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The Influence of Cycling Deformation and Annealing on the Elastic/Inelastic Properties of PTFE-Based Nanocomposite Filled with 7.5wt% Fe Cluster-Doped CNTs

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(Presented by Academy Member Ramaz Katsarava)

For the development of PTFE-based nanocomposites with the regulated technological mechanical and parameters it is necessary to reveal the correlation between their structural and dynamical-mechanical properties. The researches in this direction were performed using a low-frequency internal friction technique. The behavior of the elastic/inelastic properties of PTFE-based nanocomposite material filled with the optimal (7.5 wt%) concentration of Fe atom cluster-doped carbon nanotubes (CNTs), depending on high amplitude cycling deformation and post-deformation annealing was investigated using amplitude-independent (AIIF) and amplitude-dependent (ADIF) internal friction measurements. The characteristics of dynamical-mechanical strengthening of the Fe cluster doped PTFE-based polymeric materials were determined for the first time, and the possible mechanisms of strengthening have been analyzed. It was shown that high-amplitude cyclic deformation leads to a considerable reduction in activation energy (H, kcal/mole) of β(crystalline) and α(amorphous) relaxation processes, the magnitude of critical amplitudes (ε_c) of microplastic deformation beginning and shear modulus ($G \sim f^2$) in comparison to those for the initial sample before cyclic deformation. It was also found that the post-deformation annealing of the cyclically deformed sample at 150°C/30 min ensures a complete restoration of the above parameters to the values exceeding those for the initial sample. *© 2020 Bull. Georg. Natl. Acad. Sci.*

PTFE, nanocomposite, Fe cluster-doped CNT, internal friction, shear modulus

The unique combination of physico-mechanical properties and structural peculiarities of virgin PTFE [1-3], caused by its particular molecular structure and semi-crystalline multi-phase composition [4-7] that distinguish it from other conventional polymeric materials create a big potential for the development of a wide range spectrum of advanced PTFE-based nanocomposite/

composite materials with the excellent physical, mechanical and functional characteristics, by modifying the polymer matrix with several nano/micro-particles of fillers. The reviews of the last decade literature [8-11] showed that a distinct effect on friction and wear behavior of the PTFE may be caused by micro-scale as well as nano-scale inorganic fillers (ceramics and carbon nanoform particles, CNFs). Compilation of data regarding the modifying of PTFE matrix by ceramic nanoparticles [8, 10] as well as by carbon nanoforms (CNTs, CNPs) [11], showed that the optimal concentrations of the nanometer-sized filler particles of both types are ~2÷10wt%, while a more typical optimum for polymer composites made with micrometer-sized filler particles is on the order ~25÷30wt%. Here should be noted that the use of CNFs nanoparticles as a filler for the PTFE matrix would provide a considerable improvement in the heat- and electric conductivities coupled with the increase in its strength that is impossible in the case of ceramic nanoparticle fillers.

Along with the development of CNF nanoparticles production technology during the last decade, preferably of core-shell-type nanoparticles of CNFs (CNTs, CNPs) doped with the ferromagnetic atom (Fe, Co, Ni) clusters [12,13], as the hybrid fillers for PTFE matrix, has deserved a considerable attention. However, few data have been reported on the structure-properties relationship in the PTFE-based nanocomposite materials filled with the ferromagnetic atom clusters-doped CNTs. The frictional, wear and damping responses of the developed new PTFE-based trial nanocomposite materials filled with the Fe atom cluster-doped CNTs were first studied in the authors' recent works [14, 15]. Consequently, for further development of the above-type advanced multi-functional nanocomposite materials for the diversified applications, it is important to study their inelastic/elastic properties in the wide range of temperatures and deformation rates, using such a structure-sensitive multi-parametric measuring technique as a low-frequency mechanical spectroscopy [16]. Thus, the aim of the proposed paper is the amplitude-independent (AIIF) and amplitude-dependent (ADIF) internal friction and shear modulus study of inelastic/elastic behavior of the new trial PTFE-based nanocomposite material filled with the optimal amount (7.5 wt%) of Fe atom cluster-doped carbon nanotubes, depending on the cyclic deformation and thermal treatment.

Experimental

The choice of the PTFE-based nanocomposite material containing 7.5wt% of Fe-cluster-doped CNTs as filler was caused by our recent results leading to the conclusion that the above content of the filler is optimal for the drastic improvement of physico-mechanical properties and functional parameters of the PTFE-based new nanocomposites obtained using the unique hybrid filler such as Fe-cluster-doped CNTs. The test bulk samples were synthesized by powder metallurgy route according to the similar diagram of main steps of the preparation process described by the authors in [15]. The internal friction $Q^{-1}(T,\varepsilon)$ and shear modulus $G \sim f^2(T,\varepsilon)$ spectra were recorded for one and the same initial sample before and after cyclic deformation ($\varepsilon=1\cdot10^{-3}$, N=500) and after post-deformation annealing at 150°C/30 min as well, using a relaxometer with the reverse torsional pendulum. The measurements were performed in vacuum ~10^{-3} torr at the frequencies of 0.5÷5 Hz, the amplitude of deformation 10^{-5}÷10^{-3}, and the rate of heating ~2°C/min, over the temperature range 20÷350°C.

Results and Discussion

Fig. 1. a and b respectively, demonstrate the temperature spectra of internal friction.

$Q^{-1}(T)$ and shear modulus $G \sim f^2(T)$ of the investigated nanocomposite material, recorded for one and the same initial sample before (curve 1) and after (curve 2) cyclic deformation ($\varepsilon=1\cdot10^{-3}$ and number of cycles N=500), and also after the post-deformation annealing at 150˚C/30 min. All the three measurements were performed in the heating mode with the rate of ~2˚C/min and the rate of vibrational deformation $\varepsilon \leq 2 \cdot 10^{-5}$. The selected magnitude of deformation ensured the measurement of internal friction to be performed in the amplitude-independent range. Particularly, it should be noted that all the three temperature spectra of the amplitude-independent internal friction have a similar features (Fig. 1. a).

peaks and simultaneously increases the critical temperatures of $Q^{-1}(T)$ peaks to ~50˚C and ~155˚C respectively (Fig. 1. a, curve 3). The local relaxation displacements in the range of critical temperatures lead to the reduction in bonding forces that is demonstrated by the defects of shear modulus on the $f^2(T)$ curves (Fig. 1. b, curves 1, 2, 3), and is in a good correlation with the peculiarities of the respective $Q^{-1}(T)$ curves (Fig. 1. a, curves 1,2,3). Confirmation of the rela-

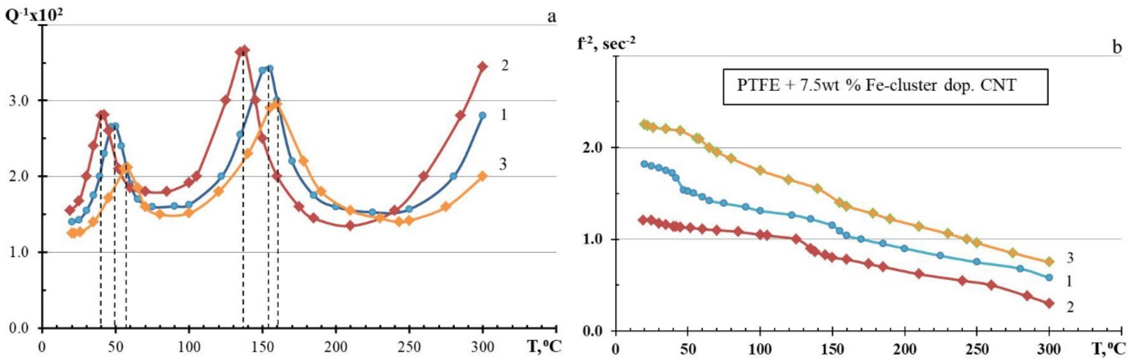

Fig. 1. The amplitude-independent internal friction $Q^{-1}(T)$ – (a) and shear modulus. $G \sim f^2(T)$ – (b) temperature spectra of the nanocomposite PTFE+7.5wt% Fe-cluster-doped CNTs sample, measured before (curve 1) and after (curve 2) cycling deformation and post-deformation annealing as well (curve 3).

Namely, two relaxation regions are revealed on the $Q^{-1}(T)$ curves in the temperature range between 0˚C and 250˚C, which are well known as β- and α-peaks of the unfilled (virgin) PTFE at ~25˚C and ~127˚C respectively [3]. For the latter, a shift of the above temperatures to higher values, depending on the increase in filler concentration, was revealed [15]. Thus, in the case of the initial PTFE+7.5wt% Fe-cluster-dop. CNTs sample, the above peaks on the $Q^{-1}(T)$ curves occur at 48˚C and 147˚C respectively (Fig. 1. a, curve 1). However, high-amplitude cyclic deformation at room temperature leads to the reduction of critical temperatures of the peaks to ~45˚C and ~138˚C, respectively and the increase in their intensity (Fig. 1. a, curve 2). On the contrary, subsequent post-deformation annealing at 150˚C/30 min, significantly decreases the intensity of the above

xation origin of β- and α- peaks [3,15] allowed to use the well-known Vert-Marx formula [16] for the calculation of activation characteristics of Q^{-1} relaxation:

$$H = RT_{\max} ln \frac{K \cdot T_{\max}}{h \cdot f_{\max}},$$

where H is activation energy, R – gas constant, K – Boltzmann constant, h – Plank constant, T_{max} and f_{max} – critical values of temperature and frequency of Q^{-1}_{max} peaks respectively. The experimentally determined (T_{max}, f_{max}) and calculated (H, τ_0^{-1}) values of activation characteristics of the relaxation processes near the temperatures corresponding to β-peak (crystalline first order transition) and α-peak (amorphous transition) for the investigated PTFE-based nanocomposite material are shown in Table 1.

Table 1. Activation characteristics of relaxation processes near the β- and α-peak temperatures in the nanocomposite PTFE+7.5 wt% of Fe-cluster-doped CNTs

PTFE +7.5wt% Fe-cluster-dop. CNT nanocomposite sample	Relaxation type		IF peaks T_{max}, °C	IF peaks f_{max}, sec^{-1}	Activation energies H, kcal/mole	Frequency factor τ_o^{-1}, sec^{-1}
Initial sample	β		48	1.30	21.5	$5{\cdot}10^{14}$
		α	147	1.24	29.6	$1{\cdot}10^{15}$
Cyclically deformed at 20°C and with ε_{max}=$1{\cdot}10^{-3}$	β		45	1.18	19.8	$3{\cdot}10^{14}$
		α	138	1.05	28.3	$8{\cdot}10^{14}$
Annealed at 150°C/30 min after cyclic deformation	β		50	1.42	22.2	$6{\cdot}10^{14}$
		α	155	1.28	30.5	$2{\cdot}10^{15}$

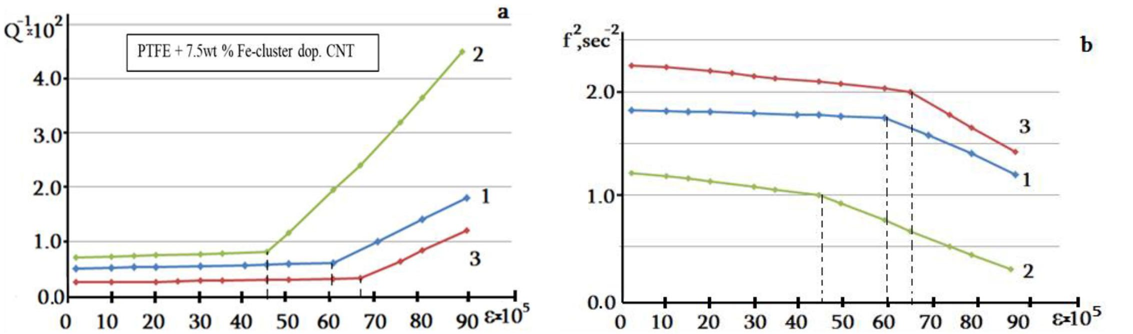

Fig. 2. The amplitude-dependent internal friction $Q^{-1}(\varepsilon)$ – (a) and shear modulus $G{\sim}f^2(\varepsilon)$ – (b) spectra of the nanocomposite PTFE+7.5wt% Fe-cluster-dop. CNTs sample, measured before (curve 1) and after (curve 2) cycling deformation and post-deformation annealing as well (curve 3).

The results of amplitude dependence measurements of internal friction $Q^{-1}(\varepsilon)$ and shear modulus $G{\sim}f^2(\varepsilon)$ for the investigated nano-composite sample, before and after identical mechanical and thermal treatments, are shown in Fig. 2.

It is obvious that in the wide range of deformation amplitudes ($10^{-5}\div10^{-3}$) at 20°C the tested sample is characterized by a single critical value of deformation amplitude of vibration ε_c that separates the permanent and linearly increasing regions of $Q^{-1}(\varepsilon)$ curves (Fig. 2. a, curves 1, 2, 3). Consequently, ε_c separates the permanent and linearly decreasing regions of the $G{\sim}f^2(\varepsilon)$ curves as well (Fig. 2. b, curves 1, 2, 3) being in a strong correlation with the $Q^{-1}(\varepsilon)$ curves. It is also clear that after cyclic deformation, the value of ε_c is considerably (25%) reduced in comparison to that of the initial sample, while the post-deformation annealing at 150°C/30 min leads to the recovery of ε_c to the value exceeding that of the initial sample for 10%. Hereby, the obtained results revealed two experimental facts: 1 – high-amplitude deformation leads to a considerable reduction of activation energy of β- and α-relaxation processes, magni-tude of critical amplitudes of microplastic deformation beginning (ε_c), and shear modulus, in comparison to those of the initial sample before cyclic deformation. 2 – The post-deformation annealing of the cyclically deformed sample ensu-res a complete recovery of the above parameters to the values even exceeding those for the initial sample.

The experimental data obtained in this work for the trial new PTFE-based nanocomposite materials, filled with CNFs doped by ferromagnetic atomic clusters, prove to be necessary to develop the methods for the prediction of physic mechanical and functional properties such as stiffness, mechanical moduli, creep resistance, heat- and electric conductivity, etc. The subsequent reverse analysis of these data will make it possible to conduct more exact calculations of service parameters and life-time of critical parts used for numerous applications in automotive, aerospace, petrochemical and other industries.

Conclusions

- The behavior of elastic/inelastic properties of the PTFE-based nanocomposite material, filed with the optimal (7.5 wt%) concentration of Fe atom cluster-doped carbon nanotubes were investigated in dependence on high-amplitude cyclic deformation and post-deformation annealing, using the amplitude-independent and amplitude-dependent internal friction measurements.
- The regularities of activation energy variation for β (crystalline) and α (amorphous) relaxation processes, shear modulus and deformation critical amplitudes (ε_c) of microplastic deformation beginning were determined depending on the above mechanical and thermal impacts. The obtained results lead to the conclusion that for the investigated nanocomposite the post-deformation annealing at 150˚C/0.5 h of the cyclically deformed sample ensures a complete restoration of the above parameters to the values even exceeding those for the initial sample.

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ფიზიკური ქიმია

ციკლური დეფორმაციის და მოწვის გავლენა 7,5 წონითი %Fe კლასტერებით დოპირებული CNT-ით შევსებული PTFE ნანოკომპოზიციების დრეკად /არადრეკად თვისებებზე

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(წარმოდგენილია აკადემიის წევრის რ. ქაცარავას მიერ)

მართვადი ტექნოლოგიური და მექანიკური პარამეტრების მქონე PTFE ფუძიანი ნანოკომპოზიციური მასალების შექმნისათვის მეტად აქტუალურია მათი სტრუქტურული მდგომარეობისა და დინამიკურ-მექანიკური თვისებების ურთიერთკორელაციური კავშირების გამოვლენა.

ასეთი კვლევები შესაძლებელია განხორციელდეს დაბალსიხშირული შინაგანი ხახუნის მეთოდის გამოყენებით. ნაშრომში პირველად იქნა გამოკვლეული Fe კლასტერებით დოპირებული PTFE ფუძიანი პოლიმერული მასალების დინამიკურ-მექანიკური განმტკიცების მახასიათებლები და გაანალიზებულია განმტკიცების შესაძლებელი მექანიზმები. შინაგანი ხახუნის ამპლიტუდაზე დამოკიდებულების გაზომვებით გამოკვლეულია 7,5 წონითი % Fe კლასტერებით დოპირებული CNT ნაწილაკებით შევსებული PTFE ნანოკომპოზიციური მასალების დრეკადი /არადრეკადი თვისებები საწყის, დიდ ამპლიტუდებზე ციკლურად დეფორმირებულ ($\varepsilon \approx 1.10^{-3}$) და დეფორმაციის შემდეგ მომწვარ (150^0C, 30 წთ) მდგომარეობებში. ნაჩვენებია, რომ დიდ ამპლიტუდებზე ციკლური დეფორმაცია იწვევს რელაქსაციური პროცესების აქტივაციის ენერგიის, მიკროპლასტიკური დეფორმაციის საწყისი კრიტიკული ამპლიტუდის (ε_c) და ძვრის მოდულის ($G \sim f^2$) მნიშვნელოვნად შემცირებას საწყის ნიმუშებთან შედარებით. ციკლურად დეფორმირებული ნიმუშების მოწვა 150^0C ტემპერატურაზე 30 წთ-ის განმავლობაში სრულად აღადგენს აღნიშნულ პარამეტრებს საწყისი მდგომარეობის დამახასიათებელ სიდიდეებამდე.

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