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Effect of Electron Irradiation on Internal Friction and Molecular Structural Alterations in Polymer-Based Composite Materials Reinforced with Mica and Asbestos

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Abstract

Effect of electron irradiation on temperature dependences of internal friction in polymer-based composites armored with mica and asbestos is studied. Characteristics of mechanical relaxation spectra and radiation-initiated molecular structural alterations in this type of composites are discussed. It is shown that structural alterations after composite irradiation depend not only on the irradiation dose but to the great extent on the dose rate. In the scissoring polymers at the absence of track and spur overlapping, increase in the dose rate causes the higher degree of polymer radiation scission at the same irradiation dose. At the values of dose and dose rate that exceed the level characteristic for the given type of the polymer binder, spur overlap leads to the decrease in the relative rate of radiation scission. The latter can be the cause of scission change to cross-linking at heightened temperatures. All the polymer binders used in the composites under study are subjected to destruction at the heightened doses of electron irradiation. Thermal processing of this type of composites can be used both for their higher radiation resistance and partial recovery of the cross-linked structure of their polymer matrix.

Introduction

This paper continues a series of experimental studies [1-5] of radiation-induced structural transformations in polymer-based composite materials and the associated alterations in the mechanical relaxation spectra. The subjects of inquiry were the composites reinforced with mica and asbestos. The detailed characteristics of these materials are given in the handbook [6]. They are commercially produced and widely used as heat-resistant elements of electrotechnical equipment, including devices operating in the fields of ionizing irradiation. Therefore, studies of their radiation resistance are of practical interest. Since mica and asbestos are highly radiation-resistant materials [6], behavior of the composites with this type of fillers under irradiation is defined by the radiation properties of the polymer binder and its interaction with the reinforcing fibers.

For the under-beam applications of any composite material, most important are the problems of recovery of its structure and properties after irradiation and prediction of the radiation-induced alterations of its characteristics. An important source of this information necessary for development of the improved radiation modifications of the composites are studies of mechanical relaxation spectra, highly sensitive to radiation-induced structural alterations.

However, there were only few publications on internal friction in composites to the end of 1990's [7,8]. Systematic studies of mechanical relaxation spectra in polymer-based composites and their alterations under ionizing irradiation were described in papers [1-5]. These studies cover such classes of materials as glass-cloth laminates, paper-based laminates, foiled dielectrics, and carbon-reinforced composites.

Since there is no information on any works on internal friction (IF) in this class of composites, this paper gives the primary identification of relaxation spectra for the typical representatives of the class that is necessary for obtaining more detailed data on structural alterations in different parts of a composite under ionizing irradiation.

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Experimental and Material

The samples of the composites were irradiated with 2 MeV electrons from the electron accelerator ELU-4. The pulse width was 5 μs at the pulse frequency of 200 Hz. The samples were irradiated at room temperature using the time-averaged dose rates of 1.0-3.8 kGy/s in the dose range of 6-17 MGy. The steady-state temperature dependences of internal friction and shear modulus were measured in the temperature range of 20-250°C at the frequency of the sample oscillations of about 1 Hz using the reverse torsion pendulum [5] constructed in Voronezh Technical University, Russia. The measurements were conducted in the original samples before irradiation and 24 hours after irradiation.

The composite LTSS-3 studied in this paper is the mica-armored material consisting of several layers of the micanite paper with the two-side glass-fiber substrate impregnated with epoxy-phenol-formaldehyde varnish LEF-3. The width of each layer was about 0.1 mm. The mica mass content in the composite was 35% and concentration of the binding substance was 45%.

The other materials under study were the mica-reinforced plastic consisting of several layers of the phlogopite mica impregnated with epoxy-phenol-formaldehyde varnish LEF-3 and the heat-resistant composite ANKHOR composed of chrysolite asbestos fibers and the rubber binder.

Internal friction in the glass-mica composite LTSS-3

Temperature dependences of internal friction and shear modulus in the original (un-irradiated) samples of the composite LTSS-3 are given in Fig. 1. Characteristics of the mechanical relaxation spectra of this material are predominantly defined by the glass transitions in the polymer matrix and in the regions of its contact with glass and mica. Relaxation processes associated with these transitions can be observed in the temperature range of 200-250°C.

As well as in the other polymer-based composites, a significant internal friction maximum (α-peak) associated with the polymer matrix transition from the glassy to the high-elastic state is observed in the temperature dependence of internal friction. This relaxation process is accompanied by the characteristic drop in the shear modulus in the vicinity of the glass transition (Fig. 1b).

In polymer-based composites α-peak is usually much wider compared with the simple Debye maximum characteristic for the processes with the single relaxation time [5]. As a rule, it is accompanied by additional IF peaks at one or both sides of the basic maximum [1-5]. These additional maxima (α'-peaks) are associated with the glass transitions in the region of the polymer binder contact with the reinforcing filler. Since the relaxation times of these processes can be very close, the IF peaks overlap strongly. In this case, α'-peaks become apparent due to specific contraflexures at the sides of the α-peak. Application of the standard procedure [5] allows peak separation. The temperatures of the separated α'-maxima are close to the contraflexure temperatures.

Figure 1 shows a rather pronounced contraflexure indicating to the α'-peak at the left side of the α-peak and a wide continuous relaxation spectra at the right side.

The experiments conducted have shown that glass can be characterized by better adhesion to the polymer binder compared with mica fibers. Therefore, it is reasonable to attribute the low-temperature α'-peak

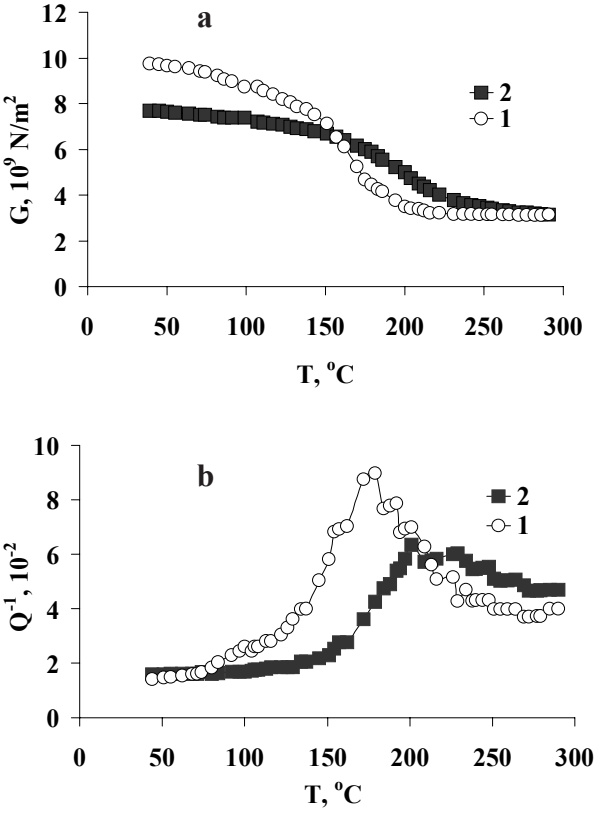

Fig. 1. Temperature dependences of internal friction (a) and shear modulus (b) in the composite LTSS-3 after the first (1) and the second (2) heating. Sample width, h = 1.0 mm.

to the vitrifying process at the boundary of mica and polymer binder, while the high-temperature α'-relaxation spectrum can be attributed to the similar structural transition at the polymer-glass layer boundary.

Figure 1 shows that after the repeated heating the heights of the α- and α'-peaks of internal friction become lower and the temperature of the IF maximums shifts to the higher temperature values.

A decrease in the heights of the internal friction peaks is proportional to the difference between the numbers of the elementary events of cross-linking and scission caused by thermal or radiation action in the corresponding structural component of the composite while the position of the IF peak in the temperature scale defines activation energy of the relaxation process associated with oscillations of the free segments of macromolecules [5].

Thus, the observed behavior of the IF peaks confirms the thermally initiated cross-linking of the polymer binder in all the structural components of the composite.

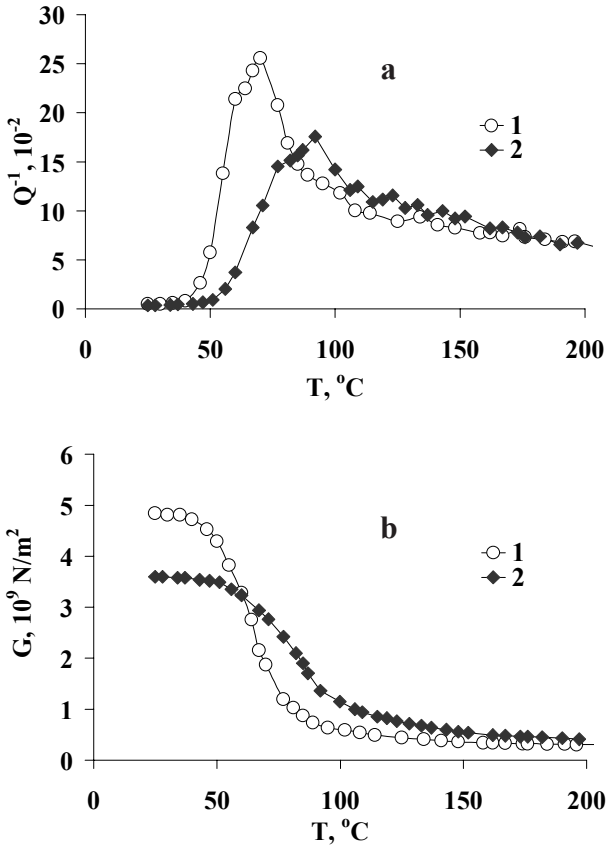

Fig. 2. Temperature dependences of internal friction (a) and shear modulus (b) in the composite LTSS-3: 1 – D = 0; 2 – D = 7 MGy (D is absorbed electron dose). Time-averaged dose rate – $\dot{D}$ = 2 kGy/s. Sample thickness, h = 1.0 mm.

Figure 2 shows that electron irradiation of the composite causes nearly the same cross-linking of the polymer binder as the composite heating up to 200°C. The relative changes in the heights of the IF peaks after irradiation or heating quantitatively correspond to the degree of the polymer cross linking after processing. Figure 3 shows that heating up the irradiated sample during the first measurement of the temperature dependence of internal friction leads to the additional polymer cross-linking and causes increase in activation energy for oscillations of the free segments of macromolecules in all parts of the composite.

The second heating of the sample up to 200°C and its irradiation to the additional dose of 6 MGy (up to the total dose of 13 MGy) causes only insignificant polymer destruction (Fig. 4). In the high-temperature region, numerous IF peaks become apparent in the temperature dependence of internal

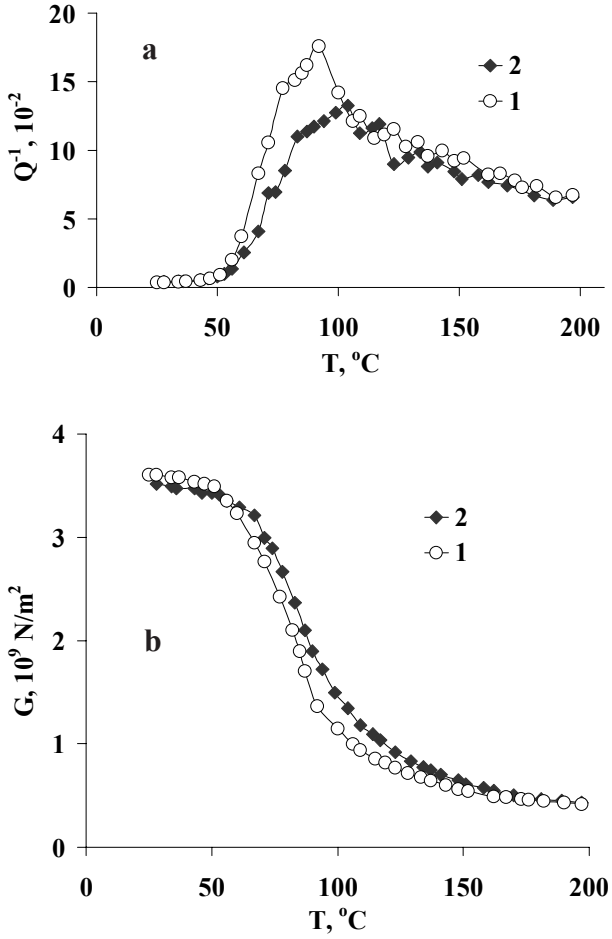

Fig. 3. Temperature dependences of internal friction (a) and shear modulus (b) in the composite LTSS-3 at the first (1) and the second (2) measurements after electron irradiation to the dose of 7 MGy. Time-averaged dose rate – $\dot{D}$ = 2 kGy/s. Sample thickness h = 1.0 mm.

friction. It indicates the discrete distribution in respect to the lengths of the molecular segments of the polymer at least in the region of its contact with the glass fibers. The temperature dependence of the shear modulus practically does not change after this type of processing (Fig. 4b).

The IF temperature dependence after direct electron irradiation of the composite up to the dose of 10 MGy (Fig. 5) shows that cross-linking really changes to scission in the vicinity of this dose. In this case, the form of the IF peaks does not change while the degree of polymer cross-linking appears to be higher than that after thermal processing of the samples before irradiation. The further increase in the irradiation dose leads to nearly proportional increase in the degree of the polymer scission (Fig. 6).

The heating of the sample irradiated to the dose of 17 MGy changes the length distribution of the molecular segments and the form of the internal friction peaks but, in whole, does not cause considerable cross-linking of the polymer matrix (Fig. 7). However, the second heating to 250°C to the great extent restores and stabilizes the cross-linked polymer structure.

Figure 7 shows that after irradiation of the sample twice-heated up to the temperature of 250°C with the additional electron dose of 6 MGy, the IF heights characterizing the number of free macromolecule segments do not exceed the heights of the relaxation maximums in the sample before irradiation. Nevertheless, the shear modulus after this processing becomes almost 5 times lower compared to unirradiated sample.

Figure 8 demonstrates an increase in the internal friction and decrease in the shear modulus in the irradiated LTSS samples as their thickness increases. This phenomenon is associated with changes in the deformation distribution as the number of composite layers increases. During bending vibrations, the inner armoring glass and mica layers are subjected to lower deformations than the well fixed outer lay-

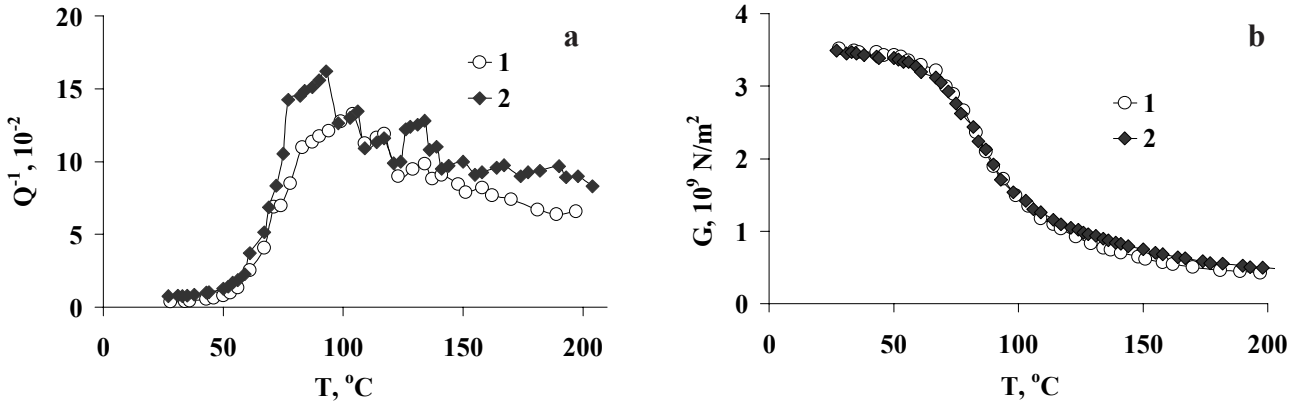

Fig. 4. Temperature dependences of internal friction (a) and shear modulus (b) in the composite LTSS-3 after electron irradiation to the dose of 7 MGy and heating up to 200°C (1) and after second heating of the irradiated sample and additional irradiation to the dose of 6 MGy. Time-averaged dose rate – $\dot{D}$ = 2 kGy/s. Sample thickness, h = 1.0 mm.

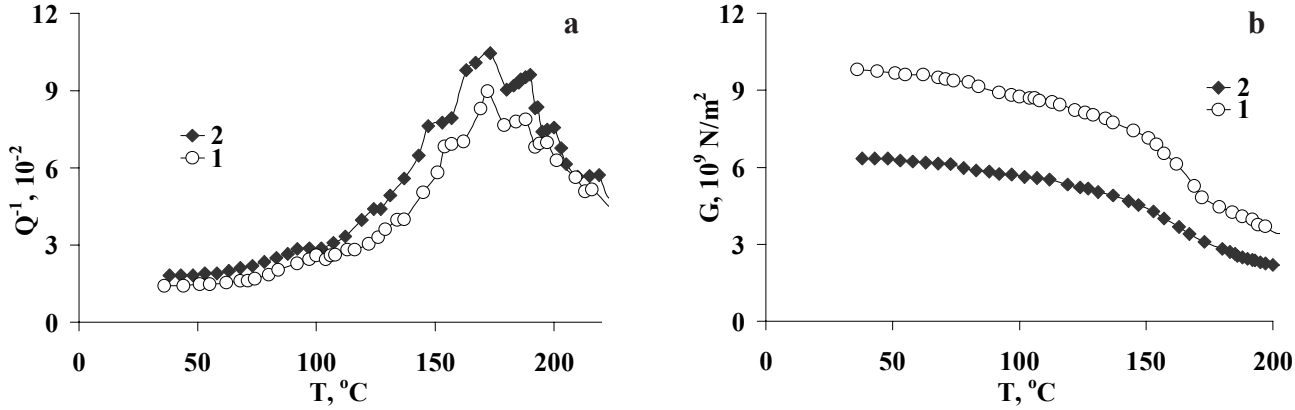

Fig. 5. Temperature dependences of internal friction (a) and shear modulus (b) in the composite LTSS-3: 1 – D = 0; 2 – D = 10 MGy (D is absorbed electron dose). Time-averaged dose rate – $\dot{D}$ = 2 kGy/s. Sample thickness, h = 1.0 mm.

ers. As a result, the composite becomes more viscous and less rigid as the number of the composite layers increases. This effect is apparent both in irradiated and un-irradiated samples; it becomes less considerable as the level of the polymer cross-linking increases.

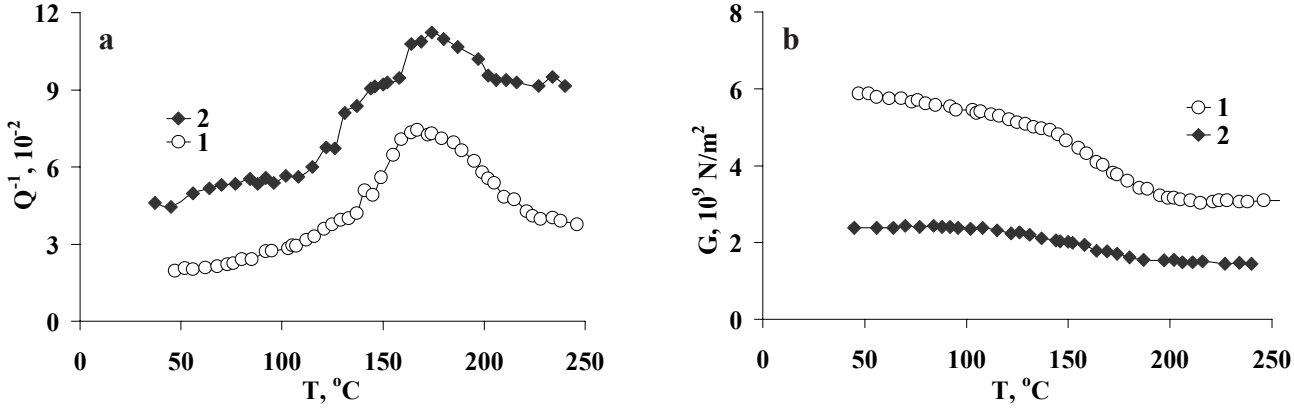

Fig. 6. Temperature dependences of internal friction (a) and shear modulus (b) in the composite LTSS-3 irradiated to different electron doses: 1–D=10 MGy, 2–D=17 MGy. Time-averaged dose rate – $\dot{D}$=2 kGy/s. Sample thickness, h=0.6 mm.

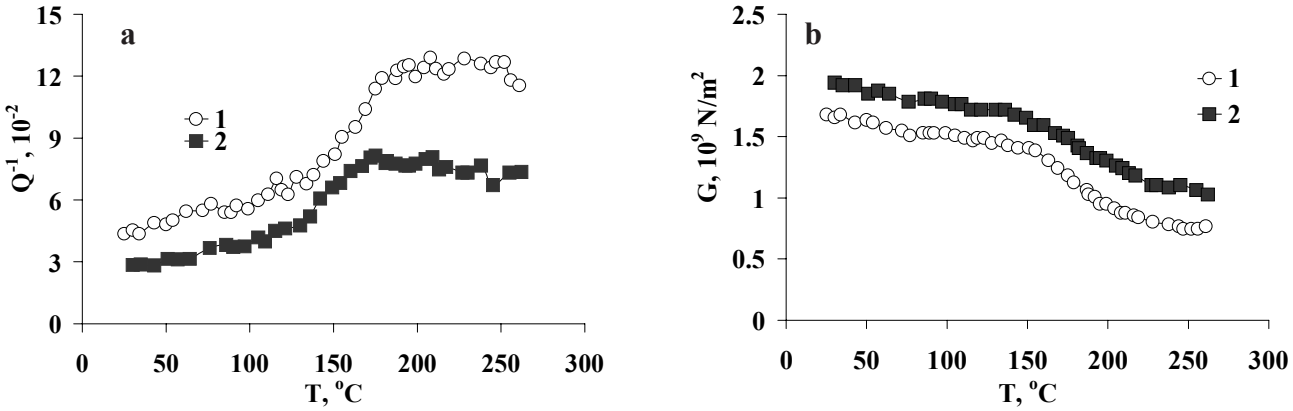

Fig. 7. Temperature dependences of internal friction (a) and shear modulus (b) in the composite LTSS-3 after electron irradiation to the dose of 17 MGy and heating up to 250°C (1) and after second heating of the irradiated sample and additional irradiation to the dose of 6 MGy. Time-averaged dose rate – $\dot{D}$ = 2 kGy/s. Sample thickness, h = 0.6 mm.

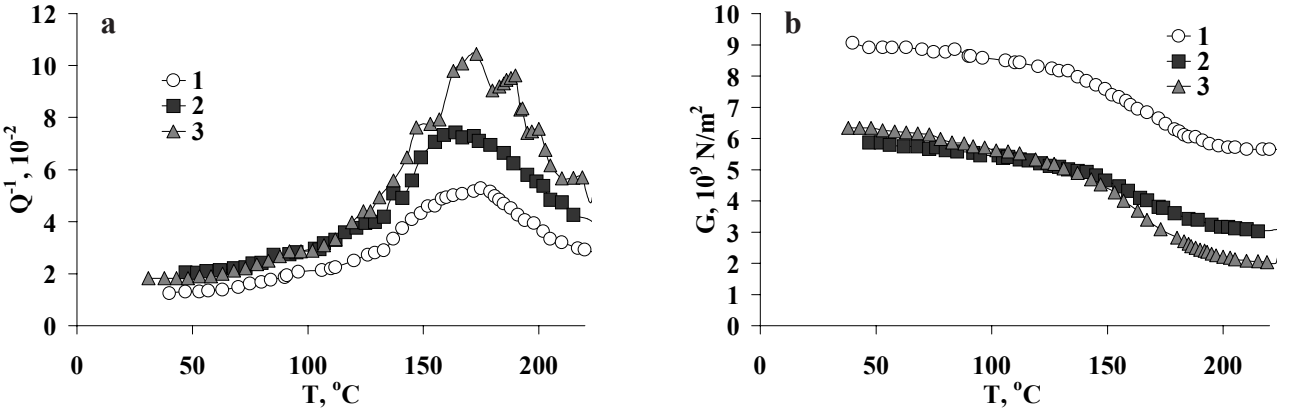

Fig. 8. Temperature dependences of internal friction (a) and shear modulus (b) in the composite LTSS-3 samples of different thickness: 1 – h = 0.5 mm; 2 – h = 0.6 mm; 3 – h = 1.0 mm. Electron dose – D = 10 MGy. Time-averaged dose rate – $\dot{D}$ = 2 kGy/s.

Generally, the experiments conducted show that small doses of electron irradiation cause cross-linking of the epoxy-phenol-formaldehyde binder in the glass-mica composite LTSS-3. Although there is no independent experimental evidence of the neat epoxy-phenol-formaldehyde cross-linking under *e*-beam, the similar behavior of this type of polymer binder was observed in the internal friction experiments on glass-cloth laminates [1,2,5].

According to the IF data, at the doses higher than 10 MGy cross-linking is changed by scissoring in all the structural components of the composite. The destructive action of the electron irradiation can be to the great extent compensated by the composite heating up to the temperature of 200-250°C before or after irradiation.

Internal friction in the mica-reinforced plastic LIFT

Application of the same type of the polymer binder in LIFT as that used in the described above glass-mica composite LTSS-3 assumes certain similarity of the mechanical relaxation spectra of these materials and their similar behavior under the action of radiation.

Figure 9 shows that the glass transition in the composite LIFT is characterized by extremely wide relaxation spectrum that confirms the availability of the free molecular segments of different length and different oscillation modes.

This type of molecular structure leads to the absence of the well pronounced temperature of the glass transition. As well as in the composite LTSS-3, electron irradiation of this material up to the dose of 7 MGy causes cross-linking of the polymer matrix and shift of the IF peaks to higher temperatures. A similar additional effect is observed after heating the irradiated samples up to 200°C (Fig. 10).

An increase in the dose rate of electron irradiation strengthens the tendency of the polymer binder to cross-linking. It becomes apparent mainly in the shift of the relaxation maximums to higher temperatures.

The probable cause of the shift of the balance of the simultaneously proceeding processes of the polymer cross-linking and scission to prevailing scission is the overlap between the electron tracks and spurs at the higher dose rates.

In the simple model [9], the threshold dose rate $\dot{D}_{th}$ and the threshold dose D_{th} for spur overlapping is given by the following equations:

$$\dot{D}_{th} = \frac{10^5 e}{\nu G \rho \tau} \qquad (1)$$

$$D_{th} = -\dot{D}\tau \ln\left(1 - \frac{\dot{D}_{th}}{\dot{D}}\right), \ \dot{D} > \dot{D}_{th} \qquad (2)$$

where e is the charge of an electron, D is dose (Gy), $\dot{D}$ is the dose rate (Gy/s), ν is the volume of a spur (cm^3/spur), ρ is density of the system (g/cm^3), G is the radiation-chemical yield of spurs (spurs/100 eV), and τ is the lifetime of spurs (s).

$\dot{D}_{th}$ was tabulated in paper [9] assuming that G = 1, ρ = 1 and that the spur is a sphere of radius r. For the reasonable values of r and τ ($r = 10^{-5}$ cm, $\tau = 10^{-6}$ s) estimation of $\dot{D}_{th}$ yields the value of 4×10^6 Gy. This value of the dose rate is close to the dose rates in pulse used in this work (1 MGy/s to 3.8 MGy/s in a pulse that corresponds to the time-averaged dose rate from 1 kGy/s to 3.8 kGy/s). The estimations show

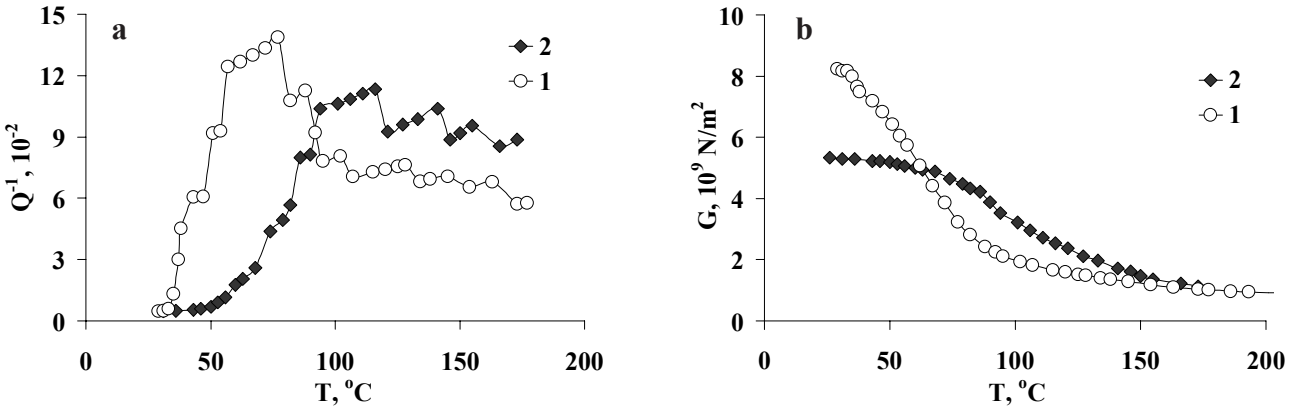

Fig. 9. Temperature dependences of internal friction (a) and shear modulus (b) in the mica-reinforced composite LIFT: 1 – D = 0; 2 – D = 7 MGy (D is absorbed electron dose). Time-averaged dose rate – $\dot{D}$ = 2 kGy/s. Sample thickness, h = 1.0 mm.

that the spur overlap is probable in the experimental conditions of this study (Fig. 11).

High concentration of radicals in small volumes eliminates steric hindrances for their recombination. It hinders disproportionation reactions leading to stabilization of the torn-off molecule ends and finishing the scission event. As a result the relative fraction of the molecule cross-linking events becomes higher.

When irradiated to the doses exceeding 10 MGy, the polymer binder of the composite LIFT is destroyed as well as in the case of the glass-mica composite LTSS-3. The process of radiation scission can be detained by thermal processing of the composite (Fig. 12).

Figure 12 shows that heating of the composite LIFT sample irradiated to the dose of 7 MGy up to the temperature of 200°C and its subsequent irradiation to the dose of 6 MGy (up to the total dose of 13 MGy) does not lead to the molecule scission. The result of this processing is the change in the length distribution of free macromolecule segments accompanied by the shift in the IF peaks to higher temperatures and some increase in the shear modulus in the vicinity of the glassy transition.

Internal friction in the asbestos-reinforced composite ANKHOR

It is interesting to compare the data on mechanical relaxation spectra of the mica- and glass-mica armored composites impregnated with the epoxy-phenol-formaldehyde binder with the behavior of internal friction and shear modulus in the heat-resistant composite ANKHOR composed of chrysolite asbestos fibers and the rubber binder.

The characteristic feature of relaxation spectrum in the composite ANKHOR is the availability of the

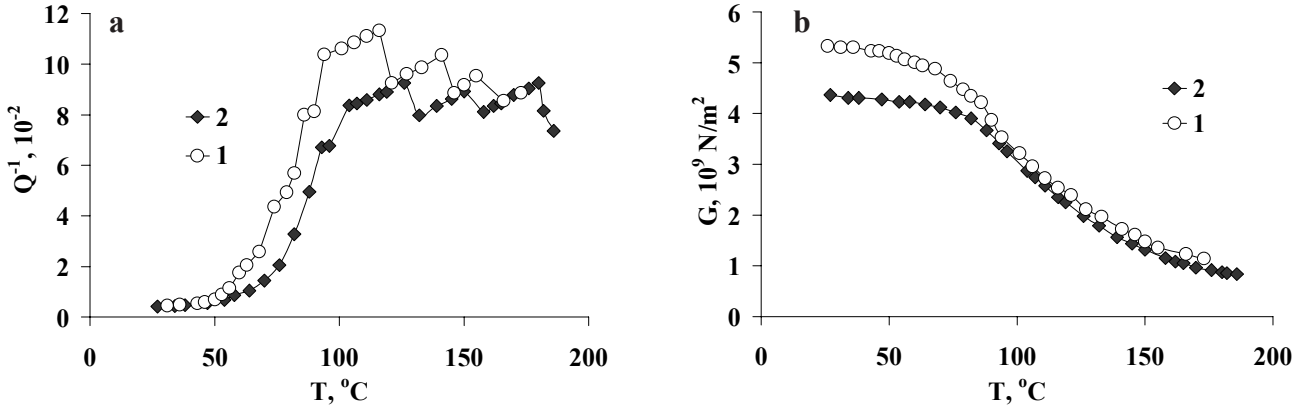

Fig. 10. Temperature dependences of internal friction (a) and shear modulus (b) in the mica-reinforced composite LIFT after electron irradiation to the dose of 7 MGy (1) and subsequent heating of the irradiated sample up to 200°C (2). Time-averaged dose rate – $\dot{D}$ = 2 kGy/s. Sample thickness, h = 1.0 mm.

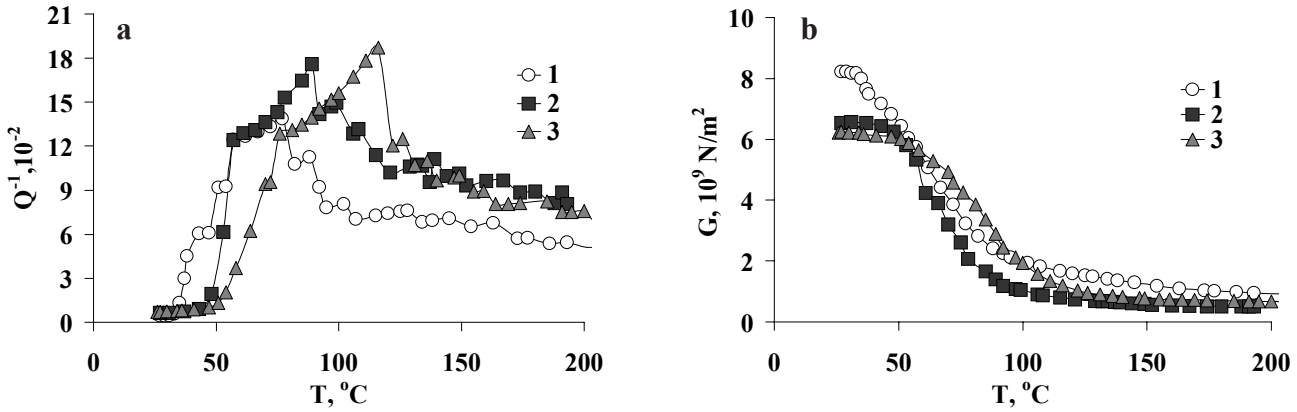

Fig. 11. Temperature dependences of internal friction (a) and shear modulus (b) in the mica-reinforced composite LIFT after electron irradiation to the dose of 6 MGy at different dose rates: 1 – unirradiated sample, 2 – Time-averaged dose rate – $\dot{D}$ = 1.2 kGy/s; 3 – $\dot{D}$ = 3.8 kGy/s. Sample thickness, h = 1.0 mm.

well-pronounced maximum associated with the glass transition at about 170°C (Fig. 13). In the high-temperature region the observed spectrum is the superposition of at least three IF relaxation peaks probably associated with specific characteristics of the glass transition in the area of the polymer matrix contact with asbestos.

Figure 13 shows that electron irradiation of the ANKHOR samples to the dose of 7 MGy causes considerable destruction of the rubber binder accompanied by a decrease in the shear modulus of the composite.

Heating of the irradiated sample up to 230°C does not change the form of the IF α-peak; it only shifts the peak to its original position in the temperature scale characteristic for the un-irradiated sample (Fig. 14). The height of the peak after heating is only 17% higher compared with the maximum IF value in the un-irradiated sample. Thus, heating of the sample up to 230°C almost completely restores and stabilizes the molecular structure of the polymer binder. The repeated heating of the sample up to 230°C does not lead to noticeable changes in the temperature dependences of internal friction and shear modulus.

Figure 15 shows that after irradiation of the ANKHOR sample to the dose of 7 MGy and thrice-repeated heating, additional irradiation to the dose of 6 MGy also does not cause substantial changes in mechanical relaxation spectrum and in the temperature dependence of shear modulus.

In the contrast to the composites with epoxy-phenol-formaldehyde binder, increase in the dose rate of electron irradiation leads to the higher scission degree of the polymer binder in the composite ANKHOR (Fig. 16).

Thus, in the similar irradiation conditions, effects associated with the spur overlapping are considerably less pronounced in the rubber matrix. In the

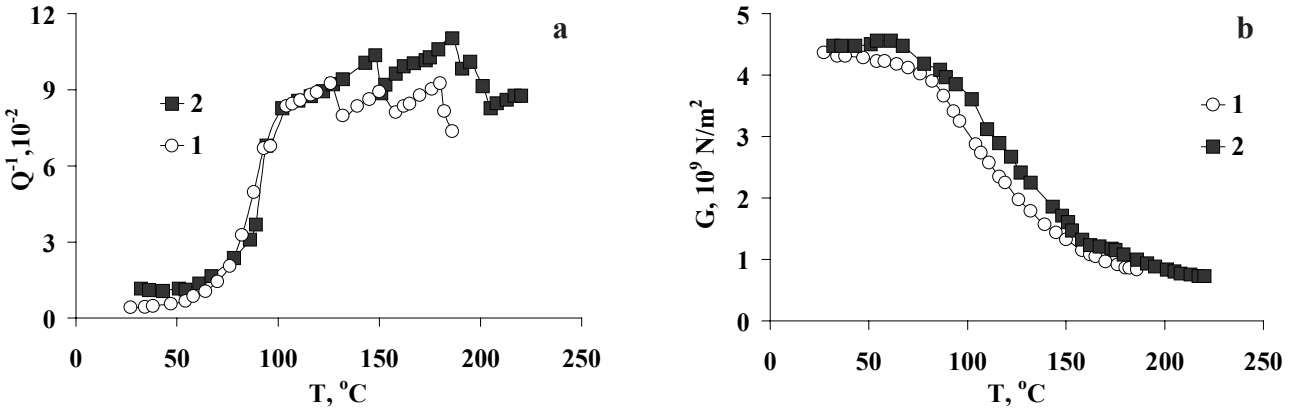

Fig. 12. Temperature dependences of internal friction (a) and shear modulus (b) in the mica-reinforced composite LIFT after electron irradiation to the dose of 7 MGy (1) and after subsequent heating of the irradiated sample up to 200°C and additional irradiation to the dose 6 MGy. Time-averaged dose rate – $\dot{D}$= 2 kGy/s. Sample thickness, h = 1.0 mm.

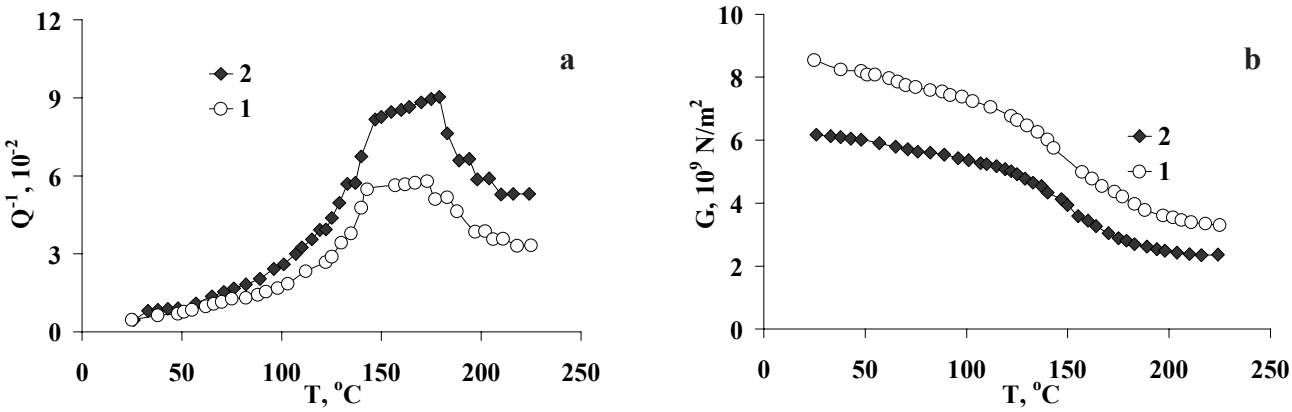

Fig. 13. Temperature dependences of internal friction (a) and shear modulus (b) in the asbestos-reinforced composite ANKHOR: 1 – D = 0; 2 – D = 7 MGy (D is absorbed electron dose). Time-averaged dose rate – $\dot{D}$ = 2 kGy/s. Sample thickness, h = 1.1 mm.

absence of these effects, increase in the dose rate leads to increase in the accumulation rate of the radicals that appear as a result of the breaks of C–C and C–H bonds. These radicals are responsible for macromole-

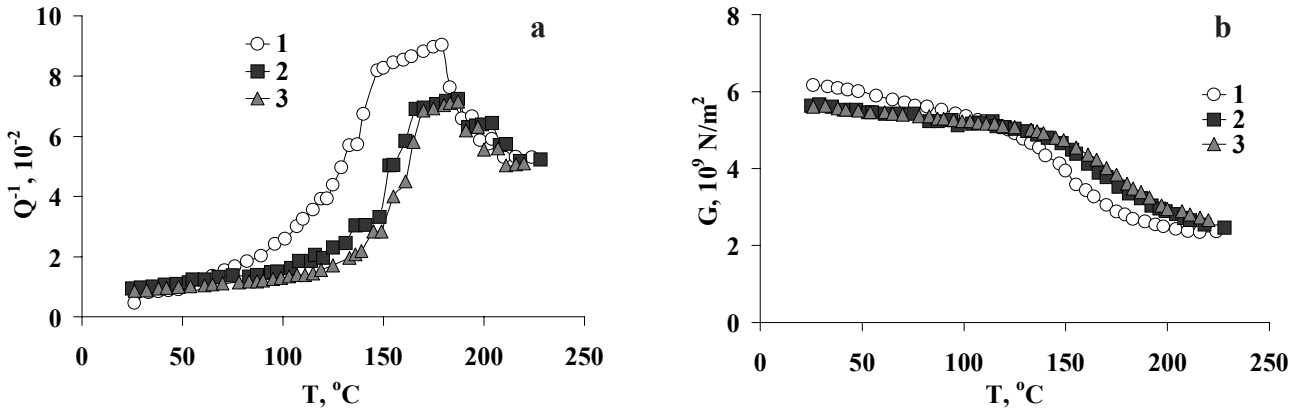

Fig. 14. Temperature dependences of internal friction (a) and shear modulus (b) in the asbestos-reinforced composite ANKHOR after electron irradiation to the dose of 7 MGy (1), after heating irradiated sample up to 230°C (2) and after repeated heating up to 230°C (3). Time-averaged dose rate – $\dot{D}$ = 2 kGy/s. Sample thickness, h = 1.1 mm.

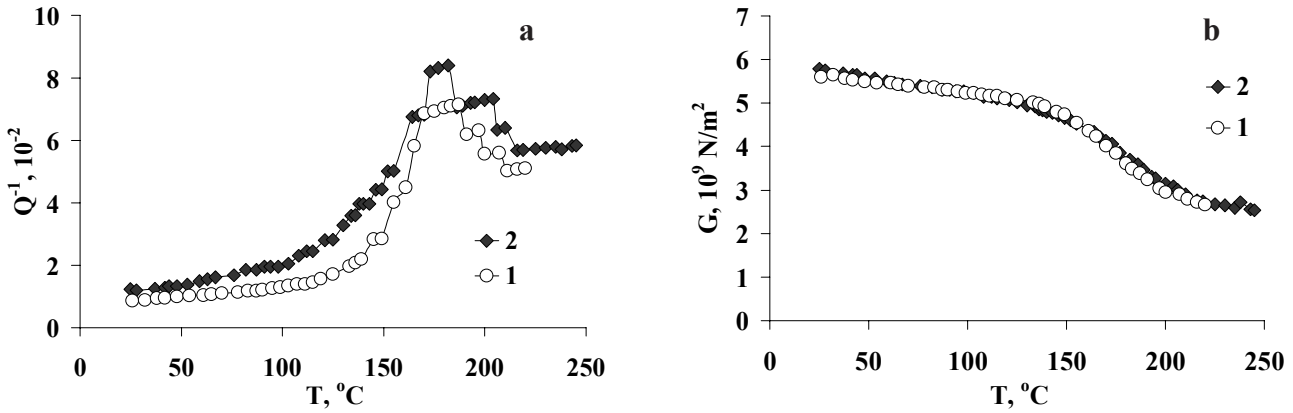

Fig. 15. Temperature dependences of internal friction (a) and shear modulus (b) in the asbestos-reinforced composite ANKHOR after electron irradiation to the dose of 7 MGy and twice repeated heating of the irradiated sample up to 230°C (1) and after the third heating and additional irradiation with the dose of 6 MGy. Time-averaged dose rate – $\dot{D}$ = 2 kGy/s. Sample thickness, h = 1.1 mm.

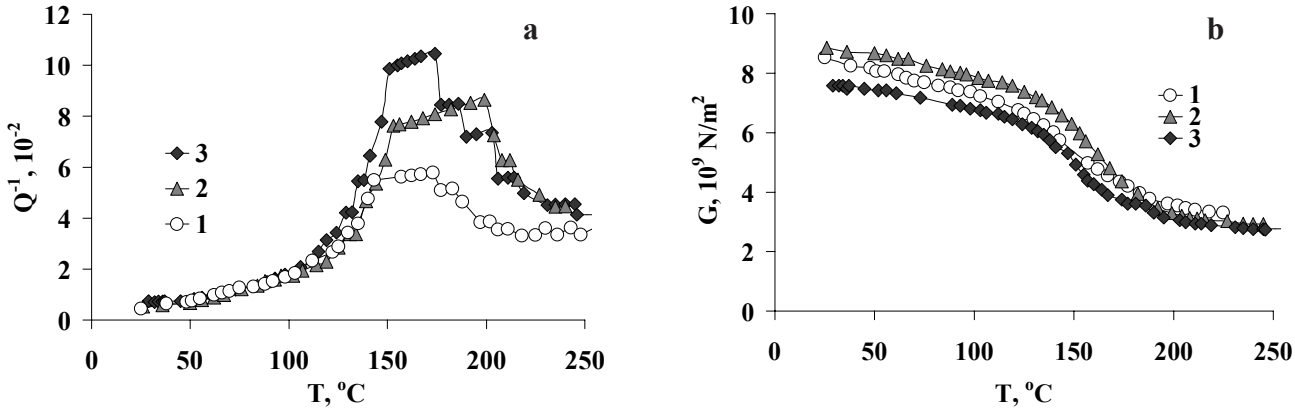

Fig. 16. Temperature dependences of internal friction (a) and shear modulus (b) in the asbestos-reinforced composite ANKHOR after electron irradiation to the dose of 7 MGy at different dose rates: 1 – unirradiated sample; 2 – Time-averaged dose rate – $\dot{D}$ = 1.2 kGy/s; 3 – $\dot{D}$ = 3.8 kGy/s. Sample thickness, h = 1.1 mm.

cule scission and cross-linking, respectively. The difference in the numbers of the elementary events of scission and cross-linking becomes higher as the dose increase; the latter leads to the prevailing destruction of the polymer binder.

Conclusions

It follows from the experiments conducted that in the polymer-based composite materials reinforced with mica and/or asbestos fibers radiation-induced processes of scission and cross-linking of the polymer binder have the same direction in different structural components of the composite. Phenomena associated with changes in the molecular structure in the area of the polymer contact with the armoring fibers play substantially less important role compared with such composites as glass-cloth or hardened paper laminates [1-3].

The results of this study show that structural alterations after composite irradiation depend not only on the irradiation dose but to the great extent on the dose rate. In the degrading type of polymers in the absence of track and spur overlapping, an increase in the dose rate causes the higher degree of polymer radiation scission at the same irradiation dose. At the values of dose and dose rate that exceed the level characteristic for the given type of the polymer binder, spur overlap leads to the decrease in the relative rate of radiation scission. The latter can be the cause of the scission change to cross-linking at higher doses and dose rates.

All the polymer binders used in the composites in this study are subjected to destruction at the higher doses of electron irradiation. Thermal processing of this type of composites can be used both for their higher radiation resistance and partial recovery of the cross-linked structure of their polymer matrix.

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