



THE INFLUENCE OF HYBRIDE FILLERS ON SILICATE MATRIX ON THERMOPLASTIC POLYMER PROPERTIES

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ABSTRACT

The hybrid fillers have been obtained on the base of alkali silicate solution and oligomers of epoxidiene resin intercalated with polyvalent metals. The technological features of the formation of the high-dispersed hybrid products from the metal-organosilicate solutions are considered. The properties and structure of the hybrid fillers have been studied. The physico-mechanical and triboengineering properties of the materials based on phenylon modified by the developed fillers have been investigated.

Keywords: alkali silicate solution, epoxidiene resin, polyvalent metals, hybrid filler, structure, properties, composite, phenylon

1. INTRODUCTION

One of the major objectives of materials science is the elaboration of new composite materials with refined service characteristics. The elevation of the polymer matrix properties is conditioned by the characteristics and the size of the target fillers, thus by the physico-mechanical processes running at the binder-filler interface. Within a broad range of the fillers used for thermoplastic-based materials organo-silicate nanocomposites based on a silicate matrix [1-3] present a special interest. The modification of the silicates by organic agents enables to achieve highly dispersed hybrid compounds that display a perfect chemical resistance and a mechanical strength in combination with optimal thermophysical characteristics. In addition, they ensure elevated service characteristics of the composites for different functional purposes [4-7].

In order to form hybrid nanocomposites with a specific molecular structure and specific physico-mechanical properties, it is worthwhile using a sol-gel method [1, 3]. The advantages of the sol-gel synthesis are the probability of combining the initial reagents in the solution, to alter the fragments of the organic and inorganic components at the molecular level and to produce the products in the ultra-dispersed state by performing a

direct synthesis of the organo-silicate nanocomposites. By varying the nature of the introduced organic components and the thermodynamic parameters of the sol-gel process, it is possible to purposefully change the structure of the products being synthesized. The gel-formation process ensures transition of the system from a free-dispersed state into a bound-dispersed one, which results in either the precipitation of the ultra-dispersed product from solution or the formation of a hybrid gel. The nanocomposites obtained by the above method are related to a condensation type in which the nanocomposites are “assembled” from inorganic and organic molecules and fragments in the course of the phase transformations. Notice that all the products of the sol-gel synthesis present nanomaterials [7-8]. By converting the sol into a gel, one may obtain the materials with a wide range of physico-chemical properties, namely, insulating, high-porous, block and dispersed ones, special additives in the form of pigments and chromophores, luminophors and so on.

The aim of the present work was to obtain functionally active dispersed organo-silicate nanocomposites and to study the vistas of their use as thermoplastic fillers.

2. TESTING METHODOLOGY

The subject of this investigation is the composition materials obtained by means of the sol-gel technology from the systems based on alkali-silicate precursor presented by the water solution of sodium silicate (SWS; $n=2.9$). The highly dispersed composites based on a silicate matrix were obtained by means of a sol-gel technology from SWS or SWS modified with epoxidian resin ED-20 (ER), where the transition metals (Me = Cr, Fe, Co, Ni, Cu) are intercalated as a result of the phase transition [4, 6, 7]. The water solutions of transition metals' sulfates were used as precursors of the corresponding metals' ions.

The synthesized metal-epoxy-silicate nanocomposites were investigated as the fillers for polyamide (phenylon C-2 FS). A part of the compositions was obtained with an additional introduction of thermally expanded graphite (TEG) as a filler.

The metal-epoxy-silicate nanocomposites were produced following a sol-gel procedure of combined systems on the base of alkali-silicate precursors in the form of sodium silicate aqua solution (SSS) ($n = 2.9$; $\rho = 1.49 \text{ g/cm}^3$). To obtain a dispersed hybrid filler, the alkali-silicate solution was modified by the epoxydianic resin (ER) ED-20, after which the organo-silicate matrix (OSM) was injected with the ions of transient metals (Me = Co, Cr, Cu, Fe, Ni) by the method proposed elsewhere [5-7]. To terminate the process of physico-chemical interaction thus formed, the nanocomposites underwent a thermal treatment under a two-stage regime: in standard conditions till a constant weight, and thermally at 120°C or 160°C. The fraction with below 50 μm dispersion was used for investigations.

The resultant fillers presented air-dry high-dispersed metal-epoxy-silicate products in which the ions of transient metals are intercalated into the epoxy-silicate matrix (ESM) obtained, in its turn, by the modification of alkaline-silicate solution of epoxidiane resin.

Thermally expanded graphite is obtained via oxidizing natural graphite by ammonia sulfate in a sulfuric medium followed by a thermal treatment in a muffle furnace under up to 1200 K. Its structure is formed as a result of splitting the initial graphite crystal along the crystallographic axis *C* into thin strips of a few strongly deformed planes with the formation of a folded structure that imparts unique properties to graphite. In our work, we have used a thermally expanded graphite that looks like inflated, black in color 0.2-10.0 mm in size chains of 5 kg/m³ loose weight.

The thermoplastic-based compositions were prepared by mixing the dispersed components in a rotating electromagnetic field [6]. The test samples were obtained by compression molding.

The samples were studied following a standard procedure. IR spectra of produced compositions were recorded by the IR-Fourier spectrometer NICOLET 5700 within the range 500-4000 cm^{-1} . The samples underwent a thermal analysis on the derivatograph Q-1500D of the system Paulic-Paulic-Erdel. The tests were conducted in the ceramic crucibles in air, within 298-963 K temperature range and the heating rate of 5.0°C/min. The degree of chemical cross-linking of the components during formation of the activated filler was determined by the method of sol-gel analysis, using a Soxhlet apparatus in aqua medium proceeding from the criterion of a sol-fraction content in a solidified system. The real density was found by a bottle method, the bulk density was measured on a loose shacked-down material. The size, state and phase composition of the powders was determined by the method of transmission electron microscopy (TEM) on the electronic transmission microscope EM 125. The phase composition was found on the base of the microdiffraction images of the electron diffraction patterns and the X-ray phase analysis. The X-ray radiography was conducted using a diffractometer DRON-3.0 in Cu-K_α radiation.

The specific heat capacity and the heat conduction ratio were measured by IT-S-400 and IT- λ -400 devices. The strength characteristics ($\sigma_{0.2}$ - the breaking strength at deformation 0.2%), and the elasticity modulus at compression (E) of the thermoplastic-based composite materials were found on a tearing machine FP-100. The triboengineering characteristics of the composite materials were determined on the friction machine SMT-2 under the sliding velocity of $v=0.5$ m/s and the load of 10 MPa.

3. RESULTS AND DISCUSSION

The rheodynamic investigations showed that during the introduction of the salts of polyvalent metals into SWS, there occur the processes structuring within the systems [9], which significantly accelerate in case of the salt concentration increase and result a rapid increase of the solutions' viscosity (Fig. 1). Only in small concentrations of the modifier the structure-formation processes flow very slowly and the viscosity remains almost the same with the time course. The investigation of kinetics of changing the rheological properties of SWS modified with polyvalent metals' salts ($C=0.01-0.3$ M) showed that binary systems with the molar concentration of salts of $0.01=0.1$ M are the most stable. The dynamic viscosity values of such systems remain almost the same at standard conditions, during 72 hours. In this case, the dynamic viscosity of SWS modified with cobalt sulfate is twice as big as that of the dynamic viscosity of SWS modified with nickel and copper sulfates, which testifies to higher system cohesion and a more intense structure-formation process course. In case of increasing of the salt up to 0.3 M within SWS, the solution's dynamic viscosity grows by 2–3 times (Fig. 1). The curves of systems' flow are of non-Newton mode, which testify the structure-formation processes occurring within them.

The structural viscosity of modified sols increases at the growth of metal ions concentration and the structure relaxation period, due to the formation of the inorganic polymer net. The systems are structurized with the time running and the obtained structure's stability is increasing in proportion to the formation period. The increase of the systems' dynamic viscosity, and consequently, of the acceleration of the gel-formation process, agrees with the activity of the introduced metal in the following direction: $\text{Cu} \rightarrow \text{Ni} \rightarrow \text{Co} \rightarrow \text{Fe}$. We can suggest that the introduced metals in parallel systems take part in specific interactions. The visual observations have shown that the solutions colour changes when the compositions are formed: salt solution \rightarrow salt-SWS solution \rightarrow xerogel compositions of salt-SWS (Table 1).

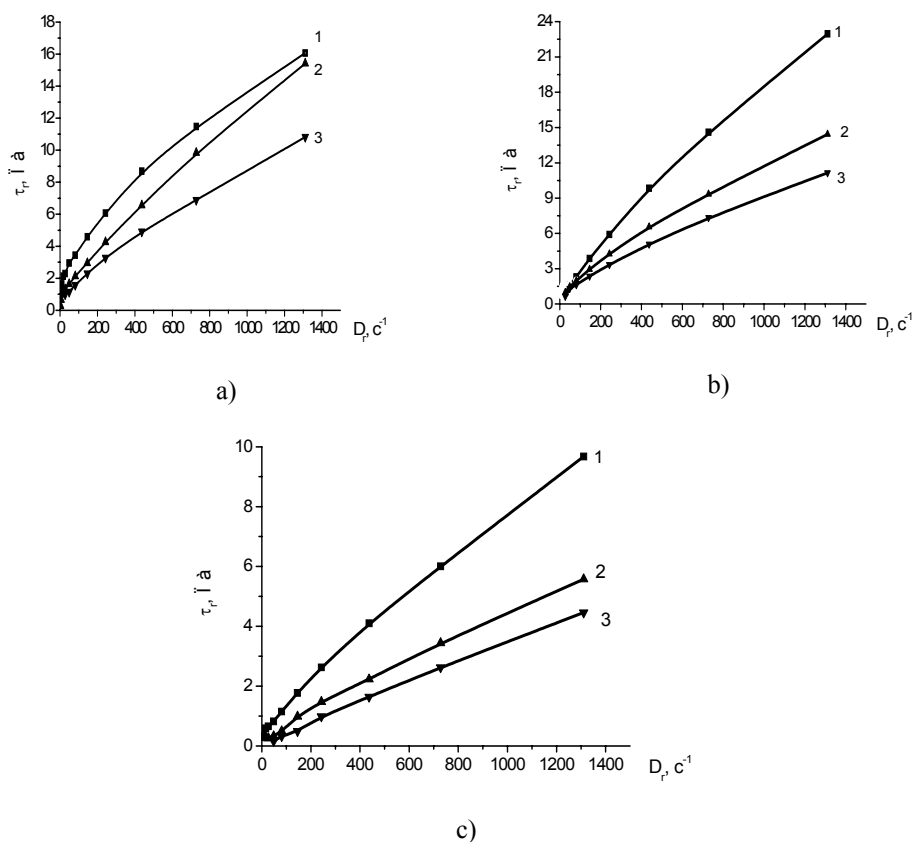


Fig. 1. Dependence of the shift velocity of SWS on the salt concentration (a, b – 0.3 M; c – 0.1 M) and on the exposure period (a – 15 min.; b, c – 24 hours): 1 – CoSO₄, 2 – NiSO₄, 3 – CuSO₄

The color change is obviously conditioned by the change of ligands (or by their number) and testifies the participation of the metal ions in the process of systems' structure formation [9]. Most probably, the metals are catalysts of the sol-gel transition and promote it via aqua systems, thus accelerating the dehydration process. A certain inhibition effect of the phase transition by means of copper is probably connected with the formation of stronger systems by metal, which results in the structure-formation kinetics decrease.

Table 1. The properties of metals and their salts

Metal	Standard electrode potential		Ion radius ϑ^{2+} , r_i , nm	Metal salt	Color		
	Electrode	E° , B			of salt (solid)	of salt solution	of xerogel
Fe	Fe/Fe ²⁺	-0.44	0.078	FeSO ₄	light brown	white	yellow
Co	Co/Co ²⁺	-0.27	0.076	CoSO ₄	crimson	pink	lilac
Ni	Ni/Ni ²⁺	-0.25	0.069	NiSO ₄	turquoise	green	light green
Cu	Cu/Cu ²⁺	+0.34	0.073	CuSO ₄	blue	darkblue	light blue

The results of IR-spectral analysis confirm the suggestion on the metals' participation in the process of sol-gel transition.

IRS data analysis shows that the absorption bands of 890-930 cm^{-1} and 864 cm^{-1} characterizing the presence of silicon orthoions in the xerogel of the initial SWS disappear in the modified xerogels. At the same time, the intensity increases at the significant absorption band expansion within the range of $\sim 1000\text{--}1070 \text{ cm}^{-1}$, which is conditioned by silicon and oxygen atoms fluctuations in Si–O–Si bridge links. The increase of the band intensity can be explained by the growth of Si–O–Si-links share and the expansion can be explained by the formation of the silicon-oxygen chains of different length. Besides, all the compositions show the shift of the major band characterizing the inorganic frame formation into the high-frequency area. The shift value is defined by the nature of the metal-containing modifier: 14.1; 11.7 and 9.6 cm^{-1} correspondently for FeSO_4 , CoSO_4 and NiSO_4 and it depends on the cation type. In IRS modified with SWS, there disappears the band of 1436.7 cm^{-1} connected with the formation of the natrium carbonate during the formation of silicon-oxygen gel, which testifies to the carbonate formation process inhibition by a metal-containing modifier.

The analysis of the obtained xerogels by means of X-ray diffraction analysis confirmed the significant difference in the structures of xerogels obtained from the systems BPC–metal containing reactant. According to the XRD data, there are no compounds containing Fe_2SiO_4 ($d = 2.50$; 2.83; 1.78), Co_2SiO_4 ($d = 2.61$; 3.6; 3.37), Ni_2SiO_4 ($d = 2.43$; 3.47; 2.74), CuSiO_3 ($d = 7.22$; 2.58; 4.03) in xerogels obtained from the systems BPC–salt. The obtained metal-silicate product possess an individual structure determined by the type of the introduced metal. It was stated that the diffraction pictures of the obtained xerogels with IV period d -metals ions: Cu, Ni, Co, Fe intercalated into the silicate matrix are characterized by the presence of the diffusive peak at the values of $2\theta_{\text{Cu}}$: 8.65; 7.7; 7.7 and 5.5, correspondently.

The elements intercalation into the silicon-oxygen matrix leads to significant structural changes of the initial silica, these changes providing for the wide diversion of physico-chemical properties of the obtained disperse products (Table 2).

Table 2. The dependence of the composite properties on the type of the introduced transition metal

Introduced metal	Gel-fraction, %	Properties of the disperse metal-silicate *			
		Density		Porosity, %	Compactness, %
		Gravel, g/cm^3	Proper, g/cm^3		
–	1.6	0.78	2.07	62.3	37.7
Fe	75.7	0.29	1.53	81.1	18.9
Co	69.2	0.31	1.48	79.1	20.9
Ni	72.5	0.33	1.43	76.9	23.1
Cu	83.5	0.41	1.41	70.9	29.1

* – particles size $d < 50 \mu\text{m}$

The obtained results showed that introducing polyvalent metals ions into the silicate matrix increases the values of the disperse products' gel-fraction and the decrease of gravel density values. The comparison of thermal resistance of the obtained products are cited in Table 3.

Table 3. The thermal properties of metal-silicate nanocomposites

Composite composition	T_0^* , K	T_5 , K	T_{10} , K	T_{15} , K	T_{20} , K
FeSO ₄ → SWS	318	353	388	495	>1273
CoSO ₄ → SWS	318	383	423	620	>1273
NiSO ₄ → SWS	318	377	424	629	1269
CuSO ₄ → SWS	318	377	459	1273	>1305

* – T_0 , T_5 , T_{10} , T_{20} – initial temperature and the temperatures of 5, 10, 20 % of mass loss, correspondently

Table 4. The properties of hybrid fillers

Composite composition	Gel-fraction, %	Density *		Porosity, %	Compactness, %
		Gravel, g/cm ³	Proper, g/cm ³		
Fe→ ESM*	53.9	0.441	1.636	73.0	27.0
Co→ ESM	54.6	0.449	1.568	71.4	28.6
Ni→ ESM	56.4	0.460	1.514	69.6	40.4
Cu→ ESM	61.3	0.476	1.490	68.1	41.9

* – epoxysilicate matrix, organic component's content of 6%;

** – disperse particles size $d < 50 \mu\text{m}$

The sol-gel synthesizing of metal-epoxysilicate (Me→ESM) nanocomposites allowed for holding a set of physico-chemical interactions among the combined reactants, which led to the formation of the highly dispersed hybrid products (Table 4) significantly different because of the metal type. The porosity of the metal-organosilicate nanocomposites decreases, while their compactness increases.

Obtaining all the investigated composites of Me → ESM type was accompanied by the interaction of the metal with the matrix formed in situ. According to IRS analysis it was stated that in case of modifying SWS with epoxidian resin at the components' overlapping within the system there occurs the interaction between ES epoxy group and the hydroxyl group of the sodium silicate, with the formation of a simple ether group and a new hydroxyl one, resulting in the formation of the spatial silicate-polymer pattern.

The comparison of IR-spectra shows that the composition of the salt introduced into the SWS–ES system significantly influences the structure of the obtained product, and the main effect is that of the cation [7]. All xerogels spectra show a wide band within the range of 900–1200 cm⁻¹, conditioned by the valent asymmetrical fluctuations of silicon and oxygen atoms in the Si–O–Si bridge links. The intensity growth of this band in composites as compared to SWS xerogel is connected with the increase of the Si–O–Si-links share in the course of the structure-formation and the formation of the inorganic net. The major peak shift into the high-frequency area of the spectrum testifies to the course of silica polymerization process. The major band shift observed in all the specters of Me→ESM composition seems to be conditioned by the intercalated metal's type: 24.2; 23.8; 27.4; 6.2 (as compared to the IR-spectrum of SWS) and 8.4; 9.2; 15.7 and 0.0 cm⁻¹, correspondently (as compared to the IR-spectrum of Me→ SWS systems) at the content of Fe, Co, Ni and Cu. Such band shift can be explained by the participation of metals in the process of the composite formation and its integration into the silicate matrix structure as Si–O–Me fragment.

Figure 2 presents electronic-microscopic shots of the nanophase structure of the xerogels depending on the introduced metal's type. The microstructure analysis shows that in the process of phase transition during the metal sulphates' introduction into the epoxysilicate emulsion the flexible matrix is formed, which looks like of rather regular-shaped spherulites whose size depends on the introduced metal's type.

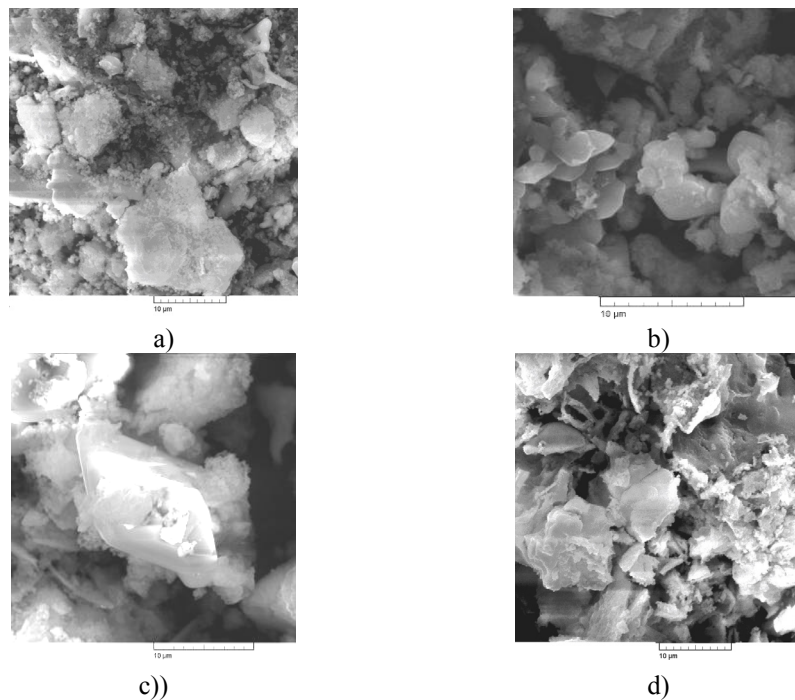


Fig. 2. The microstructure of xerogels based on the epoxysilicate matrix intercalated by metal of: a) – iron; b) – cobalt; c) – nickel; d) – copper

TEM studies of the nanophase structure of the products obtained from the systems $\text{Me} \rightarrow \text{ESM}$ (Fig. 3) have visualized that the structure of the resultant hybrid nanocomposites is characterized as a mixed-hybrid because the disperse particles of the content $\beta\text{-Na}_2\text{Si}_2\text{O}_5$ and SiO_2 , sized 5-50 nm and $\text{Me}_2(\text{SiO}_3)_n$ and $\text{Me}_2(\text{Si}_2\text{O}_5)_n$, sized 15-25 nm are intercalated into the formed epoxysilicate nanoclusters ($\text{ES-Na}_2\text{Si}_3\text{O}_7$, $\text{ES-Na}_6\text{Si}_8\text{O}_{19}$).

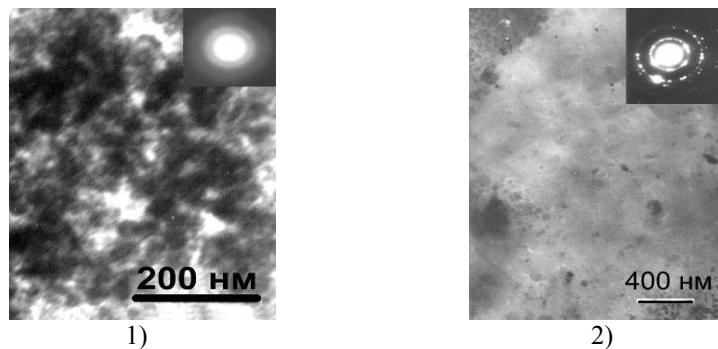


Fig. 3. TEM microphotographs and images of the microdiffraction of corresponding areas of dispersed products obtained from the system $\text{Cu} \rightarrow \text{ESM}$ under standard conditions (1) and with additional microwave heating (2)

It has been found out experimentally that the additional microwave exposure of the combined systems leads to the polymerization of silicon-oxygen matrix (the formation of the amorphous and crystalline phases $\beta\text{-Na}_2\text{Si}_2\text{O}_5$ and $\text{Na}_6\text{Si}_8\text{O}_{19}$), in which SiO_2

particles up to 15 nm in size are dispersed, during which the crystallinity degree of the hybrid composites increases.

The physico-chemical interaction of the components leading to the formation of net-organization products with intercalated metal-silicate and organic fragments conditions the high values of the thermoresistance of the obtained nanocomposites ($T_{10}=640\div 670$ K; $T_{20}=910\div 1000$ K).

Thus, the obtained metal-organosilicate fillers were examined as the fillers for thermoplastics.

The study of hybrid dopes intended for phenylon filling has shown that their introduction into the thermoplastic matrix increases the heat conductivity by 14.7-20.8%, the elasticity modulus by up to 12.3% and the compression strength by up to 16.2%. In addition, this reduces the friction coefficient 1.2 times. The verification of the efficiency of the filler effect depending on the electron structure of the metal intercalated into the epoxy-silicate matrix has proved that to refine the mechanical properties of the phenylon-based material it is more expedient to use the filler of the composition (Cr→ESM), to improve triboengineering properties, the most efficient are (Co→ESM) and (Ni→ESM), and to raise thermal stability (Fe→ESM) and (Co→ESM). It was established that the variations in the thermophysical characteristics of the material are correlated with the nucleus charge and the atomic radius of the intercalated metal.

The analysis of the effect of the operation regimes (the pressure and the sliding velocity) on the triboengineering characteristics of the material (Fig. 4) with an optimum filler content (composition: TEG/(Co→ESM)=1/1) showing the best combination of thermo-physical and mechanical characteristics (Fig. 5) makes grounds for the following conclusions.

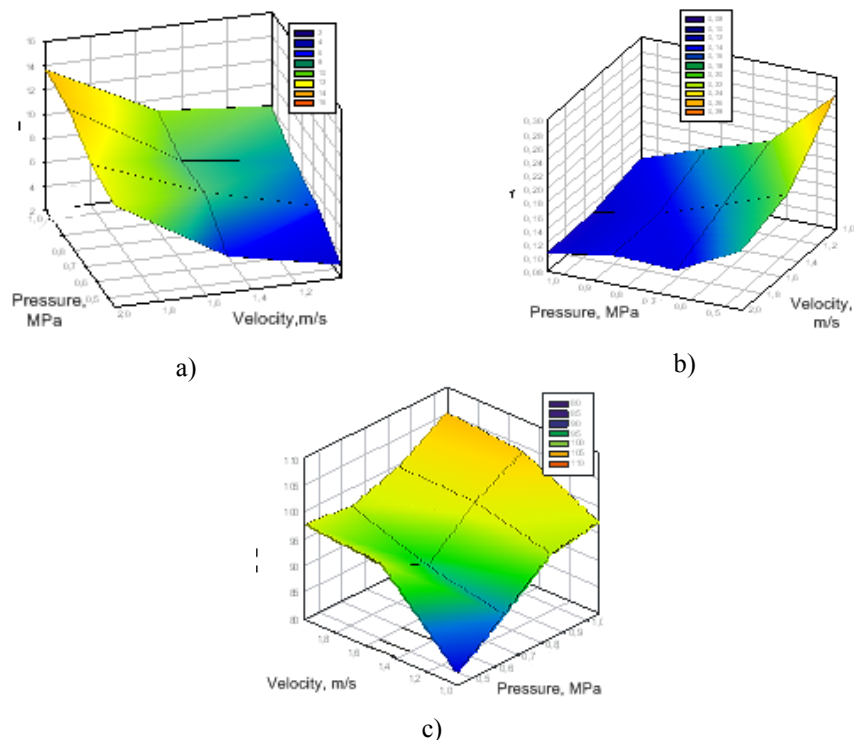


Fig. 4. The linear wear rate (a), the friction coefficient (b) and the temperature (c) in the contact zone versus the sliding velocity and the pressure (steel 45, HRC 52, $R_a=0.17$ μm) for the phenylon-based composite with a hybrid filler (TEG/(Co→ESM)=1/1)

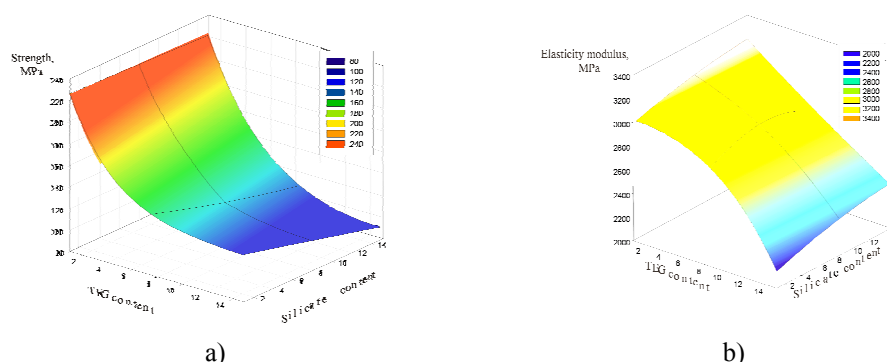


Fig. 5. The strength (a) and the elasticity modulus (b) dependence at compression versus the formula of phenylon-based composite, modified by TEG and (Co→ESM)

The temperature and the wear in the contact zone are varying symbiotically, whereas the friction coefficient is decreasing when the pressure and the sliding velocity are growing, wherein the temperature in the contact zone under similar (p.v) values is lower in the case of a higher sliding velocity, i.e., the friction contact duration is less. The surface of the composite samples within the studied load range is glassy, which is a sign of the fatigue wear mechanism.

The obtained results have proved that the combined use of the fillers leads to their mutual activation and synergetic effect enabling to vary the thermophysical, physico-chemical and triboengineering properties of the material in a wide range.

4. CONCLUSION

The conducted investigations have visualized that the synthesized metal-epoxy-silicate materials can be used as functionally active fillers for thermoplastics.

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