ISSN 1027-5495. Functional Materials, 27, No.4 (2020), p. 786-793.
doi:https://doi.org/10.15407/fm27.04.786

Cyclic structuring of epoxy polymers under the influence of microwave electromagnetic radiation

V.Kashytskyi, P.Savchuk, V.Malets, O.Sadova, O.Hulai

Lutsk National Technical University, 75 Lvivska Str.,
43018 Lutsk, Ukraine

Received April 2, 2020

For epoxy polymer compositions, the influence of the duration of treatment with electromagnetic ultra-high-frequency radiation on the amount of released thermal energy is determined in the article. The optimum duration of exposure of the epoxypolymer compositions in the electromagnetic field at the first stage and the temperature to which it is necessary to cool the composition to obtain the optimum amount of thermal energy have been determined. The dynamics of temperature change in time on the surface of the compositions was investigated depending on the volume of the samples, their shape and the duration of processing. Fractograms of destruction of epoxy polymers structured by cyclic processing under the action of microwave electromagnetic radiation have been investigated. The expediency of using a cyclic mode of treatment of the compositions in an electromagnetic field to intensify the structuring process of epoxy polymers is shown.

Keywords: electromagnetic field, thermal energy, epoxy polymer composition, fracture planes, cleavage lines.

Циклічне структурування епоксиполімерів під впливом електромагнітного випромінювання НВЧ діапазону. *В.П.Кашицький, П.П.Савчук, В.М.Малець, О.Л.Садова, О.І.Гулай*

Визначено вплив тривалості обробки епоксиполімерних композицій під дією електромагнітного надвисокочастотного випромінювання на величину генерації теплової енергії. Визначено оптимальну тривалість витримки епоксиполімерних композицій на першому етапі в електромагнітному полі та температуру, до якої необхідно охолодити композицію для отримання оптимальної кількості теплової енергії. Досліджено динаміку зміни температури у часі на поверхні композицій залежно від об'єму зразків, їх форми та тривалості обробки. Досліджено фрактограми зламу епоксиполімерів, які структуровані за циклічним режимом обробки під впливом електромагнітного випромінювання надвисокочастотного діапазону. Показано доцільність застосування циклічного режиму обробки композицій в електромагнітному полі для інтенсифікації процесу структурування епоксиполімерів.

Определено влияние продолжительности обработки эпоксиполимерных композиций под действием электромагнитного СВЧ излучения на величину генерации тепловой энергии. Определена оптимальная продолжительность выдержки эпоксиполимерных композиций на первом этапе в электромагнитном поле и температуру, до которой необходимо охладить композицию для получения оптимального количества тепловой энергии. Исследована динамика изменения температуры во времени на поверхности композиций в зависимости от объема образцов, их формы и продолжительности обработки. Исследовано фрактограмы излома эпоксиполимеров, которые структурированы по циклическому режиму обработки под воздействием электромагнитного излучения СВЧ диапазона. Показана целесообразность применения циклического режима обработки композиций в электромагнитном поле для интенсификации процесса структурирования эпоксиполимеров.

1. Introduction

Currently, methods of modifying the structure of thermoreactoplasts at the stage of molding by the inoculation of monomers or under the external influence of vibrations of the ultrasonic frequency range, vibration treatment, infrared radiation, etc. have become widespread [1]. However, these types of chemical and physical modifications, to a certain extent contributing to the improvement of the physicochemical properties of polymeric materials, are expensive and not sufficiently technological, and in some cases are harmful to the human body, which limits their widespread use in industrial production [2–5]. Therefore, it is very effective and promising in this direction to use electromagnetic radiation of the ultrahigh frequency (microwave) range to modify the structure and intensify the processes of structuring polymer materials, which has a number of advantages over the use of other physical fields. Intensification of energy exchange in a substance by converting the radiation energy into the kinetic energy of molecular vibrations provides uniform processing of the substance in full; high stability of the energy flow is ensured due to the absence of inertia and there is no need to use additional components to transform the structure of the substance [6, 7].

Microwave treatment in an electromagnetic field (EMF) should be considered as an alternative technology for thermal treatment of polymers based on epoxy oligomers [8]. Unlike traditional heating methods used in the synthesis of these polymers, microwave treatment in EMF provides a fast polymerization process, which allows you to get high productivity, shorten the production cycle of products and eliminate the use of catalysts [9].

In particular, the authors of [10] established the possibility of the influence of electromagnetic radiation of the microwave range on the process of curing thermosetting polymers. It was found that there is an improvement in the physical and mechanical properties of the reactants. The result is polymers with high rigidity of macromolecular chains, which are of great practical importance as heat-resistant materials that do not lose their physical and chemical properties under the influence of high temperatures (over 350°C).

In [11, 12], the theoretical concepts of the expediency and effectiveness of the use of microwave radiation for structuring polymers and improving their operational characteristics were investigated. It was found that when structuring the polymer with a specific energy of microwave radiation in the range of 102.5–205.8 kJ/kg and the processing time is not more than 3 min, the strength of the insulating material increases by 2 times, water absorption is reduced by 2.5 times, the three-dimensional electrical resistance increases and the glass transition temperature increases by 3–7°C.

According [13], the explanation of the mechanism of structuring the polymers under the influence of microwave radiation can be found in the polarization effects, their specific properties in the range of ultra high frequencies. Due to this effect, under the influence of external microwave radiation, conformational transformations occur in the macromolecules of the polymer without compromising the integrity of the chemical bonds. Under the influence of microwave radiation, the molecular packing density of the cross-domain regions changes, resulting in a change in operational properties. Consequently, high-frequency electromagnetic fields are ideally suited for structuring reactive plastics. In [14, 15] the technology of rapid processing of polymers in EMF microwave radiation was used to initiate and accelerate chemical reaction kinetics of reactions, diffusion behavior change and creating gradients in polymer layers.

However, in [16, 17] it was shown that, despite the large number of scientific publications in domestic and foreign publications on the use of technologies of structuring reactants in EMF, there are still unresolved theoretical and practical questions. Therefore, studies of the effect of microwave radiation on the structure and physical and mechanical properties of thermosetting materials are relevant for the creation of more efficient methods and modes of structuring; this will allow for energy efficient processing to improve the physical, mechanical and operational characteristics of polymer materials.

2. Experimental

The starting material for the formation of epoxypolymers was epoxy-dianon resin brand ED-20, which is a highly viscous transparent liquid. The mass fraction of epoxy groups is 20.0–22.5 %, volatile substances — 0.2–0.8 %. For curing of epoxy polymer coatings, polyethylenepolyamine — PEPA was used, which is intended for structuring epoxy resins at room and lower temperatures in conditions of high humidity.

The epoxy resin samples were formed to obtain a homogeneous mass of the required components. The components were mixed at a low speed of rotation of the mixer blades in the prepared vessel for 2–3 min to ensure a high homogeneity of the system. The resulting composition was poured into disposable forms and placed in the installation chamber for treatment with microwave electromagnetic radiation. The duration of the treatment of the composition and the modes of structuring the epoxy polymers were set according to the study plan. The samples were cooled in air at room temperature.

The step-by-step heat treatment of the epoxy polymers was carried out after holding the samples for 24 h under normal conditions in the following mode: 1 h at 50°C, 1 h at 100°C and 4 h at 140°C. The reduced heat treatment of epoxy polymers was carried out after treatment in the electromagnetic field in the following mode: 0.5 h at 50°C, 0.5 h at 100°C and 2 h at 140°C.

The compressive strength was measured according to GOST 4651-82. Samples in the form of cylinders with a diameter of 10±0.5 mm and a height of 15 mm were subjected to compression with a speed of convergence of the planes of 2 mm/min. Impact toughness was determined according to GOST 4647-80. Samples of rectangular shape with a square cross section of 10×10 mm^2 and a length of 60 mm were subjected to dynamic loading on a pendulum net with a charging angle of 160°. The temperature was measured by a contactless infrared thermometer at a distance of 10–15 mm from the test surface. The structure of the epoxy composite material was studied using an electron microscope EVO 50.

3. Results and discussion

Structuring of epoxy polymers occurs due to the formation of chemical bonds between segments of macromolecules of epoxy resin and a hardener; the process takes a long time to complete. To intensify the structuring process of epoxy polymers, a system with additional energy is required, in particular, the energy of physical fields. However, intensive structuring causes the formation of local bonds, which leads to an increase in residual stresses and the appearance of structural defects. To optimize the process of structuring epoxy polymers, the system with sufficient energy is needed, that can initiate the chemical reaction of bonding between system components and provide a uniform distribution of chemical bonds over the polymer volume. When epoxy-polymer compositions are processed by ultra-high-frequency radiation in an electromagnetic field, thermal energy is generated due to vibrations of segments of epoxy resin and polyethylene polyamine macromolecules. The peculiarity of this treatment is that electromagnetic waves are able to penetrate the epoxy polymer composition and initiate the structuring process simultaneously in all micro-volumes of the system. With convection heating, the outer layers first receive thermal energy, and then, due to thermal conductivity, energy enters the bulk of the composition. Accordingly, the outer layers form primary chemical bonds, the concentration of which is higher than that of the central zone.

The processing of epoxypolymer compositions in EMF requires, first of all, the determination of the exposure time, which ensures an increase of thermal energy. Measurement of the surface temperature of the epoxypolymer composition after exposure in the EMF allows us to determine the amount of thermal energy generated in the sample volume as a result of oscillations of the atoms of epoxy resin and polyethylene-polyamine macromolecules under the influence of electromagnetic radiation. It has been experimentally found that the treatment of epoxypolymer compositions for more than 40 sec leads to a sharp increase in thermal energy, which causes the release of volatile substances and intensifies the process of structuring the porous structure.

Exposure of epoxy polymer compositions in the form of cylinders with a volume of 0.4 cm^3 in the EMF for 40 sec leads to an increase in the temperature on the surface of the samples (48–50°C); however, intensive structuring does not occur, because at room temperature, due to the large surface area and temperature gradient, the samples begin to rapidly lose heat (Fig. 1). To avoid this, the specimens can be placed in a thermostat or thermal chamber with a temperature not lower than 50°C. However, this requires additional equipment and increases the duration of the technological process, which causes additional costs.

The exposure of the samples in the EMF for 10 sec, 20 sec and 30 sec leads to their heating (23–35°C), after which there is a uniform cooling of the composition. After 5 min, the epoxy polymer compositions were cooled to a temperature of 22–24°C without solidification. It is obvious that the thermal energy was not enough to initiate the structuring process of the epoxy polymer composition.

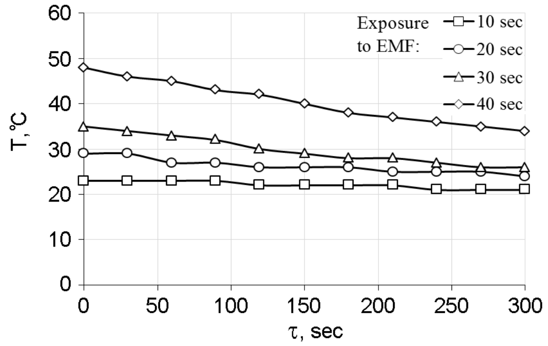


Fig. 1. Dynamics of temperature change versus treatment time on the surface of cylindrical epoxy polymer samples exposed to EMF.

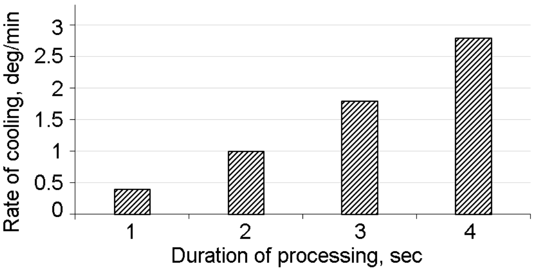


Fig. 2. Cooling rate of the sample surface depending on the exposure time in EMF: *1* — 10 sec; *2* — 20 s; *3* — 30 s; *4* — 40 s.

After exposure to EMF for 10 s at room temperature in air, the cooling rate of cylindrical samples is 0.4 deg/min. (Fig. 2), and for samples after exposure for 20 s, it increases 2.5 times ($\nu = 1$ deg/min). This increase in cooling rate is associated with the higher temperature gradient ($\Delta t = 17°C$) on the surface of the sample exposed for 20 s and the air temperature compared to the temperature gradient ($\Delta t = 5°C$) for the samples exposed for 10 s. The cooling rate of cylindrical specimens exposed in EMF for 30 s was 1.8 deg/min; and for specimens with the exposure time of 40 s the cooling rate was 2.8 deg/min. The cooling rate of the samples with the exposure time of 30 s increases 1.8 times compared to the samples exposed in EMF for 20 s. The subsequent increase in the cooling rate is registered for the samples exposed in EMF for 40 s, which is 1.5 times higher than for the samples exposed for 30 s. Note that the increase in cooling rate is slower for compositions that have a longer EMF exposure compared to ones with shorter exposure time. This is due to the slowdown in the growth rate of the structure of the composition, which determines the thermal conductivity of the epoxy polymer, since the small volume samples generate a small amount of thermal energy, and also due to the high simple surface, the generated heat energy is exhausted.

It was of interest to investigate the intensity of thermal energy generation and the cooling rate for 25×25×25 mm cubic samples ($V = 15.5$ cm^3), which differed from the previous ones in shape and volume (Fig. 3). It was found that exposure of the samples to EMF leads to the generation of a larger amount of thermal energy, since the measured temperature of 34°C was 10°C higher than the temperature of the cylindrical samples exposed for 10 sec. The exposure of cubic samples for 20 sec and 30 sec resulted in an increase in surface temperature up to 44°C and 54°C, which is higher by 15°C and 20°C, respectively, compared to cylindrical specimens with similar exposures. A temperature increase of 30°C occurs for cubic specimens compared to cylindrical specimens with exposure to EMF for 40 sec, which is due to the larger volume of the composition and the larger number of macromolecules whose groups of atoms are able to generate more thermal energy during oscillation.

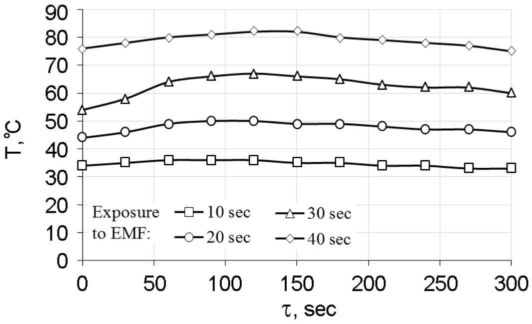


Fig. 3. Dynamics of temperature change on the surface of cubic epoxypolymer samples ($V = 15.5$ cm^3), depending on the exposure time in EMF.

After removing the cubic samples from the chamber for processing in EMF for the first two minutes at room temperature, an increase in the surface temperature by 2°C to 12°C was observed, and then the composition was cooled. The rise in temperature is the result of a flattening of the temperature gradient caused by the low thermal conductivity of the epoxy resin composition. The rate of the temperature increase was 0.4 deg/min for the compositions exposed to EMF for 10 s and 1.2 deg/min for the compositions after exposure for 20 s, i.e. 3 times higher (Fig. 4). The highest rate of the temperature rise was registered for the

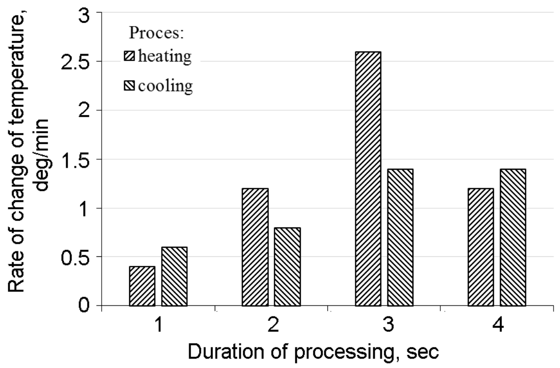


Fig. 4. The dependences of the rate of change of temperature on the surface of the samples from the exposure of the composition in the EMF: *1* — 10 s; *2* — 20 s; *3* — 30 s; *4* — 40 s.

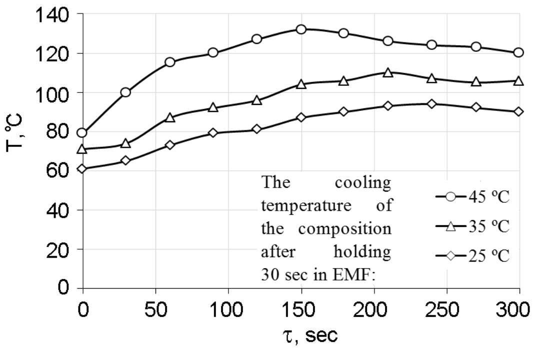


Fig. 5. Time dynamics of temperature changes on the surface of cubic epoxypolymer samples (V = 15.5 cm^3), which were processed in EMF for 30 s, cooled to a predetermined temperature and re-processed in EMF for 40 s.

compositions after exposure to EMF for 30 s, which is 2.2 times higher than the rate for the compositions after exposure for 20 s. For compositions after exposure for 40 sec, the rate of the temperature increase was 1.2 deg/min; this is due to intensive structuring, as a result of which the thermal conductivity increases and the temperature gradient quickly levels out. After the first two minutes of being in normal conditions, the samples begin to cool. The cooling rate of the samples exposed to EMF for 10 s was 0.6 deg/min, and for the compositions exposed for 20 s, this value was 0.8 deg/min. Exposing the compositions to EMF for 30 s and 40 s resulted in a cooling rate of up to 1.4 deg/min, however, this rate is stabilized for the compositions after their exposure to EMF for 40 sec, which is related to the processes of structuring the composition. It is obvious that increasing the thermal conductivity of the composition indicates an increase in the volume of the structured part of the epoxy polymer.

Since increasing the duration of exposure of the epoxy compositions to EMF leads to a sharp increase in thermal energy within the sample volume, but does not provide a uniform structuring of the system or leads to the formation of defects in the structure, cycling the compositions would provide alternate exposure of the composition in the EMF under normal conditions without the influence of electromagnetic radiation. This would ensure the uniformity of chemical bonds in the polymer network and would not allow a sharp increase in thermal energy.

It is important to determine the optimal cooling time after exposure to EMF in order to reach a certain temperature, which will ensure the loss of excess heat, but retain some of the heat required to ensure a uniform structuring of epoxy polymers.

When the composition is exposed to EMF for 30 s, cooled to a temperature of 25°C and then exposed to EMF for 40 s, the temperature of the composition increases to 60°C. When holding the samples without exposure to electromagnetic radiation at room temperature, an unexpected increase in the temperature of the composition to 94°C within 4 min is possible (Fig. 5). After the first stage of EMF treatment, when the composition is cooled to 35°C and then exposed to EMF for 40 s, the sample temperature rises to 70°C and then to 110°C. It was found that cooling the composition to a temperature of 45°C after the first stage of processing and subsequent processing in EMF for 40 s leads to heating of the composition to a temperature of 80°C, followed by an increase in temperature to 130°C.

Since the treatment cycle (treatment in EMF for 30 s + holding without treatment + treatment in EMF for 40 s) did not ensure the transition of the epoxy composition to the solid state, the treatment cycle was repeated; after that the content of the gel fraction of epoxy polymers was 70–75 %.

The microstructure of epoxy polymers was studied on samples structured according to the following treatment modes (Table): I mode (step heat treatment), II mode (basic treatment in EMF), III mode (basic treatment in EMF and reduced heat treatment), IV mode (basic and additional processing in EMF). The classic technology of structuring the epoxy polymers is stepwise heat treatment in the following mode (mode I): 1 h at 50°C, 1 h at 100°C, 4 h at 140°C. This mode provides the best mechanical characteristics due to the completed structuring and formation of a homogeneous structure, but the process is long (6 h).

Basic processing in EMF (mode II) can intensively transform the composition from a viscous state to a solid, but does not provide the maximum values of the mechanical characteristics of epoxy polymers due to the incomplete structuring processes.

Combined treatment (mode III) (main treatment in EMF and short-term heat treatment (0.5 h at 50°C, 0.5 h at 100°C, 2 h at 140°C) allows you to reduce the duration of the technological process and increase the impact strength of the material by 4.3 times compared to step heat treatment. An alternative to the combined processing is a cyclic processing (IV mode), which consists of basic and additional processing of epoxy polymers in the EMF. Additional processing consists in cyclic exposure of epoxy polymer samples to electromagnetic radiation for 30 min (10 min at each stage) with cooling the samples for 5 min. As a result of the cyclic EMF treatment, the structuring duration is reduced by 3 times compared to the combined mode III. The cyclic treatment provides a 10 % increase in the compressive strength (85 MPa) and a 38 % increase in the toughness (8.4 kJ/m^2) of the epoxy polymers due to the formation of a high structured homogeneous system with low stress.

On the surface of epoxy polymers structured by the step-by-step heat treatment (Fig. 6, a), a large number of small cleavage lines with a length of 0.1–0.2 mm are present. The cleavage lines have an elongated arcuate shape and are deepened with their apex inside the polymer. Because the initiation and propagation of cracks in the epoxy polymers occurs in places with a small number of chemical bonds or the presence of a stress state, the small cleavage lines indicate a high degree of structuring and homogeneity of the epoxypolymer mesh. The quality of these epoxy polymers is due to the long-term step-by-step heat treatment, which ensures a high content of gel fraction in the system and a uniform arrangement of chemical bonds in the polymer bulk.

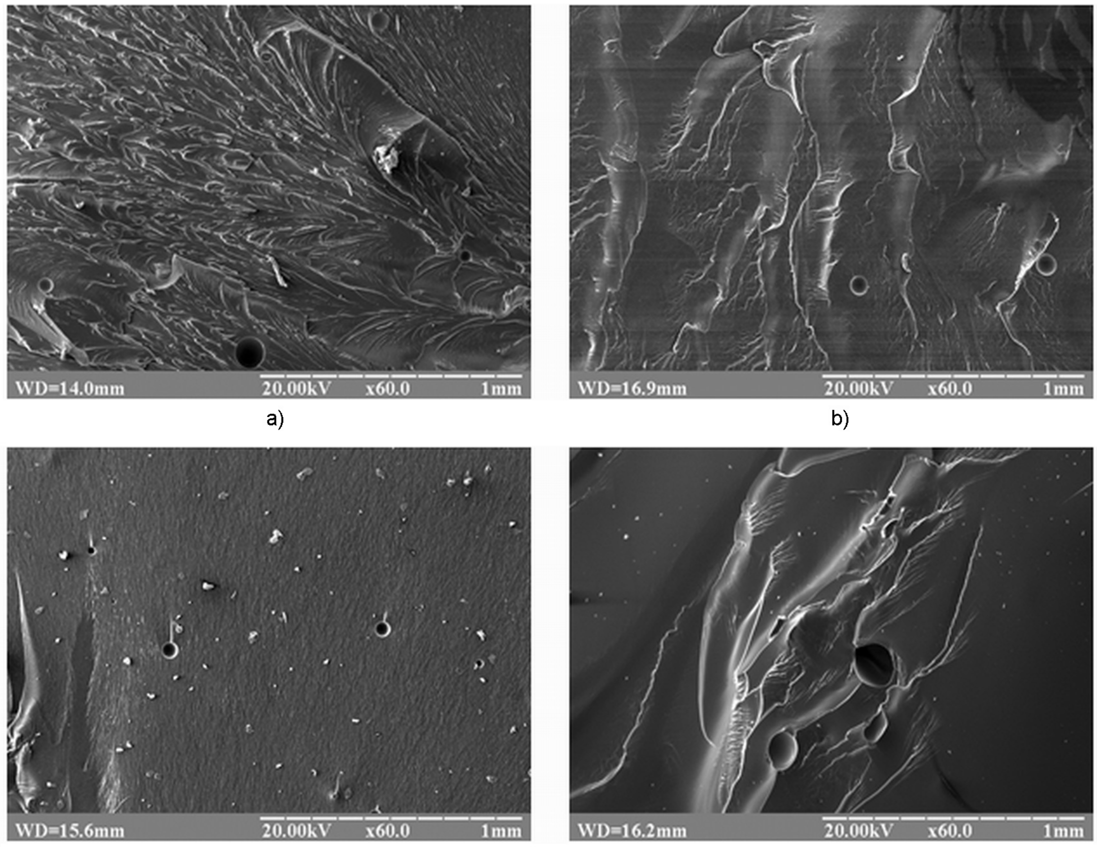
Table. Modes of structuring the epoxy polymers

Mode number	Structuring modes
1	Step-by-step heat treatment
2	30 s + cool + 40 s + cool + 30 s + cool + 40 s + cool + 40 s
3	30 s + cool + 40 s + cool + 30 s + cool + 40 s + cool + 40 s + cool + reduced heat treatment

EMF processing in the basic mode leads to the appearance of long unidirectional chipping lines with a length of 1–2 mm on the fracture surfaces, as well as a small number of small chipping lines with a length of 0.1–0.2 mm, which branch off from the long lines (Fig. 6, b). The presence of a small number of small cleavage lines indicates a low degree of structuring of the epoxy polymer. Additionally, the lack of chemical bonding causes the formation and propagation of trunk cracks that can move with less energy than microcracks. Highly structured microcracks can appear in defective areas and not propagate over long distances due to the large number of chemical bonds, the destruction of which requires additional energy. However, the uneven distribution of individual planes containing a branched network of short cleavage lines indicates the formation of an inhomogeneous structure with a large number of local zones with high stress state, and therefore the epoxy polymer has low impact strength (0.6 kJ/m^2).

On the surface of the fracture of the epoxy polymer, structured according to the combined treatment mode (the basic treatment mode in the EMF and short heat treatment), there are small lines of cleavage within one plane (Fig. 6, c). In this case, the structuring under electromagnetic radiation consists in the formation of primary chemical nodes uniformly located in the polymer epoxy polymer network due to the synchronous generation of thermal energy under the influence of EMF. As a result, under dynamic loading of the epoxy polymer, one fracture plane appears, indicating the formation of a system with a low stress state. Subsequent shortening of heat treatment leads to the formation of new chemical bonds, resulting in the appearance of small unidirectional lines of cleavage on the fracture surface due to the heat flow from the surface layers to the inner ones. These small cleavage lines are evenly spaced, since additional chemical bonds occurred within the supramolecular formations.

Additional treatment of epoxy polymers in the EMF after the main treatment (Fig. 6, d) causes the deformation of pores, which are air inclusions. The additional treatment generates thermal energy in the epoxy polymer, which softens the inadequately structured epoxy polymer mesh and deforms pores to form ovals. The ovals are oriented



a) b) c) d)

Fig. 6. Fractograms of fracture of epoxy polymers structured by different modes: a) — step heat treatment; b) — the main processing in the EMF; c) — processing in EMF and reduced heat treatment; d) — basic and additional processing in EMF.

in one direction, which is characteristic of pores located near the outer surface of the specimen. This is due to the temperature gradient: the temperature of the sample center is higher than that of the outer surface of the sample. The fracture planes, which are bounded by 0.8–1.5 mm long chipping lines, have a curved surface and a small area, indicating an increase in the toughness of the epoxy polymer.

The curved surface of the fracture planes indicates that significant mechanical energy is required for crack propagation, since the additional EMF treatment causes secondary structuring of epoxy polymers. This is due to the formation of new chemical bonds between the epoxy groups of the epoxy macromolecules, which did not participate in the formation of the polymer network, and the reactive groups of the macromolecules of the hardener, which were activated by electromagnetic radiation. Secondary structuring leads to the formation of local zones of epoxypolymer mesh with a high density of chemical bonds. At the boundaries of the local areas, the chemical bond density is lower because the chemical reaction is complicated by the large distance between the reactive component groups.

4. Conclusions

It is established that in the first stage, the optimum exposure duration of the epoxy compositions in the electromagnetic field is 30 s, which allows the system to generate enough heat due to oscillations of atomic groups of macromolecules. After this exposure to EMF, a temperature of 35°C is registered on the surface of the cylindrical specimens and the surface of the cubic specimens has a temperature of 55°C; this indicates that a larger system generates more heat. It is determined that the temperature rise above 60°C leads to intensive structuring and formation of the system with high stress state.

It is established that the rate of temperature change on the surface of epoxypolymer compositions increases with the duration of sample exposure to EMF, since the amplitude of atomic vibrations under the action of electromagnetic radiation increases and stabilizes at the stage of formation of primary chemical bonds between reaction groups.

It is found that the epoxy polymer compositions after the first stage of exposure to EMF for 30 s should be cooled to an optimum temperature of 25–30°C. The cooling provides removal of part of the thermal energy, the excess of which negatively affects the formation of a homogeneous structure of the polymer network. The optimum temperature provides the amount of thermal energy required to form uniformly distributed chemical bonds in the volume of the epoxy polymer.

The fracture surfaces of epoxypolymer specimens structured by cyclic processing in EMF were found to be curvilinear and bounded by short chipping lines. This indicates the formation of local zones with a high degree of structuring of the system; this is associated with the secondary structuring and increasing the number of chemical bonds under the influence of additional processing in the EMF. The cyclic electromagnetic processing in EMF leads to an increase in the impact strength of epoxy polymers by 38 % due to the formation of a homogeneous structure with a low stress state. An increase in the compression strength by 10 % indicates an increase in the degree of structuring of epoxy polymers, since secondary structuring provides an increase in the number of chemical bonds.

References

1. I.Zlobina, N.Bekrenev, *Mater. Engin. Techn. Product. Process. II: Solid State Phenomena*, **870**, 101 (2016).
2. A.V.Buketov, P.D.Stukhlyak, I.H.Dobrotvor, et al., *Strenght Mater.*, **41**, 431 (2009).
3. I.H.Dobrotvor, P.D.Stukhlyak, A.V.Buketov, *Mater. Sci., Chem. Mater. Sci.*, **45**, 790 (2009).
4. M.V.Brailo, A.V.Buketov, N.N.Yakuschenko et al., *Mater. Perform. Character.*, 7, 135502 (2002).
5. PA.V.Buketov, A.A.Sapronov, N.N.Buketova *et al., Composites: Mechanics, Computations, Applications: Intern. J.*, **9**, 157 (2018).
6. W.Liang, T.Huang, D.Lu et al., *Polymers*, **11**, 133 (2019).
7. P.Savchuk, V.Kashytskyi, V.Malets et al., Proc. Int. Conf. Actual Problems of Engineering Mechanics, APEM 2019, Odesa, Ukraine, v.968 MSF (2019), p.176.
8. S.Hara, S.Watanabe, K.Takahashi et al., *Polymers*, **10**, 1083 (2018).
9. C.Zimmerer, C.S.Mejia, T.Utech et al., *Polymers*, **11**, 535 (2019).
10. D.Bogda, P.Penczek, Ja.Pielichowski, A.Prociak, *Adv. Polymer Sci.*, **163**, 51 (2003).
11. R.Hoogenboom, U.S.Schubert, *Macromolec. Rapid Commun.*, **28**, 368 (2007).
12. F.Wiesbrock, R.Hoogenboom, U.S.Schubert, *Macromolec. Rapid Commun.*, **25**, 1739 (2004).
13. M.Chen, E.J.Siochi, T.C.Ward, J.E.McGrath, *Polymer Engin. Sci.*, **33**, 1092 (1993).
14. V.V.Azharonok, A.G.Anisovich, V.V.Biran et al., *Surf. Engin. Appl. Electrochem.*, **50**, 300 (2014).