საქართველოს მეცნიერებათა ეროვნული აკადემიის მოამბე, ტ. 15, №1, 2021
BULLETIN OF THE GEORGIAN NATIONAL ACADEMY OF SCIENCES, vol. 15, no. 1, 2021

Physical Chemistry

The Effect of High-Amplitude Deformation and High-Frequency Magnetic Field Exposure on the Elastic/Inelastic Properties of PTFE-Based Hybrid Nanocomposite Filled with Fe Cluster-Doped CNTs

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(Presented by Academy Member Ramaz Katsarava)

The influence of high-amplitude torsional deformation ($\varepsilon \sim 10^{-1} \div 10^{-2}$) and high-frequency (2.4 GHz) magnetic field treatment on elastic/inelastic properties of PTFE-based new hybrid nanocomposites modified with a two-component filler (2.5 wt% Fe-cluster-doped CNT nanopowder + 5wt% chalcopyrite micropowder) was studied using low-frequency amplitude-independent (AIIF) and amplitude-dependent (ADIF) internal friction measurements. The behavior of elastic/inelastic properties of the new trial PTFE-based hybrid nanocomposite modified by a two-component filler (Fe-cluster-doped CNTs + chalcopyrite micro-particles) was investigated in dependence on high-amplitude torsional deformation ($\varepsilon \sim 10^{-1} \div 10^{-2}$) and post-deformation high-frequency (2.4 GHz) magnetic field exposure and additional thermal treatment, using AIIF and ADIF measurements. It is shown that self-healing of micro/nano-cracks nucleated in the deformed samples of the nanocomposite may be properly performed via their exposure to high-frequency magnetic field and the additional annealing at 200°C that leads to the recovery of the values of microplastic deformation beginning critical amplitude (εc) to the values even exceeding its initial magnitude by ~38%. *© 2021 Bull. Georg. Natl. Acad. Sci.*

PTFE, hybrid nanocomposite, Fe-cluster-doped CNTs, chalcopyrite, magnetic field, internal friction

Polytetrafluoroethylene (PTFE) is a universal polymeric material that has a vast potential of numerous applications because of the possibility of considerable improving its physical, mechanical and functional properties by modifying. The reviews on this topic containing several researches on this problem conducted in the last decades [1-4] show that a distinct effect on friction and wear behavior of PTFE may be caused by micro-scale as well as nano-scale inorganic fillers (ceramics and carbon nano-form particles). In both cases the shape, size, aspect ratio, composition, volume fraction and specific area of the added micro/nanoparticles of the filler have been found to greatly affect the complex physicomechanical and functional properties of the synthesized PTFE-based composite/nanocomposite materials. Recent works of the authors [5-7] demonstrated for the first time the efficiency of micro-sized particles of chalcopyrite as well as nano-sized magnetic particles of Fe-cluster-doped CNTs as the fillers for the preparation of PTFE-based new wear-resistant frictional/antifrictional composite and nano-composite materials respectively. It is also known that a combination of micro-scale and nano-scale carbon fiber fillers provides a positive protective effect on PTFE matrix [8]. It should be pointed out that only a few data have been reported regarding this correlation between the functional and structural properties of the PTFE-based hybrid composite materials, depending on the kind of the combined multicomponent fillers. Incorporation of magnetic nano-particles into polymeric matrix is also of significant interest for the induction heating of thermally remendable self-healing com-posites/nanocomposites [9]. Consequently, for further development of the above-type advanced multifunctional PTFE-based hybrid composite materials for the diversified applications, it is important to study their inelastic/elastic properties in the wide range of temperatures, deformation rates and after the exposure to high-frequency magnetic field. Thus, the aims of the proposed work are: to study the effect of high-amplitude deformation and high-frequency magnetic field treatment on the elastic/inelastic behavior of the PTFE-based new trial hybrid nanocomposite material modified by a two-component (Fe-cluster-doped CNTs nanopowder + chalcopyrite micro-powder) filler, using a low frequency AIIF and ADIF measurements. It is expected that this research can be helpful for the application of the PTFE hybrid composites/nanocomposites in practice.

Experimental

The choice of the PTFE-based new trial hybrid nanocomposite material filled with a two-component filler (2.5 wt% Fe-cluster-doped CNTs+5 wt% chalcopyrite) was conditioned by the authors' recent results obtained for the PTFE-based composites filled with different amount of chalcopyrite micropowder [5]. The standard bulk test specimens for internal friction measurements were synthesized via powder metallurgy route, similar to the diagram of main steps for nanocomposite preparation process described by the authors in [7]. The only difference was that in the present study the mixture of commercial PTFE micropowder (grain sizes 0.5÷5 μm), locally produced chalcopyrite concentrate (particle sizes 1÷30 μm) milled in a vibratory mill, and the Fe-cluster-doped CNTs magnetic nanopowder suspended in ethanol were blended for 5 min in the external gradient magnetic field. After subsequent sintering of the mixture (cold compaction under 100 MPa load +holding at 365˚C/2 hours), the obtained rectangular samples of the hybrid nanocomposite with the dimensions 20×20×1.5 mm were cut into rods with the sizes 20×1.5×1.5 mm as the standard specimens for low-frequency (~1Hz) internal friction measurements. The internal friction and shear modulus spectra were recorded for the samples after high-amplitude ($\varepsilon \approx 10^{-1} \div 10^{-2}$) torsional deformation and after a post-deformation additional exposure to high-frequency (2.4 GHz) magnetic field. The measurements were performed in vacuum ~10^{-3} torr using a relaxometer with the reverse torsional pendulum, at frequencies of vibration 0.5÷5 Hz, amplitude of deformation $10^{-5} \div 10^{-3}$ and the rate of heating ~2˚C/ min over the temperature range 20÷320˚C.

Results and Discussion

Fig. 1 a and b show the temperature spectra of internal friction $Q^{-1}(T)$ and shear modulus $G \sim f^2(T)$ of the investigated hybrid nanocomposite material #19-1-Hybrid respectively.

The curves were recorded for the same sample after preliminary torsional deformation up to $\varepsilon > \varepsilon_c = 10^{-1}$. The curve 1 corresponds to the first measurement, curve 2 to the second, repeated measurement and curve 3 to the third, conducted after additional annealing at 200˚C/30 min. All the three measurements were performed in the heating/cooling mode with the rate ~2˚C/min and the rate of vibrational deformation $\varepsilon \leq 2 \cdot 10^{-5}$ that ensured the measurement of internal friction to be performed in the amplitude-independent range. Two relaxation regions were revealed in the $Q^{-1}(T)$ curves at temperatures 45˚C and 152˚C in the temperature range 20÷250˚C (Fig.1.a, curve 1) that are well known as β (crystalline) and α (amorphous) peaks respectively for both, the virgin PTFE [10] and the PTFE-based nanocomposites filled solely with the Fe-cluster-doped CNTs [7]. After the repeated measurement conducted after cooling of the sample from 320˚C with the rate of 2˚C/ min, a visible decrease in the IF background intensity over the whole temperature range 25÷320˚C, a shift of the peak towards higher temperatures and a decrease in their intensity were observed (Fig.1.a, curve 2). In addition, a slight increase in the activation characteristics was also detected. The above-mentioned peculiarities witness for the decrease in the mobility of defects involved in the relaxation dissipation of vibration

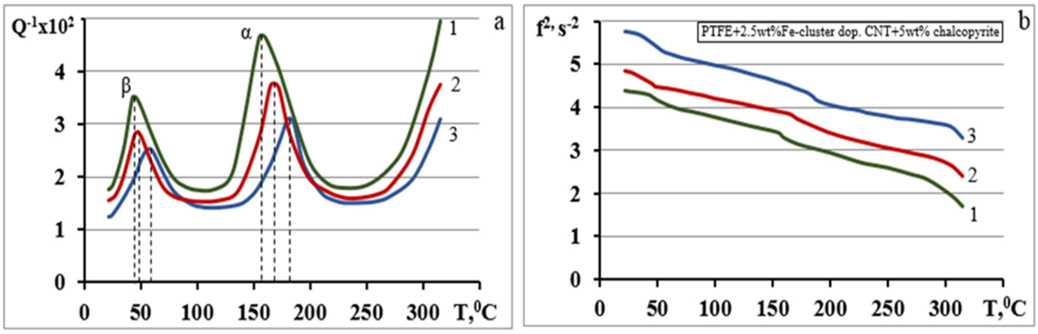

Fig. 1. Temperature dependence of internal friction (a) and shear modulus (b) of #19-1-Hybrid nanocomposite sample, preliminary torsionally deformed up to $\varepsilon > \varepsilon_c = 10^{-1}$: 1 – First measurement, f_0=2.1 sec^{-1} (the initial, deformed sample $\varepsilon_c = 10^{-1}$). 2 – Repeated (second) measurement, f_0=2.2 sec^{-1}. 3 – Measurement after the additional annealing at 200˚C/30min, f_0=2.4 sec^{-1}.

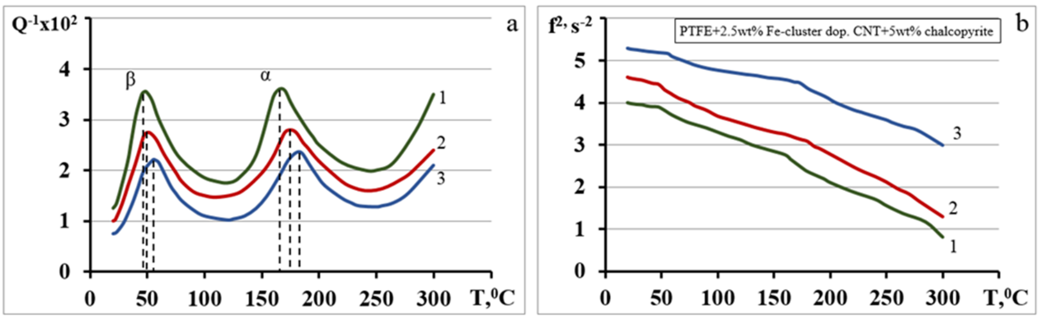

Fig. 2. Temperature dependence of internal friction (a) and shear modulus (b) of the torsionally deformed ($\varepsilon > \varepsilon_c = 10^{-1}$) #19-1-Hybridnanocomposite sample after exposure to high-frequency(2.4 GHz) oscillating magnetic field for 5 min: 1 – First measurement, f_0=2.0 sec^{-1}. 2 – Second (repeated) measurement, f_0=2.15 sec^{-1}. 3 – Measurement after the additional annealing at 200˚C/30min, f_0=2.3 sec^{-1}.

energy. Subsequent annealing at 200˚C/30 min, increasingly limits the mobility of the relaxation centers that result in the reduction of the IF peaks and the increase in their critical temperatures and activation energies (Fig. 1. a, curve 3). Some alteration of the almost linear reduction of shear modulus $G\sim f^2(T)$ is observed at the IF peaks while at the elevated temperatures (~300˚C) reduction of shear modulus is of non-linear character (Fig. 1. b, Curves 1, 2, 3).

partial recovery of their characteristics (Fig. 2. a, b, curve 3). The energy of activation (*H*) corresponding to the IF relaxation peaks were calculated by the Vert-Marx formula:

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

where *R* is a gas constant, *K* – Boltzmann constant, *h* – Planck constant, T_{max} – temperature corresponding to the IF (Q^{-1}_{max}) peak, f_{max} – the respective

Table 1. Activation characteristics ofthe IF relaxation processes in the nanocomposite #19-1-Hybrid sample, torsionally deformed at $\varepsilon > \varepsilon_c(10^{-1})$

Stages of measurement	Temperatures of the IF peaks T_{max}, ^0C	Frequencies corresponding to IF peaks, f_0, sec^{-1}	Activation energy H, ccal/moll	Frequency factor τ_0^{-1}, sec^{-1}
Imeasurement	45	2.10	18.27	$3 \cdot 10^{13}$
	152	1.55	25.09	$3.9 \cdot 10^{13}$
IImeasurement	48	2.15	18.40	$1.8 \cdot 10^{13}$
	160	1.70	25.35	$4.2 \cdot 10^{13}$
III measurement after annealing at 200^0C/30min	55	2.20	18.84	$3.2 \cdot 10^{13}$
	175	1.75	26.20	$4 \cdot 10^{13}$

Table 2. Activation characteristics of the IF relaxation processes in the nanocomposite #19-1-Hybrid sample, treated by high-frequency (2.4 GHz) magnetic field after torsional deformation at $\varepsilon > \varepsilon_c(10^{-1})$

Stages of measurement	Temperatures of the IF peaks T_{max}, ^0C	Frequencies corresponding to IF peaks, f_0, sec^{-1}	Activation energy H, ccal/moll	Frequency factor τ_0^{-1}, sec^{-1}
Imeasurement	48	2.0	18.50	$1.3 \cdot 10^{13}$
	155	1.57	24.85	$2.25 \cdot 10^{13}$
IImeasurement	50	2.15	18.55	$1.6 \cdot 10^{13}$
	160	1.60	25.15	$1.05 \cdot 10^{14}$
III measurement after annealing at 200^0C/30min	55	2.25	18.80	$1.5 \cdot 10^{13}$
	170	1.65	27.30	$1.8 \cdot 10^{14}$

It is obvious from the results on $Q^{-1}(T)$ and $G\sim f^2(T)$ presented in Fig. 2. a, b that the high-frequency (2.4 GHz) oscillating magnetic field treatment of the torsionally deformed ($\varepsilon > \varepsilon_c = 10^{-1}$) sample leads to a considerable widening of both IF peaks (β and α) while it decreases the corresponding temperatures and activation characteristics for α peaks only, dealing with the amorphous transitions (Fig. 2. a, curves -1, -2). Subsequent additional annealing at 200˚C/30 min leads to only

frequency of vibration. Frequency factors of relaxation were determined from the respective relaxation peak:

$$\tau_0^{-1} = 2\pi f_{max} \cdot exp \frac{H}{RT_{max}}.$$

The results of calculation of *H* and τ_0^{-1} are shown in Tables 1 and 2 respectively for the torsionally deformed samples and the samples additionally exposed to high-frequency magnetic

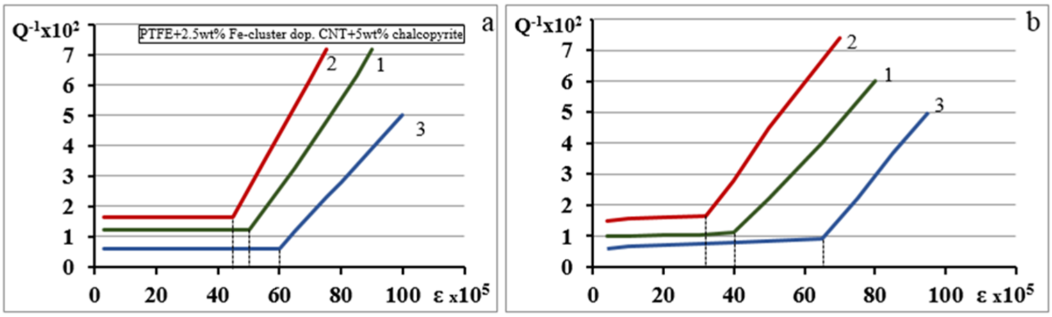

Fig. 3. The amplitude dependence of internal friction: (a) – #19-1-Hybrid nanocomposite sample, initially deformed at $\varepsilon>\varepsilon_c(10^{-1})$ and (b) – the same sample after additional treatment by high-frequency (2.4 GHz) magnetic field: 1 – first measurement, 2 – second (repeated) measurement, 3 – measurement after the additional annealing at 200˚C/30 min.

field. The measurements of amplitude-dependent internal friction (ADIF) were conducted in a$\sim10^{-2}$ torr vacuum at room temperature. The sample of #19-1-Hybrid nanocomposite deformed at $\varepsilon>\varepsilon_c(10^{-1})$ is characterized by a critical amplitude of deformation ε_c, that distinguishes two regions of weak and strong dependence of IF on the amplitude of vibrational deformation (Fig. 3. a, curves -1, 2, 3).

The behavior of ε_c in the $Q^{-1}(\varepsilon)$ spectrum (Fig.3) indicates the presence of the interacted and highly localized defects in the form of pinning centers and extensive defects such as microcracks. The additional high-amplitude cyclic deformation (n=200, $\varepsilon=1\cdot10^{-3}$) apparently leads to the frequency destruction of the interacted configurations, creates new relaxation centers, and weakens bonding forces that may be a reason of the decreasing critical amplitude of deformation ε_c (Fig. 3. a, curve 2). Subsequent annealing at 200˚C/30 min strengthens the bonding between the highly localized and extensive defects, resulting in a dynamic strengthening of the structure. The latter is exhibited by the significant increase of ε_c, proportionally to braking force.

After the exposure to the high-frequency (2.4 GHz) magnetic field, the preliminary torsionally deformed ($\varepsilon\sim1\cdot10^{-1}$) samples are characterized by all the peculiarities described above (Fig. 3. b, curves 1, 2, 3). The distinctive features are the reduced values of ε_C (critical amplitude of microplastic deformation beginning) in comparison to the previous sample, torsionally deformed at high amplitude $\varepsilon\sim1\cdot10^{-1}$ (see Table 2), and a significant influence of the additional annealing at 200˚C/30 min on the recovery of the values of $\varepsilon_C$up to the values even exceeding its initial value by ~ 38%.

Conclusions

The behavior of elastic/inelastic properties of the new trial PTFE-based hybrid nanocomposite modified by a two-component filler (Fe-cluster-doped CNTs + chalcopyrite micro-particles) was investigated in dependence on high-amplitude torsional deformation ($\varepsilon\sim10^{-1}\div10^{-2}$) and post-deformation high-frequency (2.4 GHz) magnetic field exposure and additional thermal treatment, using AIIF and ADIF measurements.

It is shown that self-healing of microcracks formed at high-amplitude deformation ($\varepsilon\sim10^{-1}$) in the new trial PTFE-based hybrid nanocomposite material can be successfully realized via exposure of the samples to high-frequency (2.4 GHz) magnetic field and the additional annealing at 200˚C/30 min, that is exhibited by the recovery of the values of microplastic deformation beginning critical amplitude (ε_c) to the values even exceeding its initial magnitude by ~ 38%.

This work was supported by the SRNSF of Georgia (Grant #STCU-2017-33) and by the STCU, Ukraine (Grant #7091).

ფიზიკური ქიმია

მაღალამპლიტუდური დეფორმაციისა და მაღალსიხშირულ მაგნიტურ ველში დაყოვნების გავლენა Fe-კლასტერებით დოპირებული CNT-ით შევსებული PTFE ჰიბრიდული ნანოკომპოზიციების დრეკად/არადრეკად თვისებებზე

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(წარმოდგენილია აკადემიის წევრის რ. ქაცარავას მიერ)

შესწავლილია მაღალამპლიტუდური გრეხითი დეფორმაციისა (ε~10^{-1}÷10^{-2}) და მაღალსიხშირულ (2,4 გჰც) მაგნიტურ ველში დაყოვნების გავლენა ორკომპონენტიანი ფილერით (2,5 წონითი% Fe კლასტერებით დოპირებული CNT ნანოფხვნილი + 5 წონითი% ქალკოპირიტის მიკროფხვნილი) მოდიფიცირებული PTFE ახალი ჰიბრიდული ნანოკომპოზიციების დრეკად /არადრეკად თვისებებზე, ამპლიტუდაზე დამოკიდებული და ამპლიტუდაზე დამოუკიდებელი შინაგანი ხახუნის გაზომვებით. ნაჩვენებია, რომ დეფორმაციით ფორმირებული მიკრო/ნანობზარების აღდგენა შესაძლებელია მაღალსიხშირულ მაგნიტურ ველში დაყოვნებისა და 200^{0}C ტემპერატურაზე დამატებითი თერმული მოწვის შედეგად.

REFERENCES

1. Biswas S.K.(1992) Friction and wear of PTFE – *Review.-Wear*, 158: 193-211.
2. Aly A.A., Zeidan El.B., Alshennawy A.A., El-Masry A. A., Wasel W. A. (2012) Friction and wear of polymer composites filled by nano-particles: a *review. World Journal of Nano Science and Engineering*, 2:32-39.
3. Jiaxin Ye., David L., Burris and Ting Xie (2016) A review of transfer film and their role in ultra-low-wear sliding of polymers. *Lubricants* 4(4): 1-15.
4. Gandotra H., Mahajan S., Jandival S., Gupta S. (2018) Effect of fillers on tribological properties of PTFE: *a review. International Journal of Scientific and Technical Advancements,* 4 (1): 147-150.
5. Gventsadze D., Kutelia E., Nadaraia L., Padgurskas J., Gventsadze L., Tsurtsumia O. (2017) The tribological properties of PTFE modified with chalcopyrite. *Proceedings of BALTRIB,* 62-65, edited by J. Padgurskas. ISSN 2424-5089/e ISBN 978-609-449-093-4.
6. Kutelia E., Gventsadze D., Tsurtsumia O., Rukhadze L., Jalabadze N., Kukava T., Dzigrashvili T. (2018) Investigation of new antifrictional/frictional nanocomposites based on PTFE matrix filled with Fe-doped carbon nanoparticles. *Advanced Materials Letters,* 9(5): 320-325 www.iaamonline.org
7. Kutelia E., Darsavelidze G., Dzigrashvili T., Kukava T., Rukhadze L., Gventsadze L.,Tsurtsumia O., Nadaraia L., Kurashvili I., Bakhtiyarov S. (2018) Internal Friction in PTFE-based nanocomposite materials filled with Fe cluster-doped CNTs. *Georgian Engineering News*, 87 (3): 5-13.
8. Shi Y., Feng X., Wang H., Lu X. (2007) Tribological and mechanical properties of PTFE composites filled with the combination of short carbon fiber and carbon nano-fiber. *Key Engineering Materials*, 334-335, 689-692.
9. Ahmed A.S., Ramanujan R.V. (2015) Curie temperature controlled self-healing magnet-polymer composites. *Journal of Materials Research*, 30 (7): 946-958.
10. 10. McCrum N.G. (1959) An internal friction study of polytetrafluoroethylene. *Journal of Polymer Science*, 34: 355-369.

Received June, 2020