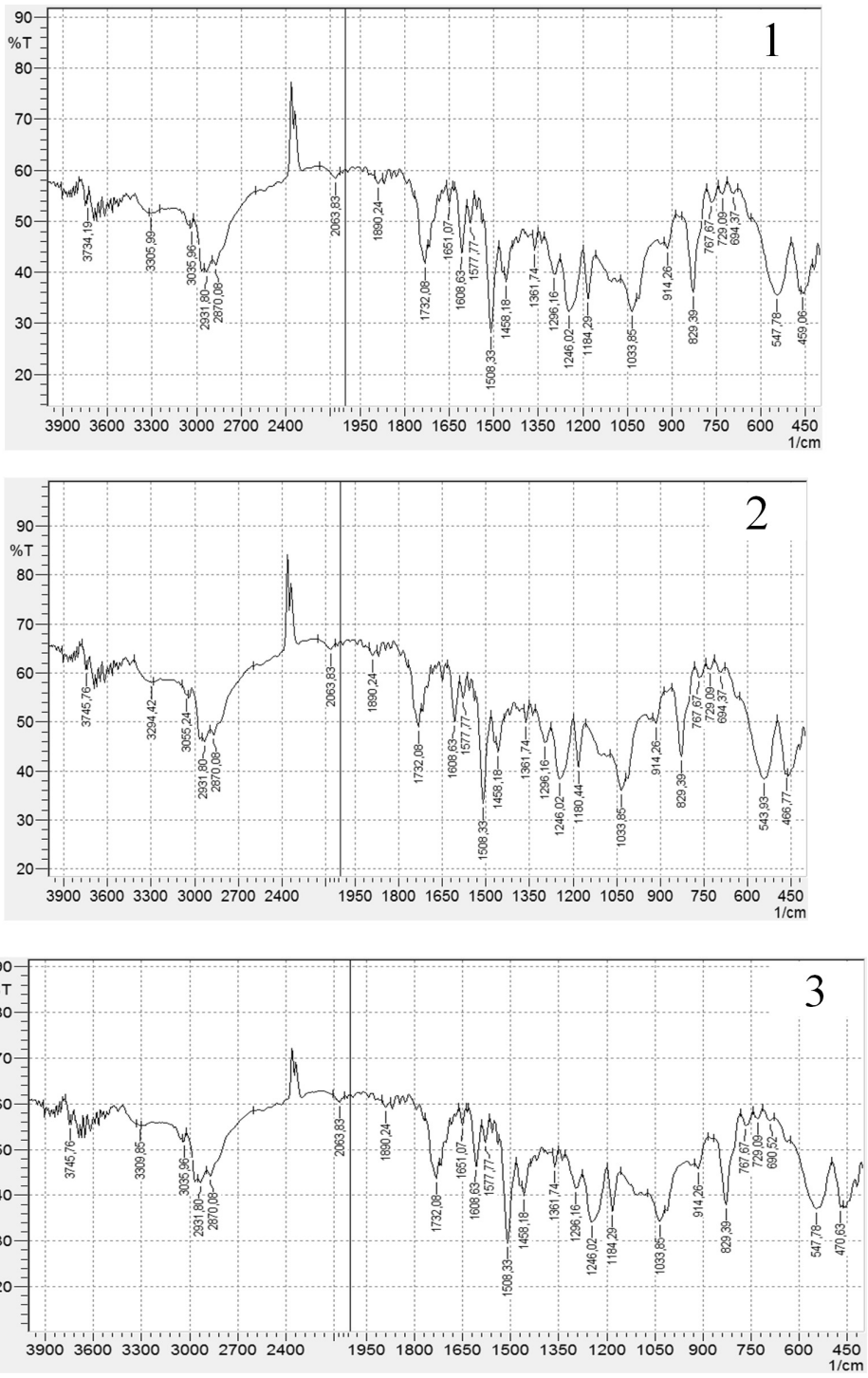

Fig.2. IR-spectra of composites with RM particles, modified by SHF-treatment: 1 — composite without treatment; 2 — composite treated by SHF EMF (30s); 3 — composite treated by SHF EMF (60s).

Further, IR-spectral analysis of composites filled with dispersed B_4C particles (dispersion 63 μm) with $q = 30$ weight parts was carried out. In all investigated CM, the presence of absorption bands in the range of wave numbers $\nu = 574.79?420.48$ cm^{-1}, characteristic for oscillations of -CH_2- groups, and benzene pair (at $\nu =$

574.79...567.07 cm^{-1}) was found (Fig. 3, spectra *1–3*), which indirectly indicates the presence of B_4C particles.

In comparison with the initial state, the IR-spectra of CM modified by SHF field show the following displacements: the line at $\nu = 1296.16$ cm^{-1} is shifted by $\Delta\nu = 3.85$ cm^{-1} towards lower wave numbers; the line at $\nu = 1454.33$ cm^{-1} is shifted by $\Delta\nu = 3.85$ cm^{-1} towards higher wave numbers. It was suggested that the revealed features are associated with increased mobility of the binding components of molecules due to the effect of SHF. In addition, the destruction of the triple bonds of -C≡N-groups was found in the range of $\nu = 2367.69...1886.38$ cm^{-1} for all investigated CMs (Fig. 3, spectra *1–3*). At the same time, the absence of absorption bands in comparison with the matrix (Fig. 1, spectrum *3*) in the range $\nu = 3552.88...3414.00$ cm^{-1} indicates the destruction of hydrogen -OH-i-NH groups.

Next, the IR-spectral analysis of composites filled with SiC dispersed particles (63 μm) with a content of $q = 30$ weight parts was carried out.

The absorption bands detected in the range of wave numbers $\nu = 771.73...420.48$ cm^{-1} are characteristic for oscillations of $-CH_2-$groups, a pair of benzene, -NH-, -CH-pendulum oscillations, of the primary amino group: $-NH_2$ (Fig. 4, spectra *1–3*). When comparing the IR-spectra of the composites filled with SiC (Fig. 4, spectra *1–3),* the minimum transmittance intensity and half-widths were found for CMs modified by SHF electromagnetic field for 30 s at the following wave numbers: $\nu = 829.39$ cm^{-1} ($T = 13.9$ %, $b = 33.2$ cm^{-1}); $\nu = 1246.02$ cm^{-1} ($T = 8.0$ %, $b = 45.2$ cm^{-1}); $\nu = 1296.16$ cm^{-1} ($T = 3.8$ %, $b = 12.7$ cm^{-1}); $\nu = 1508.33$ cm^{-1}. When using the EPR spectroscopy method, the introduction of a paramagnetic probe into composites in the presence of fillers sharply reduces the mobility of macromolecules. An additional decrease in the mobility of macromolecules is observed in the composites after the first seconds of SHF treatment. According to Sperling's research, practically all physical units in a composite break down at temperatures higher than the glass transition temperature of the polymer matrix [9]. Studies of the instantaneous modulus of elasticity have shown that at temperatures below and above the glass transition temperature, the degree of crosslinking increases, mainly due to physical crosslinking. The chemical interaction of the binder with active centers on the surface of the filler has been proven by the use of red mud. The introduction of red mud, boron carbide and silicon results in an increase in the number of nodes in the binder net, which has a physical nature. This fact is in agreement with the results presented in [10]. An analysis of the EPR spectra showed an increase in the number of paramagnetic centers in the material upon transition to a pure binder even with the introduction of a small amount of fillers. In this case, the SHF treatment changes the number of paramagnetic centers in the matrix. An increase in the elastic modulus is noticed at the temperature above the glass transition temperature of the polymer matrix. In our opinion, this should be associated with an increase in the number of bonds between the matrix and the solid surface of the filler, which do not break down at temperatures above the glass transition temperature of the binder. Probably, we observe the migration of physical bonds at the indicated temperatures on the filler surface, when macromolecules interact with -OH-groups. The surface of fillers used as suppliers is characterized by the presence of active centers of OH groups, exchange electrons, dislocations, and so on. When using red mud, chemical interaction is possible. It should be noted that the optimal time for microwave processing is 30 seconds. Further increase in the treatment duration does not improve the properties of epoxy composites. A processing time of 30 seconds is suggested to create a new CM. If IR-treatment lasts more than 30 s, the properties of materials practically do not change and are within the limits of the experiment error. Further increase in the time of IR-treatment results in destructive processes in the binder.

4. Conclusions

Using the methods of IR and EPR spectroscopy to analyze the structure of epoxy compounds, the mechanism of interaction of the matrix and the particles of the filler of different dispersion and physical nature is substantiated. Based on the studied carried out, it is established that the improved properties are characteristic of a matrix modified by superhigh-frequency electromagnetic field for 30 seconds. This is confirmed by a decrease in the bandwidth at a frequency of $\nu = 829.39$ cm^{-1} indicating an increased degree of crosslinking of -NH-, -CH-, -C–C- and primary amino groups

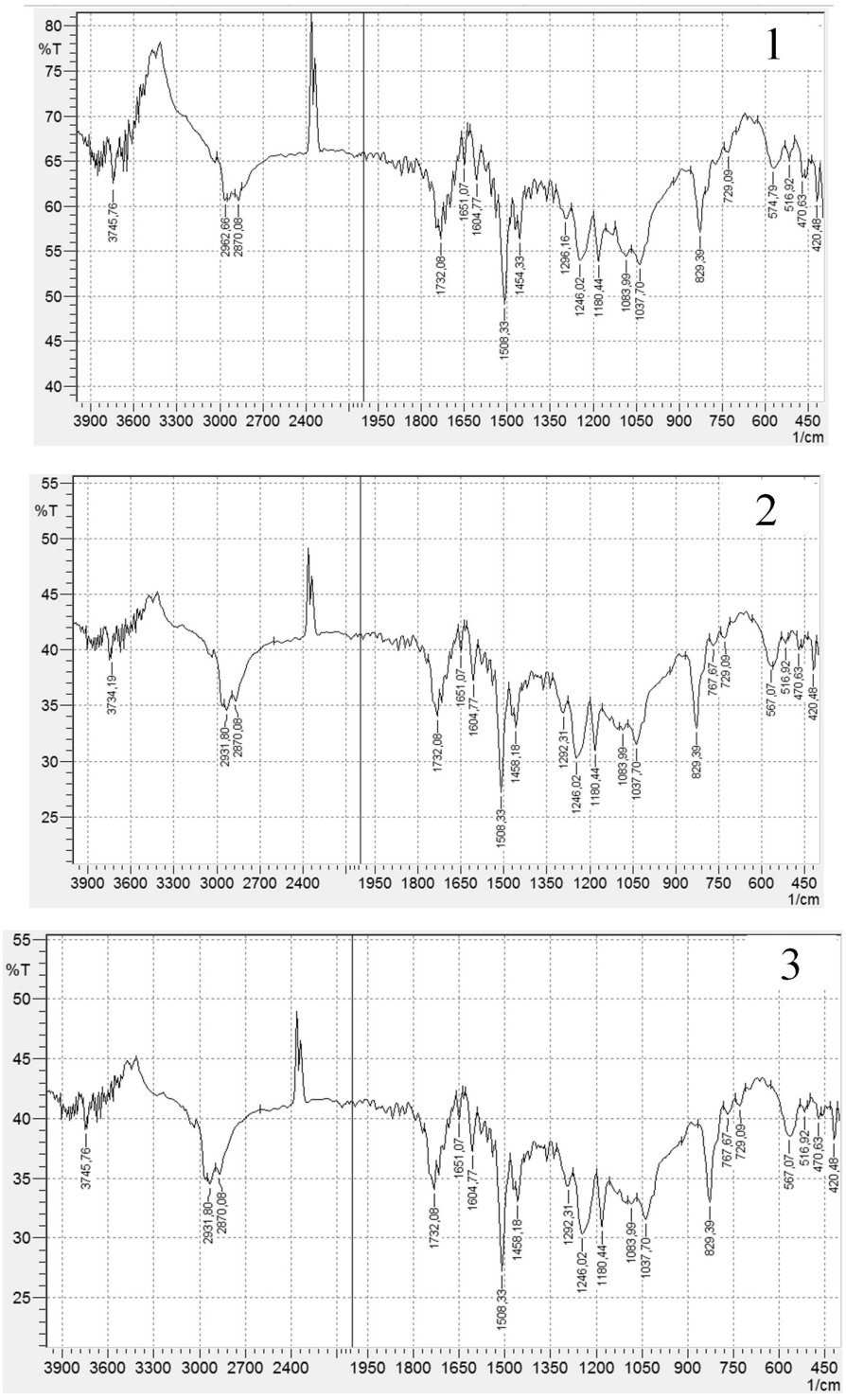

Fig.3. IR-spectra of composites with B4C particles, modified by SHF-treatment: 1 — composite without processing; 2 — composite treated by SHF (30s); 3 — composite treated by SHF (60s).

CH_2–NH_2, CH–NH_2 during the formation of the material. A decrease in the bandwidth at the frequency of $\nu = 1732.08$ cm^{-1} also indicates that the bonds of -C≡C–C=N- and -C=O-groups occur. At the same time, it should be noted that among the investigated CM the improved properties are characteristic of a composite filled with RM modified by SHF electromagnetic field for 30 s. This is confirmed by a decrease in the ab-

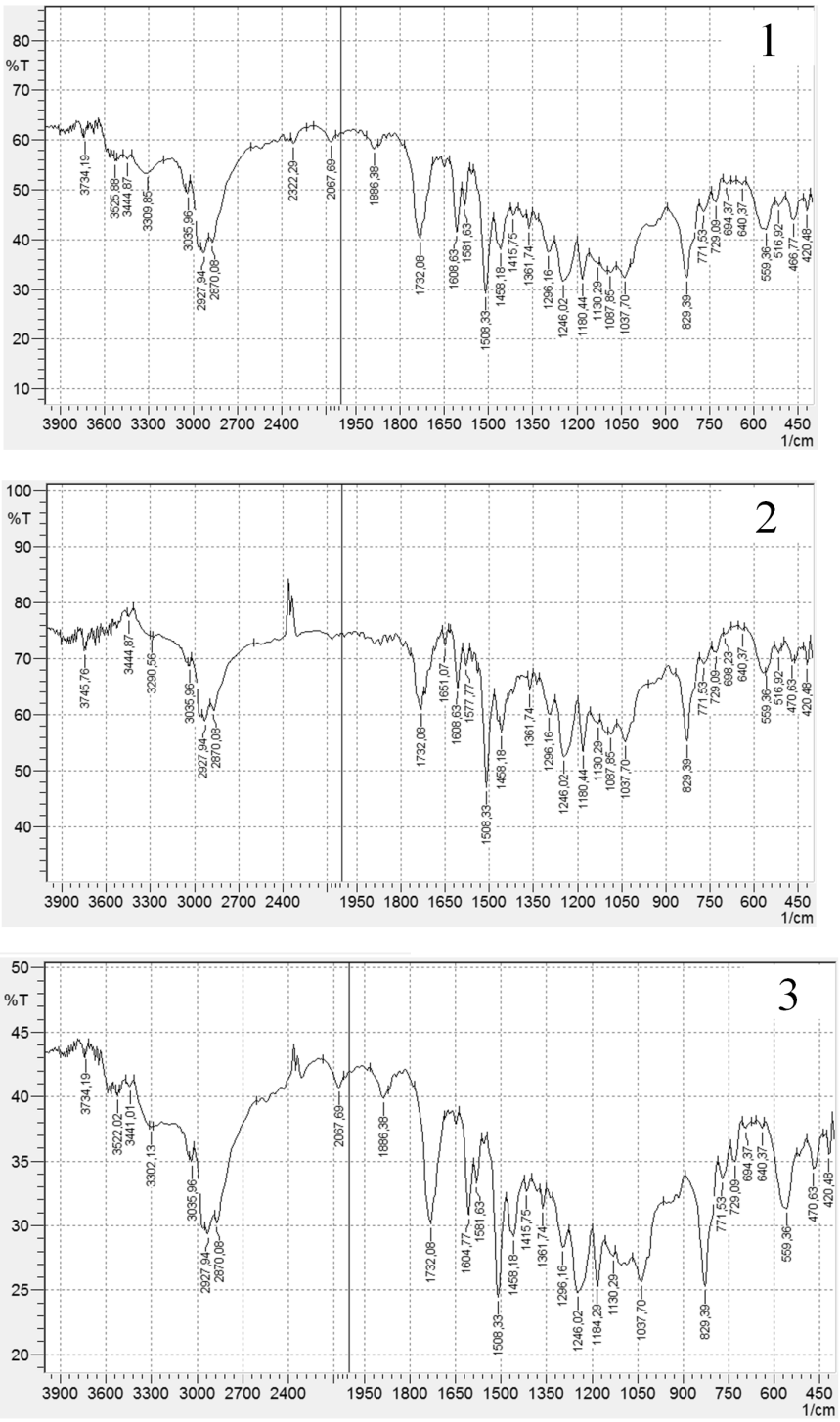

Fig. 4. IR-spectra of composites with SiC particles modified by SHF treatment: *1* — composite without processing; *2* — composite treated by SHF (30 s); *3* — composite treated by SHF (60 s).

sorption band displacement relative to the matrix in the range of wave numbers ν = 3745.76...2870.08 cm^{-1}, characteristic of valence oscillations of -CH-, methyl -CH_3–C and methylene -CH_2-groups, as well as a decrease in the transmittance intensity at half-width. EPR spectroscopy proved a change in the supramolecular organization of the polymer structure, which causes activation and subsequent interaction of macromolecules with active centres on the surface of particles with the formation of new

bonds. This ensures the formation of the material with the maximum degree of crosslinking, and, consequently, the stable physical-mechanical properties during the operation of the developed epoxy materials.

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