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INVESTIGATION OF MOLECULAR MOBILITY IN A MODIFIED EPOXY BINDER USING THE DIELECTRIC LOSS TANGENT METHOD

Ascertaining molecular mobility in the near-surface layers, relying on dielectric assessment, has shown that the creation of a phase border—brought about by incorporating dispersed additives into the polymeric matrix—markedly alters the relaxation patterns of the macromolecule at the interfacial zone. A comprehensive study was carried out to investigate the influence of electric spark hydro-impact (ESHI) treatment on the structure formation processes and relaxation behaviour of epoxy-based composites. The experimental results demonstrated that the application of ESHI leads to a noticeable shift of relaxation maximum temperatures toward higher values by approximately 30–40 K, accompanied by variations in the width and intensity of dielectric loss peaks. These changes are indicative of an increased degree of molecular cross-linking, enhanced network density, and the development of more organized surface layers within the polymer matrix. Furthermore, the modification of the oligomer by ESHI promotes the formation of a spatially homogeneous and energetically stable structure, resulting in improved thermo-mechanical stability. The combined effect of ESHI and the incorporation of the DEG-1 plasticiser has been shown to positively influence the segmental mobility of macromolecular chains, facilitating a more flexible yet robust polymer network. This synergy contributes to improved adhesive strength at the filler–matrix interface and greater resistance to thermal degradation. Overall, the obtained data confirm that ESHI treatment represents an efficient pre-processing technique for tailoring the molecular architecture of epoxy composites, providing a promising approach for enhancing their operational reliability and durability in demanding environments.

Keywords: *epoxy matrix, composite materials, structure formation, relaxation processes, dielectric losses, segmental mobility.*

СТУХЛЯК ПЕТРО, ТОТОСЬКО ОЛЕГ, СТУХЛЯК ДАНИЛО
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ДОСЛІДЖЕННЯ МОЛЕКУЛЯРНОЇ РУХЛИВОСТІ В МОДИФІКОВАНОМУ ЕПОКСИДНОМУ СПОЛУЧНОМУ ЗА ДОПОМОГОЮ МЕТОДУ ТАНГЕНСУ ДІЕЛЕКТРИЧНИХ ВТРАТ

Було проведено комплексне дослідження з метою вивчення впливу обробки електричним іскровим гідроударом (ЕІГУ) на процеси формування структури та релаксаційну поведінку композитів на основі епоксидної смоли. Експериментальні результати продемонстрували, що застосування ЕІГУ призводить до помітного зсуву максимальних температур релаксації в бік більш високих значень приблизно на 30–40 К, що супроводжується змінами ширини та інтенсивності піків діелектричних втрат. Ці зміни свідчать про підвищення ступеня молекулярного зшивання, збільшення щільності мережі та розвиток більш організованих поверхневих шарів у полімерній матриці. Крім того, модифікація олігомеру за допомогою ЕІГУ сприяє формуванню просторово однорідної та енергетично стабільної структури, що призводить до поліпшення термомеханічної стабільності. Показано, що комбінований ефект ЕІГУ та включення пластифікатора ДЕГ-1 позитивно впливає на сегментну рухливість макромолекулярних ланцюгів, сприяючи створенню більш гнучкої, але міцної полімерної мережі. Ця синергія сприяє поліпшенню адгезійної міцності на межі наповнювач-матриця та більшій стійкості до термічного розкладу. В цілому, отримані дані підтверджують, що обробка ЕІГУ є ефективною технологією попередньої обробки для адаптації молекулярної архітектури епоксидних композитів, що забезпечує перспективний підхід до підвищення їх експлуатаційної надійності та довговічності в складних умовах.

Ключові слова: *епоксидна матриця, композиційні матеріали, формування структури, процеси релаксації, діелектричні втрати, сегментарна рухливість.*

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Problem statement

The fundamental requirements for advanced composite materials and the protective or functional coatings derived from them include the comprehensive improvement of their molecular–mechanical, physicochemical, and structural characteristics. Achieving this goal is directly linked to an in-depth understanding of the mechanisms governing the formation and evolution of their internal structure. Therefore, a detailed experimental investigation of the dynamic processes associated with the structural organization of composite materials (CM) under various technological conditions and at distinct stages of material formation is of paramount importance [1].

Although significant progress has been made in the study of polymer-based composites, the physicochemical transformations occurring in epoxy matrices subjected to electro-spark hydro-impact (ESHI) treatment remain insufficiently elucidated [2–6]. The ESHI method represents a complex form of surface modification that combines the effects of localized electric discharge, mechanical shock waves, and thermal impulses. These combined influences can induce structural rearrangements at both the molecular and supramolecular levels, potentially altering the energy state, relaxation behavior, and interfacial interactions within the polymer matrix. In this regard, systematic research on the influence of ESHI on the structural characteristics, relaxation dynamics, and physicochemical properties of initial and modified materials is of particular scientific and practical relevance.

The determination of molecular mobility in the near-surface layers, based on dielectric characterization, has revealed that the formation of a phase boundary—caused by the introduction of dispersed fillers into the oligomeric matrix—significantly modifies the relaxation behavior of the polymer at the interfacial region [2, 7]. These modifications are typically expressed as a shift in the glass transition temperature (Tg), a broadening of the relaxation time spectrum, and, in some cases, the emergence of additional relaxation modes. Such effects suggest changes in the conformational freedom of macromolecules and in the structural ordering of the surface layers, which play a decisive role in determining the overall dielectric response and energy dissipation characteristics of the composite.

Moreover, the influence of conformational rearrangements is further enhanced by the energetic interactions between the surfaces of dispersed particles and the surrounding oligomeric binder [8, 9]. The nature and intensity of these interactions are strongly dependent on the chemical composition, magnetic properties, and surface energy of the filler. These parameters collectively define the strength of interfacial adhesion at the phase boundary and consequently determine the integrity, mechanical performance, and stability of the composite material as a whole.

Thus, understanding the interplay between structural relaxation, interfacial phenomena, and energy transfer mechanisms in ESHI-treated composites provides a fundamental basis for the targeted design of high-performance materials. Such materials exhibit enhanced adhesion, improved dielectric stability, and superior mechanical resilience, which are essential for their application as protective coatings, electrical insulators, and functional layers in modern engineering systems.

The aim of this study is to investigate the influence of electro-spark hydro-impact (ESHI) treatment on the molecular mobility, structural organization, and dielectric behavior of modified epoxy composite materials. The research seeks to establish the relationship between relaxation processes, interfacial phenomena, and the physicochemical transformations occurring within the polymer matrix during and after modification. By analyzing the temperature and frequency dependencies of dielectric losses using the dielectric loss tangent method, the study aims to elucidate the mechanisms of energy dissipation, polarization dynamics, and structural relaxation in both the initial and ESHI-treated epoxy systems. The ultimate objective is to determine how ESHI treatment affects the adhesion strength, stability, and functional performance of composite coatings under real operating conditions.

Research methodology

The dielectric permittivity (ε′) and the tangent of the dielectric loss angle (tan δ) of KM samples were measured during thermostatting using an E7-14 alternating current bridge. The measurements were performed at frequencies of 0.1 kHz, 1 kHz, and 10 kHz, in accordance with the standardized procedure described in [10]. Cylindrical specimens were prepared with a diameter of 30 ± 0.5 mm and a height of 5 ± 0.05 mm. The deviation in the sample thickness did not exceed 8%, thereby ensuring the uniformity of the electric field distribution and the reliability of the experimental data.

The dielectric loss factor (ε″) was subsequently calculated from the experimental results using the method outlined in [11]. The electrical resistance of the surface coatings was determined according to the protocol specified in [12], while the capacitance of the samples was obtained in compliance with the procedure detailed in [13].

These combined measurements provided a comprehensive characterization of the dielectric behavior of KM under thermal stabilization. Such an approach enabled a detailed assessment of polarization mechanisms, charge transport phenomena, and energy dissipation processes over a wide frequency range. The obtained data are essential for understanding the temperature-dependent dielectric properties of the material and for evaluating its potential applications in electronic and insulating systems.

Research results

The temperature-dependent characteristics of relaxation processes in both the initial and modified epoxy matrices were systematically investigated. Particular attention was given to determining the temperature dependencies of dielectric losses in epoxy composites subjected to electro-spark hydro-impact treatment, as well as in untreated (reference) composites. The comparative analysis of these data allowed for a deeper understanding of the influence of surface modification on the dielectric response of the material.

The study of the temperature behavior of relaxation processes in the modified composites is of significant practical importance, as it provides insight into the mechanisms governing charge mobility, dipole orientation, and energy dissipation under thermal stress. These findings are essential for evaluating the operational stability and performance reliability of composite materials (CM) when employed as protective or insulating coatings under real-world service conditions.

When examining the material based on unfilled ED-20 epoxy resin at a frequency of ν = 1 kHz, three distinct relaxation regions were experimentally identified (Fig. 1). It is assumed that these relaxation regions correspond to different types of molecular mobility within the polymer structure. The first relaxation region, observed within the temperature range ΔT = 323–373 K, is attributed to the motion of localized side groups of macromolecules (γ-transition). The second region, occurring within ΔT = 343–393 K, is associated with the mobility of polymer chain segments. The third and broadest relaxation region, observed within ΔT = 373–433 K, corresponds to the cooperative motion of entire molecular chains.

The manifestation of these relaxation processes in the temperature dependence of dielectric losses indicates that the structural formation of epoxy matrices is governed by the mobility of various kinetic units located within the adsorption and surface layers of the polymer. This suggests that both the local and collective dynamics of molecular motion play a crucial role in determining the dielectric behavior and relaxation properties of the material.

It is known [1, 2, 14] that during the formation of the material, a surface layer with properties different from those of the polymer in volume is formed. Due to its heterogeneity, areas of different density can be observed both near the surface of the filler and at a certain distance from it. The results of the studies show (Table 1) that the use of ED-20 epoxy resin as a matrix for the initial and modified EIGU causes the manifestation of three relaxation processes characteristic of molecular mobility in the adsorption and surface layers. The results obtained allow us to conclude that in such polymers there are two types of segmental mobility in the surface layer: segments and groups located in the adsorption layer, as well as segments and groups distant from the filler.

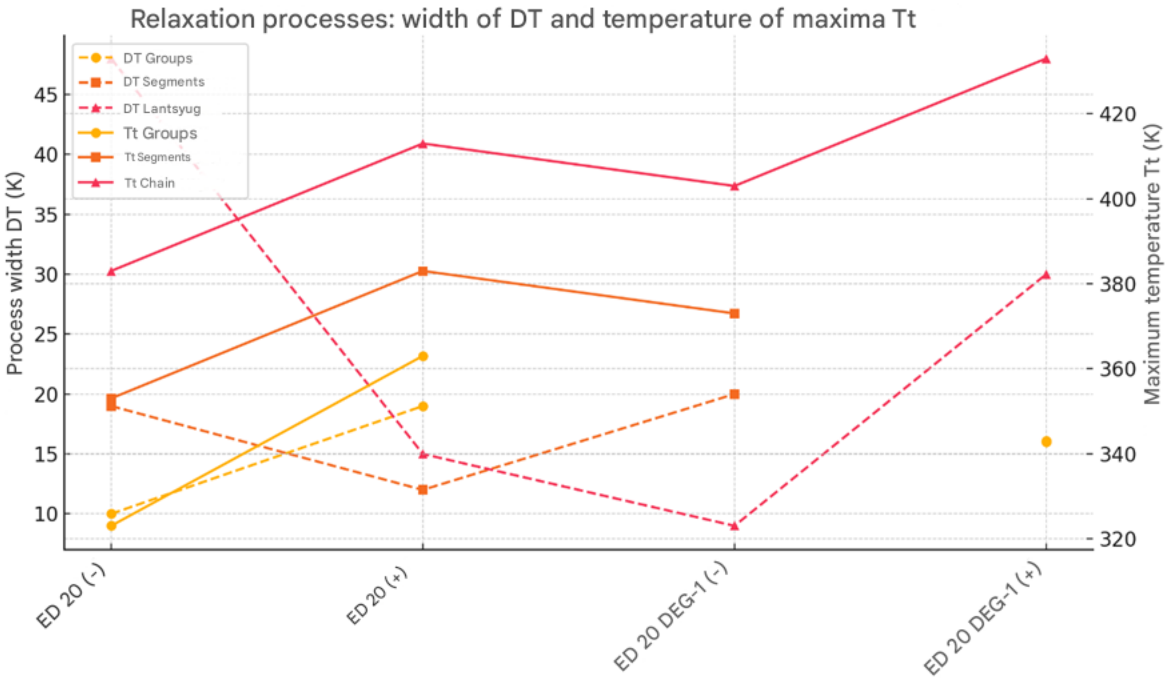

Fig. 1 – Temperature characteristics of relaxation processes in the initial and modified matrix. Concentration of matrix ingredients: ED-20 – 100 wt.%, DEG-1 – 10 wt.%, PEP – 11 wt.%; "+" "–" EIGU material treatment

Table 1 presents experimental data characterising the parameters of relaxation processes in initial and modified epoxy matrices based on ED-20 resin with DEG-1 plasticiser after treatment with electric spark hydro-impact (ESHI). A comparative analysis shows that EISH treatment causes a shift in the temperatures of relaxation loss maxima (Tm) to higher temperatures, which indicates an increase in the degree of polymer structure cross-linking. At the same time, a change in the width of relaxation peaks (ΔT) is observed, which reflects the different mobility of groups, segments and chains of macromolecules in the surface layers. Samples ED-20 (+) and ED-20 DEG-1 (+) are characterised by a broadening of the relaxation spectrum and an increase in the Tm temperature, which indicates the formation of more stable and thermally resistant structures. The introduction of the DEG-1 plasticiser contributes to a change in the relaxation mechanism and a decrease in the temperature of individual processes, which is explained by the increased flexibility of the polymer chain. The results obtained confirm the positive effect of ESHI on the thermodynamic stability and molecular order of the epoxy matrix, and also testify to the effectiveness of combined modification with the use of a plasticiser.

Table 1

Parameters of relaxation processes in initial and modified epoxy matrices after treatment with electric spark hydro-impact

Sample	ΔT group, K	ΔT segments, K	ΔT chain, K	Tm group, K	Tm segments, K	Tm chain, K
ED-20 (–)	10	22	30	335	375	395
ED-20 (+)	15	35	40	345	405	410
ED-20 DEG-1 (–)	20	10	25	350	380	400
ЕД-20 DEG-1 (+)	12	30	45	340	380	425

Note. ΔT — width of the relaxation process; Tm — temperature of maximum dielectric losses; "(–)" — samples without ESHI treatment; "(+)" — after ESHI treatment; DEG-1 — diethylene glycol-1 plasticiser.

Discussion of results

It has been established that after treatment of the ED-20 oligomer with electric spark hydro-shock, the temperature of the dielectric loss maxima (ε″) shifts to the higher temperature range for all determined relaxation processes by 30...40 K. In addition, the width of the maximum characteristic of the relaxation process of groups increases after EIS by 9 K, while for the relaxation process of segments and main chains of macromolecules, its width decreases significantly [8]. The results of the analysis of studies before and after the treatment of the epoxy resin oligomer with ESHI allow us to propose new modes of material formation. The assumption that after treatment with ESHI resin, most of the oligomer transitions to the state of surface layers has been confirmed, with the surface layers not only becoming more saturated with macromolecule segments, but also increasing in total volume. This confirms the positive contribution of the preliminary treatment of ESHI matrix components to its properties and degree of cross-linking.

The above research results indicate relaxation of segments and groups of macrochains in the surface layer areas. In this regard, it was interesting to study the dependence of the loss factor (ε″) on temperature for epoxy matrices containing the DEG-1 plasticiser. It has been established that the introduction of a plasticiser into an epoxy oligomer leads to a slightly different mechanism of composite structure formation. It was shown (Fig. 1) that, compared to the initial (untreated ESHI) ED-20 oligomer, no areas responsible for group relaxation were observed in the temperature dependence of dielectric losses. In addition, the width of the maximum loss factor (ε″) of the segment relaxation process remains almost unchanged (increasing by 1 K), but its maximum shifts to higher temperatures by 20 K compared to the initial untreated and unplasticised oligomer. It has been proven that during cross-linking in the process of structure formation, a larger amount of ED-20 oligomer, as well as DEG-1 aliphatic resin molecules, are involved. In addition, it should be noted that the behaviour of a plasticised epoxy matrix with simultaneously modified ESHI during temperature relaxation is interesting in this comparative context. When analysing the dependence of the dielectric losses of the specified epoxy composite on temperature, it was experimentally established that there is no region responsible for the relaxation of segments (Fig. 1). It should be noted that the maximum temperature characteristic of the relaxation process of groups shifts to the region of lower temperatures (by 20 K), and the maximum temperature responsible for the relaxation process of the main chain shifts to the higher temperature region (by 20 K) compared to the specified characteristics of the material based on epoxy resin modified with ESHI.

Conclusion

Analysis of the experimental data obtained allows us to conclude that a high degree of gel formation occurs in the material under study, which indicates intensive cross-linking reactions in the polymer matrix. A high rate of structure formation is observed already at the initial stages of solidification, which ensures uniform formation of the spatial network and reduces the likelihood of internal stresses in the material. This behaviour is characteristic of systems with increased activity of oligomers modified by electric spark hydro-impact, which contributes to an increase in the energy of intermolecular interactions and the strengthening of interphase bonds. The results obtained indicate that, as a result of the preliminary treatment of EIS components, a more homogeneous and thermally stable structure of the epoxy matrix with improved physical and mechanical characteristics is formed. Thus, the use of EIS at the oligomer preparation stage is an effective method for controlling the kinetics of polymerisation and optimising the process of structure formation in composite materials.

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