https://doi.org/10.15407/ujpe68.9.619

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MAGNETIC-RESONANCE AND TRIBOLOGICAL PROPERTIES OF ORGANOPLASTICS BASED ON COPOLYMER BSP-7

The properties of the copolymer BSP-7, high-strength and high-modulus Kevlar-like organic fibers (OFs) Terlon and Vniivlon as fillers, and composites BSP-7/OF have been studied using the electron paramagnetic resonance method. The presence of various defects and magnetic impurities is detected in the raw materials and the manufactured composites. Their properties are determined, and the influence of the matrix interaction with the fillers and the environment on them is revealed. A considerable concentration of nitrogen-containing radicals is detected in Terlon, which are associated with the presence of diamine monomers in its structure and which can negatively affect the physical and mechanical characteristics of composites. On the basis of the obtained data, effective BSP-7/OF organoplastics are developed. The measurements of their tribological properties show that the addition of OFs in an optimal concentration to the BSP-7 polymer matrix brings about a substantial reduction of the friction coefficient, the linear wear intensity, and the heat generation. The best results are obtained for composites with Terlon, which is explained not only by its higher elastic modulus, but also a high degree of structural crystallinity, which is in contrast to Vniivlon with its almost amorphous heterocyclic structure. In addition, the process of composite synthesis suggests the application of rather high temperatures and pressures; as a result, nitrogen radicals of Terlon are destroyed, and their negative impact on the long-term stability of composite parameters becomes eliminated.

Keywords: copolymer BSP-7, electron paramagnetic resonance, Vniivlon, Terlon, composites.

1. Introduction

Modern materials science is based on a deep understanding of the physical and chemical properties of novel materials developed for industrial needs. For example, mechanical engineering requires the creation of materials with high strength, rigidity, and wear resistance together with a long service life and a rather low cost. From this viewpoint, polymer composite materials (PCMs) created on the basis of thermoplastic binders are promising objects and form a competitive alternative to widespread metal-based materials, including those for tribotechnical applications [1]. The creation of effective PCMs requires the knowledge of the structure and physicochemical properties of polymer matrices and fillers, the dispersion degree of the latter in the composite, and

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Citation: Graschenkova M.O., Tomina A.-M.V., Burya O.I., Krasnovyd S.V., Konchyts' A.A., Shanina B.D. Magnetic-resonance and tribological properties of organoplastics based on copolymer BSP-7. *Ukr. J. Phys.* **68**, No. 9, 619 (2023). https://doi.org/10.15407/ujpe68.9.619.

Цитування: Гращенкова М.О., Томіна А.-М.В., Буря О.І., Красновид С.В., Кончиць А.А., Шаніна Б.Д. Магніторезонансні та трибологічні властивості органопластів на основі співполімеру БСП-7. *Укр. фіз. журн.* **68**, №9, 621 (2023).

the mechanisms of interaction between all composite components.

Organic fibers (OFs) of various brands created on the basis of polyamide, polyethylene, polyester, and other polymers are effective fillers for the development of PCMs with high functional properties [2–4]. Products made of organoplastics (OPs) are characterized by a low friction coefficient, a low thermal linear expansion, a high abrasive wear resistance [5], a high resistance to the influence of cyclic and dynamic loads and vibrations, a high resistance to the action of aggressive environments, a high operational stability at high humidity, and so forth. A low specific weight, high manufacturability, and minimum energy consumption (the ability to form a product within one technological cycle) make it possible to improve the repairability of OP-based products in tribological joints and practically exclude the necessity of the maintenance of the latter, which gives rise to a significant economic effect due to the prolongation of their service life [6, 7].

When developing new PCMs, including those with OFs as fillers, an important role belongs to the research of the structural, electronic, and magnetic properties of all composite components, as well as the composite as a whole. Those properties are formed at the atomic-molecular level and affect, in particular, the physical and mechanical characteristics of the created PCMs [8]. Currently, due to their unique properties, aramid fibers (Nomex, Kevlar, heterocyclic aramids, *etc.*) and OPs based on them are widely used [1,7,8]. The spectrum of their application is very wide (mechanical engineering, space technology, personal protective equipment, and others).

The aim of this work was to develop effective and relatively inexpensive tribotechnical composites based on the BSP-7 copolymer and the Kevlar-like fillers Terlon and Vniivlon, which would surpass known analogs by their tribotechnical characteristics. The task of this work was to determine the magnetic resonance properties of the examined materials (the BSP-7 copolymer, the Terlon and Vniivlon organic fibers, and their composites), compare them on the basis of the structures of selected materials, study the tribological characteristics of the created composites, compare them with the properties of competing materials, and formulate conclusions concerning the application of the developed composites.

Table 1. **Technical parameters of organic fibers [10]**

Parameter	Fiber brand	
	Vniivlon	Terlon
Fiber length l, mm	3–4	
Density ρ, g/cm^3	1.43	1.46
Tensile strength σ^+, GPa	3.8÷4.2	3.5÷3.8
Elastic modulus E^+, GPa	135	150÷184
Relative elongation ε^+, %	3.4	2.5÷2.8

2. Materials and Methods

For the OP creation, the polyarylatesulfone block-copolymer sulfaryl BSP-7 was chosen as the polymer matrix. This polymer is superior to such well-known tribotechnical materials as polyethylene, caprolon V, and polyamide 12L by such parameters as the operating temperature, the destructive tensile stress, and the hardness [7].

BSP-7 was synthesized under the conditions of acceptor-catalytic polycondensation in an organic solvent medium on the basis of 2,2-di-(4-oxyphenyl)-propane, phenolphthalein, 4,4′-dichlorodiphenylsulfone, and dichloroanhydrides of the tere- and isophthalic acids [9].

As a filler, high-strength organic fibers Terlon and Vniivlon were chosen. By their chemical composition, they are fibers based on polyparaphenylene terephthalamide (PFTA) and aromatic heterocyclic polyamide on the basis of diamine and terephthalyl chloride, respectively. The Terlon and Vniivlon OFs are characterized by a high strength and a high resistance to fire, mold, and aggressive environments. According to their technical characteristics, they are close to such well-known fibers as Kevlar and ultra-high-modulus SVM fibers, respectively, but they are much cheaper. The main properties of the applied OFs are quoted in Table 1.

The OPs based on the BSP-7 copolymer with 10–40 wt% of Vniivlon or Terlon fibers were produced using the compression pressing method and following the procedure described in work [9]. The tribotechnical parameters of sulfaryl BSP-7 and the OPs on its basis were studied in the friction without lubrication mode on a disc friction machine. A ball made of carbon steel 45 was chosen as the counter-body. The load, the sliding velocity, and the friction path were 0.6 MPa, 1 m/s, and 1000 m, respectively.

The influence of Vniivlon OFs on the abrasive wear performance of the BSP-7 copolymer at rigidly fixed abrasive particles was considered in work [11]. The analysis of the test results showed that the introduction of those high-strength OFs to the polymeric binder BSP-7 allowed the abrasive wear resistance of the latter to be increased by more than 60%. Therefore, it was expected that the introduction of the Vniivlon OFs should improve the tribotechnical characteristics of the composite measured in the tribological tests of other types as well, including the friction without lubrication regime.

The physico-mechanical properties of OPs – in particular, the tribological ones – are sensitive to their structure, in particular, to the distribution of electron density around OFs and the type of interatomic bonds. The higher the concentration of free electrons, the higher the electron density of the s-type, which favors a higher plasticity and the growth of the tensile strength. On the other hand, various structural defects in PCMs can worsen their mechanical parameters by 10–20% [1, 7, 12]. An effective method for determining the electron concentration and the densities of the free and localized electronic states is the electron paramagnetic resonance (EPR) method. In this work, EPR measurements were performed on a Radiopan X-2244 spectrometer (the microwave frequency $\nu \approx 9.4$ GHz) with the magnetic field modulation at a frequency of 100 kHz. The determination the accuracy of a g-factor was $\pm 3 \times 10^{-4}$. The absolute and relative determination accuracies of the spin concentration N_s were $\pm 50\%$ and $\pm 20\%$, respectively.

A series of comparative EPR measurements was performed using the same specimens located in evacuated quartz tubes or in the air environment. This way was used to measure the influence of paramagnetic molecular oxygen on the width of the EPR line of defects, which is proportional to the concentration of oxygen adsorbed in the specimen's pores. In turn, the specimen porosity is an indirect estimate of their density and adhesive properties, which immediately affect the mechanical parameters of composites.

3. Experimental Results

3.1. Magnetic-resonance properties

The magnetic-resonance properties of the BSP-7 copolymer, the Terlon and Vniivlon fillers, and their composites with various filler concentrations were studied. Those studies made it possible to evaluate their structural perfection from the viewpoint of the presence of para- and ferromagnetic impurities and defects, and elucidate the role of the interaction between the matrix and the fillers in the composite.

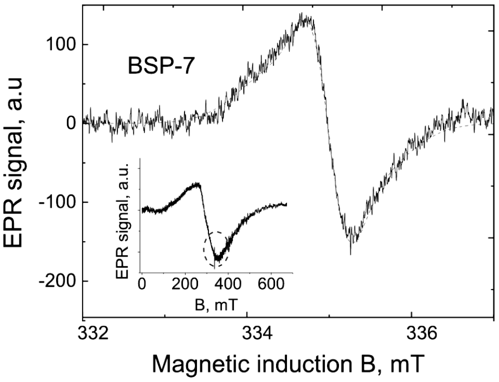


Fig. 1. EPR spectrum of BSP-7 copolymer and its approximation by formula (1) as the sum of signals 1 and 2 (the red dashed curve). The spectrum of the same specimen in a wide interval of magnetic field scanning is shown in the inset. Hereafter, the spectra are normalized to the frequency $\nu = 9392$ MHz

Figure 1 demonstrates the EPR spectrum of the BSP-7 copolymer, $F_{\text{BSP}-7}(B)$. A theoretical approximation of this spectrum with use of the ORIGIN software program showed that the dependence $F_{\text{BSP}-7}(B)$ is the sum of two resonance signals, 1 and 2, and each of them has the form of a Gaussian derivative:

$$F_{\text{BSP-7}}(B) = \sum_{i=1,\,2} A_i \frac{d}{dB} \exp\left[-\left(\frac{B - B_{\text{res},i}}{\Delta_{G,i}}\right)^2\right] =$$
$$= -\sum_{i=1,2} 2A'_i \left(\frac{B - B_{\text{res},i}}{\Delta_{G,i}}\right) \times$$
$$\times \exp\left[-\left(\frac{B - B_{\text{res},i}}{\Delta_{G,i}}\right)^2\right], \qquad (1)$$

where $A'_i = A_i/\Delta_{G,i}$ is the amplitude of the ith derivative signal ($A'_1 = 110$ and $A'_2 = 80$), $B_{\text{res},i}$ is the magnitude of the resonance field of the ith signal ($B_{\text{res},1} = 335.0$ mT and $B_{\text{res},2} = 334.95$ mT), $\Delta_{G,i} = \Delta_{1/2,i}/\sqrt{\ln 2}$ ($\Delta_{G,1} = 0.35$ mT and $\Delta_{G,2} = 0.8$ mT), and $\Delta_{1/2,i}$ is the ith Gaussian halfwidth at the half-height. The distance Δ_{pp} between the peaks of the Gaussian derivative is coupled with Δ_G via the relation $\Delta_{pp} = \Delta_G\sqrt{2}$. For Lorentzian $\Delta_{pp} = (2/\sqrt{3})\Delta_L$.

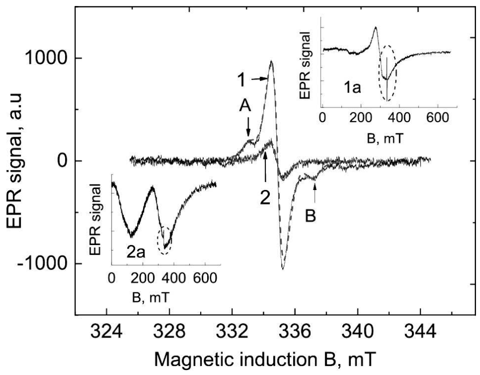


Fig. 2. EPR spectra of Terlon (curve *1*) and the BSP-7 + 10 wt% Terlon composite (curve *2*). Spectral lines A and B belong to a hyperfine structure whose origin and properties are discussed in the text. The dashed curves are the approximations by formulas (2). The spectra of those specimens in a wide interval of magnetic fields are shown in the insets

Signal 1 is emitted by paramagnetic centers (PCs) and is characterized by the g-factor value $g_1 = 2.0031$ and the linewidth $\Delta B_{pp}(1) = 0.49$ mT. For signal 2, $g_2 = 2.0036$ and $\Delta B_{pp}(2) = 1.13$ mT. The Gaussian shape of both signals testifies to the nonuniform broadening of the EPR lines.

Besides the described spectrum, an intensive broad line is also observed (see the inset in Fig. 1), which belongs to uncontrolled ferromagnetic inclusions; their nature and properties are discussed below.

Figure 2 demonstrates the magnetic resonance spectra of Terlon fibers (curve *1*) and the composite BSP-7 + 10 wt% Terlon (curve *2*) evacuated at the temperature $T = 400$ K. A theoretical approximation of the EPR spectrum of Terlon shows that it is the derivative of the sum of two Gaussians and two Lorentzians (in the formula below, these are the first and second sums, respectively):

$$F_{\text{Terlon}}(B) = \\ = \sum_{i=1,\,2} A_{i,G}\frac{d}{dB}\exp\left[-\left(\frac{B-B_{\text{res},i}}{\Delta_{G,i}}\right)^2\right] + \\ + \sum_{i=3,4} A_{i,L}\frac{d}{dB}\left[1+\left(\frac{B-B_{\text{res},i}}{\Delta_{L,i}}\right)^2\right]^{-1} = \\ = -\sum_{i=1,2} 2A'_{i,G}\left(\frac{B-B_{\text{res},i}}{\Delta_{G,i}}\right)\exp\left[-\left(\frac{B-B_{\text{res},i}}{\Delta_{G,i}}\right)^2\right] - \\ - \sum_{i=3,4} 2A'_{i,L}\left(\frac{B-B_{\text{res},i}}{\Delta_{L,i}}\right)\left[1+\left(\frac{B-B_{\text{res},i}}{\Delta_{L,i}}\right)^2\right]^{-2}, \quad (2a)$$

where $A'_{1,G} = 90$, $A'_{2,G} = 110$, $B_{\text{res},1} = 333.4$ mT, $B_{\text{res},2} = 336.7$ mT, $\Delta_{G,\,1} = 0.6$ mT, $\Delta_{G,\,2} = 0.7$ mT, $A'_{3,L} = 1500$, $A'_{4,L} = 100$, $B_{\text{res},3} = 334.9$ mT, $B_{\text{res},4} = 335.05$ mT, $\Delta_{L,\,3} = 0.7$ mT, and $\Delta_{L,\,4} = 0.6$ mT.

In the composite BSP-7 + 10 wt % Terlon, the presence of the latter increases the values of the g-factor of PC signals 1 and 2 in BSP-7, namely, $g_1 = 2.0039$, $\Delta B_{pp}(1) = 0.7$ mT, $g_2 = 2.0043$, and $\Delta B_{pp}(2) = 1.3$ mT. The composite spectrum was approximated by the derivative of the sum of two Gaussians,

$$F_{\text{composite}}(B) = -\sum_{i=1,2} 2A'_{i,G}\left(\frac{B-B_{\text{res},i}}{\Delta_{G,i}}\right) \times \\ \times \exp\left[-\left(\frac{B-B_{\text{res},i}}{\Delta_{G,i}}\right)^2\right], \quad (2b)$$

where $A'_{1,G} = 75.0$, $A'_{2,G} = 40.0$, $B_{\text{res},1} = 334.87$ mT, $B_{\text{res},2} = 334.8$ mT, $\Delta_{G,\,1} = 0.5$ mT, and $\Delta_{G,\,2} = 0.9$ mT.

The most intense EPR line of Terlon is emitted by PCs with $g = 2.0037$ and $\Delta B_{pp} = 0.81$ mT. Its Lorentzian shape testifies to the uniform broadening character.

In the course of the experiments, it was found that the values of the g-factor and the EPR linewidth of Terlon fibers depend on the observation conditions. Namely, those values slightly decreased, when the specimens were evacuated at an elevated temperature (in the reported experiments, at $T_{\text{ann}} = 400$ K). Figure 3 illustrates the dependence of the kinetics of those processes on the time interval during which the evacuated specimen was held in the air environment. One can see that, in the course of the specimen–air contact, the values of the g-factor and the EPR linewidth of Terlon gradually increased and became stable after 1–1.5 h.

A somewhat different behavior was observed for the Vniivlon specimens. In Fig. 4, the EPR spectra of the Vniivlon fibers and the composite BSP-7 + 20 wt% Vniivlon are compared. In contrast to the Terlon case, the EPR line of Vniivlon has a Lorentzian form with the g-factor $g = 2.0034$ and the width $\Delta B_{pp} = 0.51$ mT. The approximation of the EPR signals of Vniivlon and the BSP-7 + 20 wt% Vniivlon composite gave the following results:

$$F_{\text{Vniivlon}}(B) = -2A'_{1,L}\left(\frac{B-B_{\text{res},1}}{\Delta_{L,1}}\right) \times$$

$$\times\left[1+\left(\frac{B-B_{\mathrm{res},1}}{\Delta_{L,1}}\right)^2\right]^{-2}, \qquad (3a)$$

where $A'_{1,L} = 1300$, $B_{\mathrm{res},1} = 334.96$ mT, and $\Delta_{L,1} = 0.44$ mT; and

$$F_{\mathrm{composite}}(B) =$$
$$= -2A'_{1,G}\left(\frac{B-B_{\mathrm{res},1}}{\Delta_{G,1}}\right)\exp\left[-\left(\frac{B-B_{\mathrm{res},i}}{\Delta_{G,i}}\right)^2\right] -$$
$$-2A'_{2,L}\left(\frac{B-B_{\mathrm{res},2}}{\Delta_{L,2}}\right)\left[1+\left(\frac{B-B_{\mathrm{res},2}}{\Delta_{L,2}}\right)^2\right]^{-2}, \qquad (3b)$$

where $A'_{1,G} = 700$, $A'_{2,L} = 500$, $B_{\mathrm{res},1} = 334.9$ mT, $B_{\mathrm{res},2} = 334.82$ mT, $\Delta_{G,1} = 0.45$ mT, $\Delta_{L,2} = 0.9$ mT, $\Delta_{pp,G1} = \Delta_{G,1}\sqrt{2}$, and $\Delta_{pp,2L} = 2\Delta_{L,2}/\sqrt{3}$.

The characteristics of the paramagnetic signals registered from the researched specimens after their long-term (for more than 1 month) storage in the air environment are quoted in Table 2.

Intensive broad signals depicted in the insets in Figs. 1, 2, and 4 were observed as concomitant in all examined specimens, except for the Vniivlon one. The nature of those signals is most likely associated with the presence of uncontrolled magnetic nanoparticles. The latter are present, in particular, due to the peculiarities of the composite preparation technology, which includes the stage of magnetic mixing of the initial mixtures [7–9]. Depending on their size, nanoparticles can exhibit ferromagnetic or superparamagnetic (SPM) properties. In the studied specimens, SPM nanoparticles were characterized by the g-factor $g = 2.237$ and the linewidth $\Delta B_{pp} = 104$ mT in BSP-7 and the composite with Vniivlon, $\Delta B_{pp} = 34.7$ mT in Terlon, and $\Delta B_{pp} = 58$ mT in the composite with Terlon. The spread of the widths of those signals is associated with the dispersion of both the sizes of SPM particles and the values of the total particle spins [8]. This dispersion is substantially lower in Terlon and in the BSP-7/Terlon composite. The other rather weak signal was ferromagnetic; it was observed at low resonance magnetic fields of 60 mT in the composites and 120 mT in Terlon. In general, the obtained EPR data testify that Terlon had the most ordered structure among the examined specimens.

3.2. Tribological properties

The measurements of the tribological properties of the developed OPs (see Table 3) showed that the introduction of OFs into a polymer matrix leads to a 1.2–2.2-fold reduction of the friction coefficient, a 2.3–17.6-fold reduction of the linear wear intensity, and a 1.3–2.2-fold reduction of the heat generation.

In Fig. 5, the microstructures of the friction surfaces of the BSP-7 copolymer (*a*) and the organoplastics based on it (*b* and *c*) are shown. From Fig. 5, *c*, one can see that the OP with Vniivlon fibers has undergone a substantial deformation. In particular, squeezed zones are observed on its surface, which emerged in the regions of the "composite-steel counter-body" contact under the load influence. At the same time, in the case of the OP with Terlon fibers

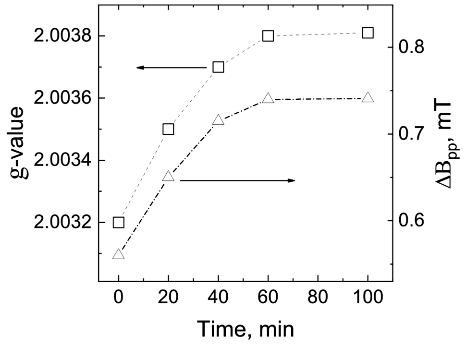


Fig. 3. Dependences of the g-factor (squares) and the EPR linewidth ΔB_{pp} (triangles) for a Terlon specimen preliminary evacuated for 1 h at $T = 400$ K on the time of its exposure in air. The specimen–air contact begins at $t = 0$

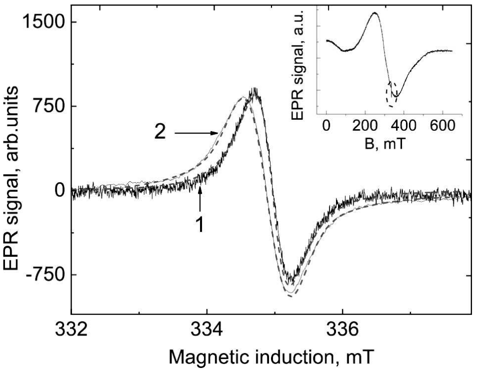


Fig. 4. EPR spectra of the Vniivlon fibers (curve *1*) and the bulk specimen of the BSP-7 + 20 wt% Vniivlon composite (curve *2*). The dashed curves are the approximations by formulas (3b). The spectrum of the composite specimen in a wide interval of magnetic fields is shown in the inset, $\nu = 9392$ MHz

Table 2. **EPR characteristics of the researched specimens**

Specimen and signal number	g-factor	EPR line width ΔB_{pp}, mT	PC concentration N_s, 10^{15} g^{-1}	Hyperfine spectrum structure
BSP-7, Signal 1	2.0031	0.49	1.5	–
BSP-7, Signal 2	2.0036	1.13	5.7	
Terlon			45.9 (in total)	$2A_{zz} = 3.3$ mT
Signal 1	2.0037	0.85		
Signal 2 (peak NTV A)	–	0.99		
Signal 3 (peak NTV B)	–	0.81		
Signal 4	2.0028	0.92		
BSP-7 + 10 wt% Terlon				Not registered
Signal 1	2.0039	0.71	3	
Signal 2	2.0043	1.3	3.6	
Vniivlon	2.0034	0.62	12.8	–
BSP-7 + 20 wt% Vniivlon				–
Signal 1	2.0037	0.64	7.9	
Signal 2	2.0043	1.04	22.6	

Table 3. **Tribotechnical characteristics of organoplastics based on BSP-7 copolymer**

Parameter	Content of Vniivlon/Terlon organic fiber C, wt%				
	0	10	20	30	40
Friction coefficient, f	0.46	0.37/0.34	0.31/0.29	0.25/0.25	0.25/0.21
Linear wear intensity, $I_h \times 10^{-8}$	10.58	4.59/4.35	2.47/1.92	1.24/0.60	2.18/0.68
Heat release intensity, q, kJ/(m^2 s)	276	222/204	186/170	150/147	156/126

(Fig. 5, *b*), the friction surface is more uniform, which testifies to its higher resistance to deformations. In general, as one can see from Table 3, the friction surfaces of OPs are characterized by a higher resistance in comparison with that of pure BSP-7 (Fig. 5, *a*).

4. Discussion of Results

Let us consider the paramagnetic properties of the basic BSP-7 polymer, the Terlon and Vniivlon fillers, and their composites, as well as the tribological properties of the latter.

First of all, we note that the BSP-7 copolymer has a complicated structure, in which carbon can be in two fundamentally different positions: close to or far from the CH_3 structural groups [13]. The parameters of EPR signal 1 (Fig. 1) are typical of defects like dangling carbon bonds in polymer chains [8]. At the same time, signal 2 with a larger g-factor and a substantially larger width is associated with the dangling carbon bonds at the structural positions near the CH_3 carbon-hydrogen groups [13]. The latter affect the PC parameters via the superfine interaction of the PC electron with the hydrogen nuclei. This interaction is also responsible for the nonuniform broadening of the EPR line in BSP-7.

As concerning Terlon and its paramagnetic properties, this is a Kevlar-like copolymer based on poly-(p-phenylene terephthalamide). However, unlike Kevlar, it contains 10–15% of diamine monomers [12]. It is known that the concentration of paramagnetic defects in the as-synthesized Kevlar fibers is insignificant, but it can substantially increase under external influences (pressure, ultraviolet, gamma or electron irradiation, annealing at temperatures $T > 370$ °C, and so forth) [14–18]. The EPR spectrum of defects in Kevlar consists of a single line with $g = 2.003 \div 2.004$ and the linewidth $\Delta B_{pp} \cong 2$ mT. It is important that the concentration of radicals and their stability over time depend on the fiber humidity and the concentration of nitrogen or oxygen in the immediate environment [18].

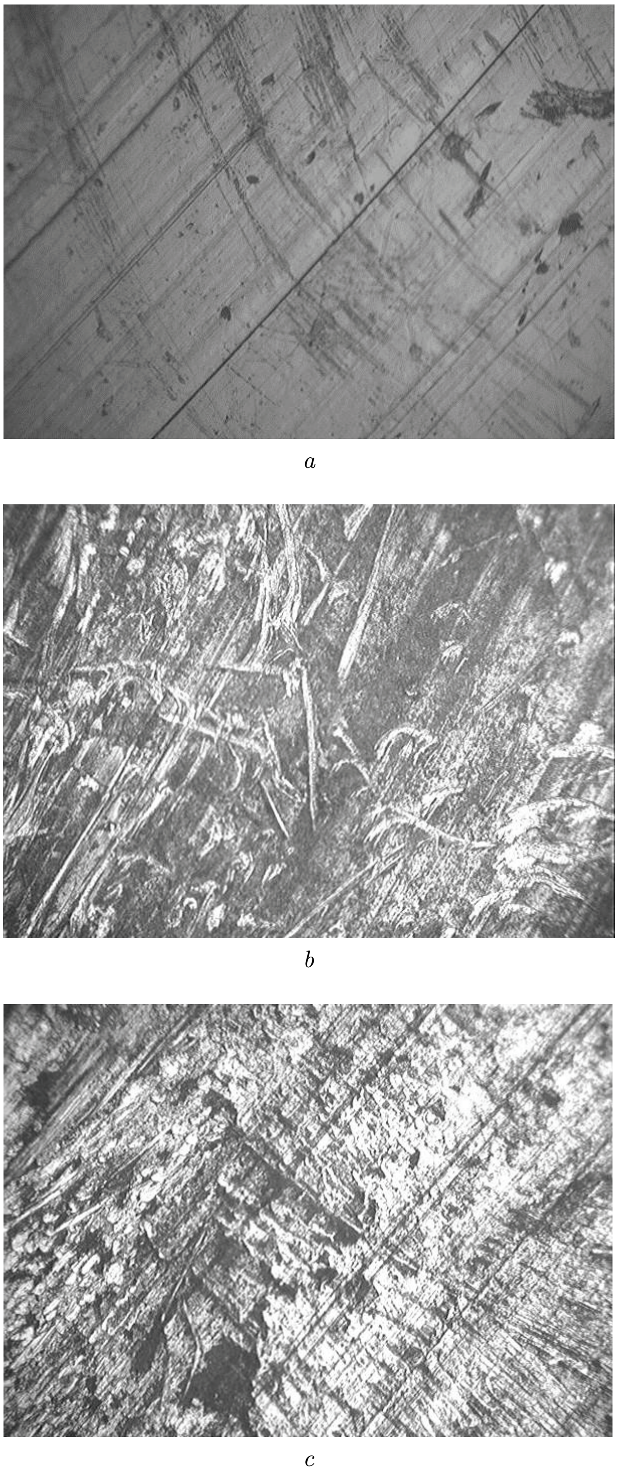
In contrast to Kevlar, the EPR spectra of the studied Terlon specimens consist of three lines (see Fig. 2). Lines A and B in Fig. 2 are a manifestation of the hyperfine spectrum structure with the hyperfine interaction constant $A = 1.65$ mT. Most likely, the PC is related to the nitrogen of the amide groups; its nuclear spin equals $I = 1$ and, accordingly, the hyperfine lines belong to the nuclear spin projections $I_z = \pm 1$. The central component with $I_z = 0$ is hidden under a more intense signal with $g = 2.0037$. This conclusion about the nature of PCs in Terlon is in agreement with the results of the recent work [19], where a nitrogen triplet was observed in the EPR spectrum of a Terlon specimen held in the nitrogen dioxide atmosphere.

The data presented in Fig. 3 allow the assumption that the Terlon specimens had a significant number of pores that could adsorb paramagnetic molecular oxygen. The spin-spin interaction of O_2 molecules with paramagnetic defects in Terlon led to the broadening of their EPR line and a shift of the g-factor.

The difference between the paramagnetic characteristics of Kevlar and Terlon may probably stem from the presence of 10–15% of monomers (diamines) in Terlon [12]. It follows from our experiments that the presence of diamines stimulates the formation of nitrogen-containing radicals, even if the Terlon specimens were not specially doped with nitrogen oxides, as was done in work [19]. At the same time, nitrogen-containing radicals were not registered in the BSP-7/Terlon composite (Fig. 2, curve *2*). It can be assumed that such radicals are destroyed in the course of composite formation at rather high temperatures and pressures [9, 11].

Another filler is the high-modulus aromatic heterocyclic polyamide Vniivlon (later, SVM$^{\mathrm{TM}}$) [12]. Those fibers have high mechanical characteristics. However, they also possess a low crystallinity degree as a result of the asymmetry between the chemical structures of initial monomers, which can connect arbitrarily (head-to-head or head-to-tail) with one another at the synthesis [20].

From the data in Table 2, one can see that the concentration of paramagnetic defects in Vniivlon was approximately 3.5 times lower than in Terlon, to a


a

b

c

Fig. 5. Microstructures (×150) of the friction surfaces of (*a*) the BSP-7 copolymer, (*b*) the BSP-7 + 30 wt% Terlon composite, and (*c*) the BSP-7 + 30 wt% Vniivlon composite

great extent owing to the absence of nitrogen-related radicals. Unlike the case of Terlon, the EPR parameters of Vniivlon did not change, when the specimens were evacuated, which indirectly testifies to their low porosity. By its parameters, the broad signal in the BSP-7/Vniivlon composite (see the inset in Fig. 4) is similar to those in BSP-7 (Fig. 1) and the BSP-7/Terlon composite (Fig. 2), but it is more intense.

As was already noted, the EPR spectra in the BSP-7, BSP-7/Terlon, and BSP-7/Vniivlon specimens consist of two signals belonging to essentially different defects. The width of both ΔB_{pp} signals in the composites almost does not change in comparison with that in pure BSP-7, but the value of the g-factor increases considerably (see Table 2). This fact testifies to the enhancement of the spin-orbit coupling, the increase of the p-component of the electronic states, and, accordingly, the strengthening of the interatomic covalent bonds in the composite due to the presence of Terlon or Vniivlon.

As concerning the tribological properties of the developed OPs, the Terlon OFs are the most effective for the improvement of the tribotechnical characteristics of the basic polymer (see Table 3). This may probably occur, because the elastic modulus of Terlon is 35% higher than that of Vniivlon (see Table 1). As a result, the OP reinforced with Terlon fibers is characterized by better damping properties (the ability to withstand multiple loads), which is evidenced by the analysis of the friction surfaces (Fig. 5). In this sense, a positive factor is the high crystallinity of the Kevlar-like Terlon structure, whereas the composites with the Vniivlon filler (the latter has an almost amorphous heterocyclic structure) can be less resistant to the intensity of a linear wear under dynamic loads.

Uncontrolled nanocluster impurities of iron oxides were present in all synthesized composites. However, their influence on the tribological composite properties was not detected. Note, however, that the controllable presence of the magnetic and/or conductive nanoclusters in polymer composites can be used to achieve the electromagnetic screening effect [8].

5. Conclusions

The EPR spectroscopy data show that paramagnetic centers are observed in the pure BSP-7 polymer, the Terlon and Vniivlon fibers, and the BSP-7/Terlon and BSP-7/Vniivlon composites. Those PCs are related to various defects in polymer chains and radicals emerging due to the presence of nitrogen atoms in amide groups. The parameters of those defects are appreciably different, which allowed us to determine the structure-dependent electronic properties of all components of the composites and the character of polymer interaction with the fillers and the air environment.

The Terlon structure differs from that of Kevlar by the 10–15% presence of diamines, which favor the spontaneous formation of nitrogen-containing radicals. The presence of the latter can substantially worsen the mechanical properties of Terlon and, after a long-term storage, even lead to the destruction of fibers [19]. However, according to the results of EPR measurements, such radicals were not detected in the researched BSP-7/Terlon composites because of their destruction during the composite synthesis at relatively high temperatures and pressures.

A comparison of the BSP-7/Terlon and BSP-7/Vniivlon composites shows that the former has better tribological properties, which is associated with a higher elastic modulus of Terlon and, probably, its scalier (pseudographite) structure. The latter conclusion is indirectly confirmed by the EPR data demonstrating that the Terlon structure is more porous than the Vniivlon one. Furthermore, it should be taken into account that Vniivlon is a heterocyclic OF and, accordingly, has a low degree of structural crystallinity. Under dynamic loads typical of tribotechnical applications, organoplastics with such OFs as fillers can be less effective than OPs with highly crystalline OFs. The developed ecological and inexpensive organoplastics are effective substitutes for ordinary tribotechnical materials (caprolon B, polyamide 12, polyethylene, and others) and can be recommended for the practical implementation.

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Received 19.07.23.
Translated from Ukrainian by O.I. Voitenko

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МАГНІТОРЕЗОНАНСНІ ТА ТРИБОЛОГІЧНІ ВЛАСТИВОСТІ ОРГАНОПЛАСТІВ НА ОСНОВІ СПІВПОЛІМЕРУ БСП-7

Методом електронного парамагнітного резонансу досліджено властивості співполімеру БСП-7, високоміцних і високомодульних кевлароподібних органічних волокон (ОВ) терлону та вніівлону в ролі наповнювачів, а також композитів БСП-7/ОВ. Встановлено наявність та визначено властивості дефектів різного типу і магнітних домішок у вихідних матеріалах та виготовлених композитах. Виявлено вплив взаємодії матриці з наповнювачами та оточуючим середовищем. У терлоні зареєстровано значну концентрацію азотовмісних радикалів, пов'язаних із наявністю мономерів діамінів у його структурі, що може негативно впливати на фізико-механічні характеристики композитів. З урахуванням отриманих даних розроблено ефективні органопластики БСП-7/ОВ. Вимірювання їх трибологічних властивостей показали, що додавання оптимальної концентрації ОВ до полімерної матриці БСП-7 сприяє значному зменшенню коефіцієнта тертя, інтенсивності лінійного зношування та тепловиділення. Кращі результати показали композити з терлоном, що пояснюється не тільки його більш високим модулем пружності, а і високим ступенем кристалічності структури, на відміну від вніівлону з його майже аморфною гетероциклічною структурою. Крім того, процес синтезу композитів передбачає застосування достатньо високих температур і тиску, в результаті чого азотні радикали терлону руйнуються, і їхній негативний вплив на довготермінову стабільність характеристик композита нівелюється.

Ключові слова: співполімер БСП-7, ЕПР, вніівлон, терлон, композити.