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Investigation of epoxycomposites linking kinetics during ultrasonic treatment

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Relaxation processes depending on the time of hardening of initial and ultrasonically modified epoxy composites at different stages of formation of composite materials containing "hybrid" (fibrous and disperse) fillers of various nature are investigated. The activation of side groups and segments of epoxy binder macromolecules has been proved. The mobility of the matrix units also increases. These factors enhance the interaction at the phase separation interface in the system "filler — epoxy matrix" during the formation of surface layers. The degree of matrix cross-linking is determined by the displacement of the $\tan(\delta_{max})$ peak of the relaxation process of the segments towards smaller values of time. It proves the intensification of the cross-linking process during the composite formation.

Keywords: polymer composite material, ultrasonic treatment, relaxation process, modified epoxy composite, torsion, surface layers, activation of macromolecules aggregates.

Дослідження кінетики зшивання епоксикомпозитів при ультразвуковій обробці. *І.В.Чихіра, П.Д.Стухляк, М.М.Митник, В.В.Карташов*

Досліджено релаксаційні процеси від часу тверднення вихідних і модифікованих ультразвуком епоксикомпозитів, що містять "гібридні" (волокнисті і дисперсні) наповнювачі різної природи, на різних стадіях формування композитних матеріалів. Доведено активацію бокових груп та сегментів макромолекул епоксидного зв'язувача. Також підвищується рухливість агрегатів матриці. Дані фактори покращують взаємодію на межі поділу фаз у системі "наповнювач — епоксидна матриця" з утворенням поверхневих шарів. Визначено ступінь зшивання матриці за зміщенням піка $\tan(\delta_{max})$ процесу релаксації сегментів у бік менших значень часу, що доводить інтенсифікацію процесу зшивання при формуванні композиту у вироби.

Исследованы релаксационные процессы от времени твердения выходных и модифицированных ультразвуком эпоксикомпозитов, содержащих "гибридные" (волокнистые и дисперсные) наполнители различной природы, на разных стадиях формирования композитных материалов. Доказана активация боковых групп и сегментов макромолекул эпоксидного связующего. Также повышается подвижность агрегатов матрицы. Данные факторы улучшают взаимодействие на границе раздела фаз в системе "наполнитель — эпоксидная матрица" с образованием поверхностных слоев. Определена степень сшивания матрицы по смещению пика $\tan(\delta_{max})$ процесса релаксации сегментов в сторону меньших значений времени, что доказывает интенсификацию процесса сшивания при формировании композита в изделия.

1. Introduction

Structural processes in binders have an important influence on the properties of composites. Particular attention is paid to the processes taking place at the phase interface close to the filler surface in the "binder-filler" system. In this regard, the investigation of the process of interphase interaction in epoxy composites during their formation is an important task in multicomponent systems research [1–7]. Thus, from scientific and practical point of view, it is important to investigate the relaxation processes of composite materials containing a complex of fibrous and dispersed fillers.

The scientific basis of obtaining polymer composite materials (CM) for protection of technological equipment is based on the investigation of physical-chemical processes at the interface of "oligomer-filler" phases. The formation of the binder structure in the layers at the interface around the filler surface is important in the formation of a composite. "Soft" surface layers with low strength are due to low absorption of matrix and filler components, technological factors and the activity of fillers in relation to the epoxy binder. When operating under cyclic alternating loads, the presence of such layers causes the destruction of the adhesive joint, which leads to the formation of cracks and complete fracture of the composite in the filler-polymer matrix system. In [8], the reasons for the formation of these layers around the filler in CM are considered. It is proved that their occurrence is due to insufficient interaction of the filler surface with the binder, the presence of contaminations and air inclusions on the filler surface during the product formation. These disadvantages can be overcome by changing the method of surface preparation of the additives before the formation of CM. A significant migration of macromolecules can be provided by changing the hardening regime with the formation of supramolecular structures in the cross-linking process: "hard" surface layers are formed. These materials have high cohesive properties significantly improving the product operational life characteristics [9].

The objective of this paper is to increase physical-mechanical and operational characteristics of epoxy composites by intensifying the relaxation processes of the formation of the epoxy composite structure under the action of ultrasonic treatment. Studying the relaxation of segments and side groups of macromolecules under ultrasonic treatment (UST) make it possible to determine the technological parameters for the formation of a composite with the introduction of dispersed and fibrous fillers with high physical-mechanical and operational characteristics.

From scientific and practical point of view, it is interesting to determine the size of globules in the epoxy composite material under UST action after its formation. The size of the globules is the indicator of the intensification of cross-linking processes during the formation of the oxycomposite material. A decrease in the globule size is the indisputable condition for intensifying the processes of the structure formation due to an increase in the segmental mobility of epoxy binder macromolecules under the action of the specified force field.

2. Experimental

An epoxy diane oligomer of ED-20 grade was used, which, in comparison with other known thermosetting plates, is characterized by the following properties: high adhesive strength, hardening at low temperatures, low shrinkage, no volatile organic emissions, manufacturability while applying on the parts with complex surface profile. The developed raw basic material was selected as the main component of polymer composites. For epoxy compositions, cross-linking of polyethylene polyamine (PEPA) hardener is used, which allows the composite to be cured at room temperature. Dispersed particles of soft carbon (SC), green chrome oxide, and aluminum oxide are used as fillers. These fillers differ in their activity with respect to the epoxy binder. Glass [10], carbon [11] and basalt [12] fibers are used as reinforcing fillers. A preliminary ultrasonic treatment of the materials increases the degree of composite cross-linking [13, 14].

The fiber with the composition was additionally treated by ultrasound. The optimal duration of the treatment of the compositions (with mass $m = 30$ g) is $t = 4...6$ min [15]. After the introduction of the hardener, the oligomer composition is applied on the surface of the part.

The dynamic characteristics of the samples during hardening are investigated by means of torsion pendulum, using the TBA-Torsional Braid Analysis method [16]. A device has been designed to measure the dynamic characteristics of polymeric materials during the investigation and to determine the CM hardening kinetics [17]. The dependence of the tangent of angle of mechanical losses on the hardening time for the composite material based on epoxy resin ED-20 during torsion for fibers of different nature is investigated. When calculating the tangent of the angle of mechanical losses, the values of the initial and intermediate amplitudes of inertial disk oscillations are measured. These amplitudes are determined during one test cycle (for $t = 30$ s.). Further, the inertial disk deviation from the equilibrium position during the whole investigation time (5 h) is analyzed. The investigation results are automatically recorded in the file and then analyzed.

3. Results and discussion

The developed torsion pendulum was used to investigate the process of matrix cross-linking in the surface layers and the rate of relaxation processes during the formation of CM with a "hybrid" (fibrous and dispersed) filler [16]. It should be noted that as a result of torsion, a braid of carbon, glass and basalt fibers of the same thickness and width is formed. After evacuating the braid, the oligomer composition is applied to the torsion surface for a minimum short period of time: $\tau = 2.0...2.5$ min. This mode of CM formation is used to prevent interaction of active centers on the surface of the fibers after UST with acceptors contained in the air (oxygen and other gases). It is assumed that such period of time does not significantly increase the experiment error during the investigation of structural processes in the material.

The original and ultrasonically modified epoxy matrix formed as a braid of carbon, glass and basalt fibers is investigated on torsion. The beginning of relaxation processes in the segments was observed 10...50 min after the hardener addition, and the relaxation processes of macromolecular formations after 100...160 min. The processes of segment relaxation in CM after UST of epoxy oligomer in the presence of glass, carbon and basalt fiber were investigated. The maximum displacement of tangent of the angle of mechanical losses $\tan(\delta_{max})$ was observed towards a decrease in the time of the beginning of structuring processes in the epoxy matrix. This value also decreases relative to the original (without UST) epoxy composites. An increase in the relaxation rate and hardening processes in ultrasonically treated CM indicates an intensification of diffusion processes leading to an increase in the rate and degree of its cross-linking in comparison with the original untreated epoxy materials. The most significant shift of the value $\tan(\delta_{max})$ towards a shorter hardening time (Δt = 22 min) and a significant decrease in the value of the tangent of the angle of mechanical losses (from $\tan(\delta_{max}) = 7.5$ to 6.8) was observed for a composite with glass fiber as a result of using a binder ED-20 under ultrasonic treatment.

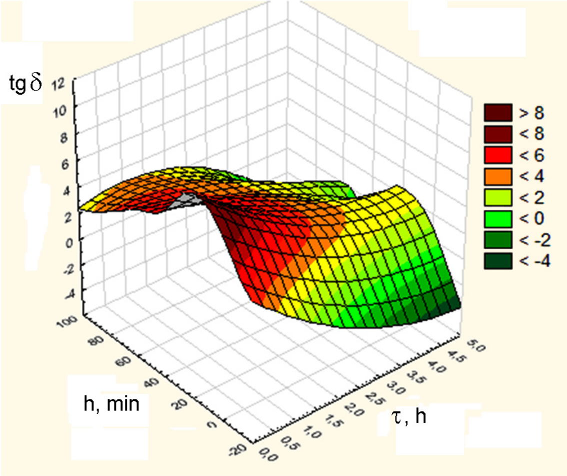

Fig. 1. The peak width (h) of the tangent of the angle of mechanical losses (tan δ) depending on hardening duration (τ) of epoxy composites after ultrasonic treatment of the epoxy matrix in the presence of basalt fiber.

The results of studying the surface layers indicate an increase in their volume due to physical-chemical processes at the "oligomer — glass fiber" interface. The results of the falling-sphere method prove an increase in the degree of matrix cross-linking already at the initial stages of material hardening after UST. In this case, the mobility of functional groups and segments of macromolecules increases in the surface layer around the fibers, providing a more intense structuring of the material both near the filler surface and in the composite as a whole, which is in good agreement with the authors' data [18, 19].

With the introduction of carbon and basalt fibers into the epoxy oligomer, a less significant shift of the loss tangent towards the left along the time axis is observed after UST of epoxy composite with hardening for Δt = 7 min and Δt = 12 min, respectively, compared to the CM containing an epoxy matrix without ultrasound treatment. The value of $\tan(\delta_{max})$ corresponding to the relaxation process of segments for CM with carbon fiber is practically unchanged, while $\tan(\delta_{max})$ corresponding to the relaxation process of segments for CM with basalt fiber decreases by 0.5 (from 8.0 to 7.5) after UST, compared to CM containing the US untreated matrix (Fig. 1).

UST intensifies the processes of structure formation in the composition. An increase in the hardening rate and a decrease in the hardening start time are in good agreement with papers [13, 15, 20].

Further, it has been determined that in the case of CM reinforcement by glass or basalt fiber, after ultrasonic treatment, the tan(δ_{max}) value corresponding to the relaxation process of the side groups is shifted towards a longer CM cross-linking time, and its absolute value decreases in comparison with the original CM. The obtained results indicate the formation of physical bonds between binder macromolecules and active centers on the filler surface when applying the investigated fibers [21].

It should be noted that the absolute value of tan(δ_{max}) decreases for all fibers, characterizing an increase in the degree of cross-linking in the material after UST. An increase in the maximum tangent of the angle of mechanical losses compared to the material which is not subjected to UST indicates a decrease in the degree of cross-linking of the material. These results confirm the presence of relaxation processes of the side groups of macromolecule chains in both adsorption and surface layers around the filler. The change in molecular mobility of macromolecules in the binder volume at different distances from the filler surface was determined. In our opinion, the shift of the maximum of the tangent of the angle of mechanical losses towards longer times indicates an increase in the relaxation time of the side groups. Investigations of physical-mechanical characteristics show that in this case the residual stresses in the material decrease, which is in good agreement with the results of [22]. Reinforcement of the epoxy composite by carbon fiber results in a decrease in the start time of the hardening process after UST and a shift of tan(δ_{max}) towards shorter start time of this process. This in turn indicates an increase in the relaxation of the side groups of the binder macromolecules in the system "binder — solid filler surface".

Further, we consider the effect of previous UST on the relaxation processes in the compositions containing dispersed fillers during hardening of CM in the presence of fibers. The maximum tangent of the angle of losses decreases from tan(δ_{max}) = 6.8 to tan(δ_{max}) = 6.0 for CM reinforced by glass and basalt fiber, regardless of the nature of dispersed filler. In the relaxation process in the area segments, an increase in the peak width of the dependence tan(δ_{max}) on the hardening time and its shift to the left along the hardening time axis in comparison with the material without dispersed particles is also observed. As it is mentioned above, a decrease in tan(δ_{max}) and its shift towards the shorter start time of cross-linking indicates a more intense relaxation process of segments. The duration of this process increases in comparison with the original reinforced matrix. The results of the study confirm the fact that the cross-linking process in the matrix surface layers is more significant under the influence of ultrasonic treatment [20].

According to the results on the relaxation of the system "carbon fiber — disperse filler — oligomer", in the case of CM with chromium oxide and soft carbon fillers, the tangent of the angle of mechanical losses for the relaxation process of segments decreases from tan(δ_{max}) to tan(δ_{max}) = 7.0...7.8.

The results of the studying the effect of UST on the composites with dispersed fillers are in good agreement with the data of [23, 24]. Ultrasonic treatment due to acoustic flows creates additional pressure at the interface, which allows removing gas inclusions and activating binder macromolecules due to cavitation processes. The ultrasonic activation enhances the chemical and physical interaction of the ingredients during matrix cross-linking. As a result, there is an increase in the rate of structural processes in the material, which is observed by the molecular mobility of the segments.

The efficiency of ultrasonic treatment includes a complex effect of the above mentioned factors on the change of the properties of the material during its cross-linking. Under the action of ultrasound, a significant reduction of gas inclusions is observed in the composite. This treatment significantly increases the cohesion characteristics of the material and is less energy consuming compared to the vacuuming process. It should be noted that the absorption of ultrasonic energy by the composite increases the mobility of macromolecules, reduces the oligomer viscosity and increases the wettability of dispersed filler particles [25]. Due to the manufacturing technology, the penetration of oligomer macromolecules into the pores on the filler surface enhances both physical and mechanical interaction at the interface. During UST, macromolecules are activated with the formation of free radicals characterized by a significant mobility; therefore, there is an enhanced interaction of macromolecules with the filler. This, in turn, improves the conditions for the formation of a spatial grid of the binder.

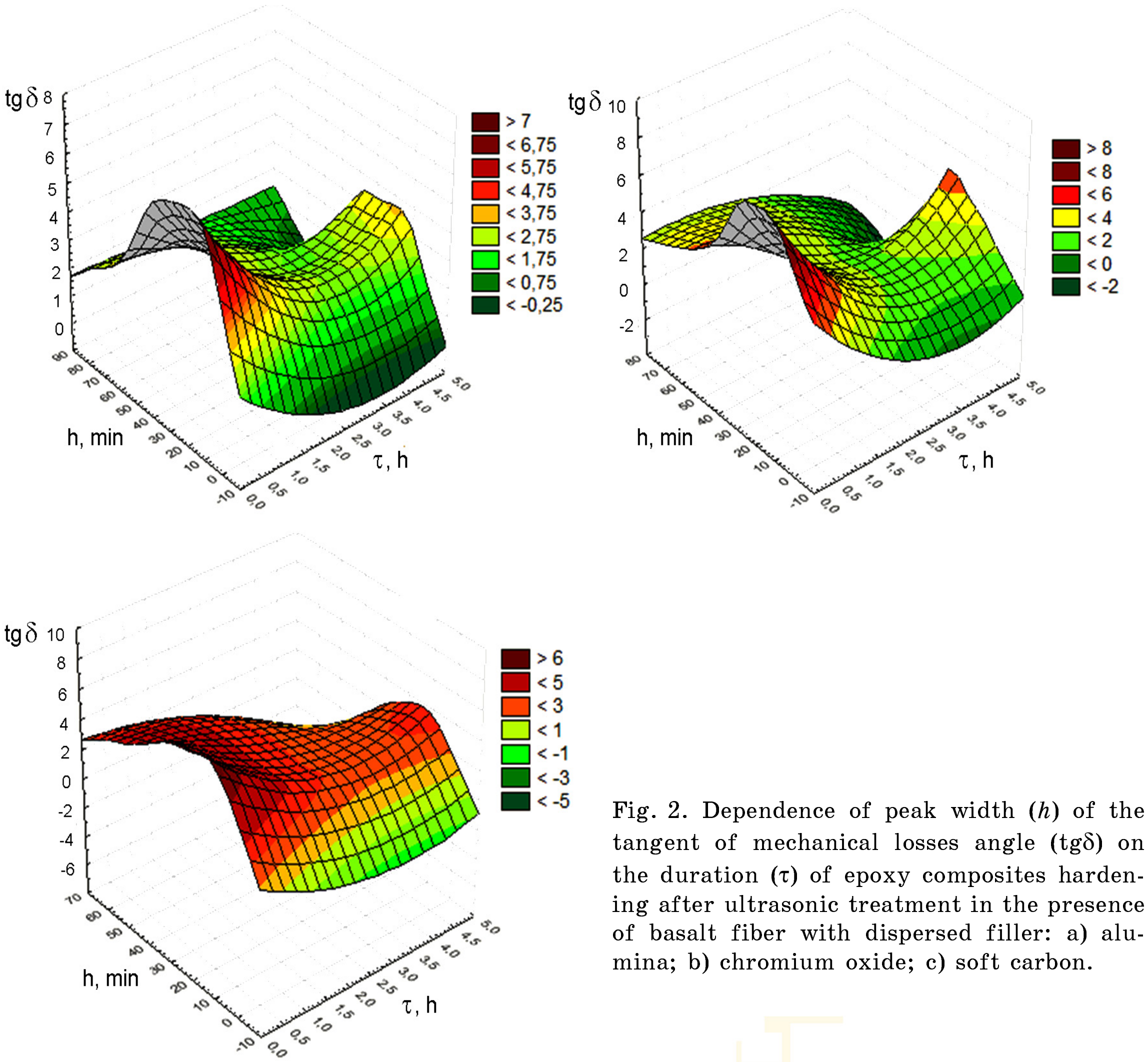

Fig. 2. Dependence of peak width (h) of the tangent of mechanical losses angle (tgδ) on the duration (τ) of epoxy composites hardening after ultrasonic treatment in the presence of basalt fiber with dispersed filler: a) alumina; b) chromium oxide; c) soft carbon.

Optical microscopy shows that the high intensity and oscillation frequency of the concentrator results in the destruction of newly formed cavitation bubbles.

Thus, structuring the composite matrix after UST is confirmed by the results of studying the molecular mobility of the side groups of CM (Fig. 2). Depending on the nature of dispersed filler, there is a shift of $\tan(\delta_{max})$ towards longer times of CM hardening. However, in the case of soft carbon (SC) as filler, the relaxation processes of the segments and side groups slightly shift to the left and right along the hardening time axis, compared to other CM containing alumina and chromium oxide.

The introduction of ferromagnetic filler soft carbon intensifies the cross-linking processes in the matrix surface layers due to the interaction of magnetic field of the dispersed filler and the magnetic moment of the domain of epoxy binder macromolecules. The introduction of ferromagnets into heterogeneous systems intensifies the processes of interaction of macromolecules with the solid surface of the fillers. The degree of cross-linking in surface layers increases, therefore, the strength properties of CM increase. An increase in the width of the $\tan(\delta_{max})$ in CM with SC filler, regardless of the fibers nature, indicates an increase in the degree of oligomer cross-linking around the surface of dispersed particles. In comparison with other investigated materials, the layers with more uniform structure are formed in this case.

The simultaneous effect of the magnetic field of ferromagnetic fillers and ultrasonic treatment resulted in the improvement in the physical and mechanical properties of the developed CM by 1.5 times. In our opinion, these results are associated with the relaxation rearrangement of the supramolecular structure of the epoxy binder during the formation of the material. Ultrasonic treatment reduces the size of globular formations and their conglomerates by 3–5 times. In our opinion, these processes are the result of a synergistic effect of both treatment itself and constant magnetic field of soft carbon fillers. Moreover, an increase in cohesive strength of the developed epoxy composite materials is observed.

4. Conclusions

An increase in physical and mechanical characteristics of epoxy composites under the action of ultrasonic treatment is proved in this paper. An additional increase in these characteristics is achieved due to the influence of fillers nature, including the magnetic component (for ferromagnets). The following dispersed fillers are used: soft carbon, green chromium oxide and alumina; and fibrous: glass, carbon, basalt fibers. It is proved that the improvement of the properties is associated with the relaxation processes in the surface layers at the interface of the "epoxy binder — filler" system.

The time intervals of the molecular mobility of the segments ($\tau = 0.3...1.0$ h) and physical bonds ($\tau = 2.0...3.0$ h) in the surface layers of the epoxy composites at the interface containing a dispersed and fibrous filler were determined experimentally.

The intensification of the cross-linking processes in the epoxy matrix after ultrasonic treatment of the composites was estimated by the displacement of the peak of the tangent of the angle of mechanical losses $\tan(\delta_{max})$ for the process of segment relaxation towards smaller values of time ($\Delta t = 5...22$ min); the reduce of the start time for CM hardening was proved experimentally.

An increase in the degree of cross-linking is proved. A decrease in the extreme value of the tangent of the angle of mechanical losses after UST is observed, moreover, the time of relaxation processes during materials formation decreases.

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