

THE EFFECT OF HYBRID FILLERS ON PHYSICO-MECHANICAL PROPERTIES OF THERMOPLASTIC POLYMERS

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Summary

Hybrid nanocomposites intercalated with polyvalent metals have been obtained based on polysilicates of alkali metals and epoxidian resin oligomer. The properties and the nanophase structure of hybrid products have been studied depending on the type of a polyvalent metal introduced into the silicate or epoxy-silicate matrix. The developed hybrid nanocomposites have been investigated as UHMWPE and Phenylon fillers. Physico-mechanical and triboengineering properties of the materials based on UHMWPE thermoplastic and phenylon modified by the developed fillers have been investigated.

Key words: hybrid nanocomposite, polysilicates of alkali metals, ED-20, filler, structure, properties, UHMWPE, phenylon, composite

INTRODUCTION

One of the major objectives of materials science is elaboration of new composite materials with refined service characteristics. Elevation of the polymer matrix properties is conditioned by just as characteristics and size of the target fillers, so by physico-mechanical processes running at the binder-filler interface. Within a broad range of the fillers used for thermoplastic-based materials organosilicate nanocomposites based on a silicate matrix present a special interest. Modification of silicates by organic agents enables to achieve highly dispersed hybrid compounds that display perfect chemical resistance and mechanical strength in combination with optimal thermophysical characteristics. In addition, they ensure elevated service characteristics of the composites of different functional purposes. The sol-gel method which can compatibilize starting reagents in solution is a most efficient means for making hybrid nanocomposites with a particular molecular structure and physicochemical properties [1,2]. The advantage of the sol-gel synthesis is that fragments of both organic and inorganic com-

ponents can be varied on the molecular level thus realizing a directional synthesis of organosilicate nanocomposites that can combine properties of ceramics and polymers. While varying the nature of the organic components, as well as the thermodynamic parameters of the sol-gel process, the structure of the synthesized nanocomposites can be changed directionally [1-4].

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.

EXPOSITION

The object of research were organosilicate nanocomposites produced by sol-gel process from compatibilized systems based on a colloidal alkaline silicate solution (ASS, $n = 2.9$). The ASS was modified by functionally reactive organic reagents (OR) – oligomer of epoxydiane resin ED-20 (ER). The sol modified by an oligomer was matured, subjected to coagulation in aqueous solution of salt of a polyvalent metal (e.g. Cr^{2+} , Co^{2+} , Ni^{2+} , Fe^{3+} or Cu^{2+}).

The prepared products were tested as fillers to polyolefins (ultra-high molecular weight polyethylene (UHMWPE)) and polyamides (phenylon S-2 (PS)). The UHMWPE- and PS-based compositions were prepared by mixing dispersed components in a rotating electromagnetic field [5, 6]. The UHMWPE- and PS-based materials were produced by compression moulding.

IR-spectra of the compositions prepared were recorded using FTIR-spectrophotometer NICOLET 5700 at 500-4000 cm^{-1} frequency range. The size, condition and phase contents of the powders were determined by the transmission electron microscopy (TEM) using TEM 125. The phase contents were determined from electron-diffraction photomicrographs and results of X-ray phase analysis. Roentgenographic studies were performed the diffractometer DRON-3.8 and Cu- K_{α} radiation. The true density was determined with a pycnometer, the apparent density – in bulk after shaking. The strength characteristics (ultimate tensile stress at 0.2% ($\sigma_{0.2}$) strain and elastic modulus in compression) of the thermoplastics-based composite materials were determined on the tensile-testing machine FP-100. The triboengineering characteristics of the composite materials were studied on friction-testing machine SMTs-2 at a sliding speed $v = 0.5$ m/s and load 10 MPa.

Hybrid composites are prepared from ASS in the following sequence: preparation of starting solution → introduction of a modifying reagent → preparation of a stable compatibilized solution → maturing of a binary sol → gel formation → drying → heat treatment of the xerogel → dispersion → hybrid nanocomposite. Synthesis of hybrid nanocomposites has made possible to realize a series of physico-chemical interactions between the combined agents and has lead to formation of highly dispersed hybrid products. The resultant fillers presented air-dry high-dispersed metal-epoxy-silicate products (Table 1) in which the ions of transient metals are intercalated into the epoxysilicate matrix (ESM) obtained, in its turn, by modification of alkaline-silicate solution of epoxidiene resin.

The formation of in fact all studied composites of the type Me → OSM was accompanied by strong interactions of *in situ* forming

metal and matrix. By the method of IRS it was established that modification of ASS by epoxidiene resin, during which the components are combined within a system is accompanied by interactions between the epoxide group ER and hydroxyl one of sodium silicate resulting in formation of a simple ether and new hydroxylic groups that bring about a spatial silicate-polymer structure.

Table 1. Properties of hybrid composites

Composition *	Density**		Porosity, %	Gel fraction, %
	in bulk, g/cm ³	true, g/cm ³		
Cr → ESM	0.28	1.94	85.6	59.8
Fe → ESM	0.29	1.53	81.1	65.7
Co → ESM	0.31	1.48	79.1	69.2
Ni → ESM	0.33	1.43	76.9	72.5
Cu → ESM	0.41	1.41	70.9	83.5

* metal incorporated in epoxysilicate matrix; organic component concentration in system – 6 wt%

** dispersed fraction size $d < 50$ μm

TEM studies of the nanophase structure of the products obtained from the systems Me → OSM have visualized that the structure of the resultant hybrid nanocomposites is characterized as a mixed-hybrid one in which along with intercalated epoxysilicate nanoclusters (ER- $\text{Na}_2\text{Si}_3\text{O}_7$, ER- $\text{Na}_6\text{Si}_3\text{O}_{19}$) one can see the regions with a dispersed filler of amorphous crystalline particles (β - $\text{Na}_2\text{Si}_2\text{O}_5$, SiO_2) 5-50 nm in size, and metal-silicate fragments of $\text{Me}_2(\text{Si}_2\text{O}_5)_n$ 15-25 nm in size.

Thus obtained epoxysilicate fillers were examined as the fillers for thermoplastics.

The results showed the crystallization degree of UHMWPE-based materials to vary negligibly (Table 2) but to depend on the incorporated metal [7].

Table 2. Crystallinity degree for UHMWPE and CM based on that

Indexes*	UHMWPE	Filler composition				
		Cr → ESM**	Fe → ESM	Co → ESM	Ni → ESM	Cu → ESM
I_1	0.079	0.104	0.096	0.089	0.097	0.08
I_2	0.082	0.085	0.083	0.078	0.092	0.077
I_1/I_2	0.96	1.22	1.16	1.14	1.05	1.04

* absorption band intensity at 1894 (I_1) and 1303 cm^{-1} (I_2);

** epoxy-silicate matrix (ESM)

Crystallinity reduction in UHMWPE modified by hybrid fillers enhances strength cha-

racteristics, especially with addition of Ni→ESM and Cu→ESM (Table 3).

Table 3. Strength characteristics of UHMWPE-based materials

Properties	UHMWPE	Filler composition				
		Cr → ESM	Fe → ESM	Co → ESM	Ni → ESM	Cu → ESM
$\sigma_{0.2}$, MPa	16.4	16.0	16.6	18.6	20.1	20.9
E , MPa	1023.7	1137.7	1196.4	1224.7	1246.2	1248.1

Hybrid fillers added to UHMWPE increase compressive strength by 27 %, elastic modulus by 22 % as a result of interaction between the polymer matrix and filler particles. The analysis of physicomecanical properties of materials show that property improvements depend on the polyvalent metal intercalated in the epoxysilicate matrix. The strength enhancement correlates with nucleus charge changes of the metal in the filler matrix in the sequence: $^{24}\text{Cr} \rightarrow ^{26}\text{Fe} \rightarrow ^{27}\text{Co} \rightarrow ^{28}\text{Ni}$ (Fig. 1). The filler composition affects the yield point and elastic modulus of the formed composites.

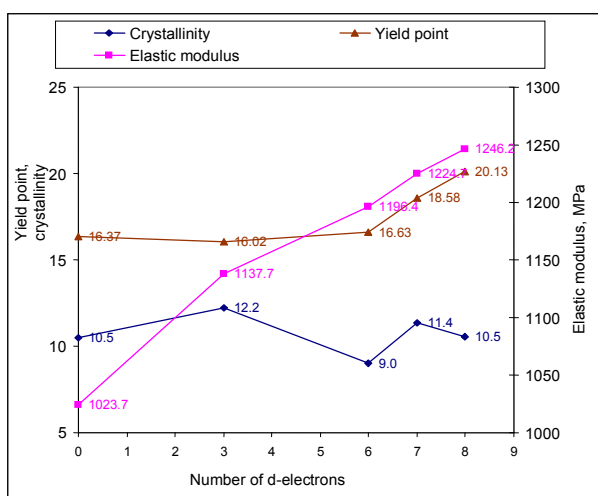


Fig. 1. UHMWPE-based material properties versus metal structure (d-electron quantity on 3d-sublevel) in the filler (Me→ESM): 0 – parent UHMWPE; 3 – Cr; 6 – Fe; 7 – Co; 8 – Ni. Crystallinity rates are: $A \times 10$

Reinforcement of the composites causes changes in the failure mode of the materials (Fig. 2).

The incorporated fillers favor more ductile failure of the composite material against brittle failure of the parent UHMWPE.



UHMWPE



UHMWPE +
(Cr → ESM)



UHMWPE +
(Fe → ESM)



UHMWPE +
(Co → ESM)



UHMWPE +
(Ni → ESM)

Fig. 2. Appearance of samples after compression testing

The initial period of failure is associated with crack development starting from an equilibrium state of the compressed region around cracks. The second period of failure – with crack development – starts from the state that developed after the loss of stability. In addition to stability loss, the parent UHMWPE samples contained cracks typical of brittle failure.

So, synthesized nanocomposites added to UHMWPE improve service characteristics of the materials, which is explained, first of all, by the filler composition and mechanism of making thermoplastic materials.

The study of hybrid fillers as fillers to phenylone showed that their introduction in a thermoplastic matrix allows the following: to increase thermal conduction by 14.7 to 20.8 %; elastic modulus by 12.3 %, and compression strength by 16.2 %; to decrease the friction coefficient 1.2 times [8]. The estimated efficiency of the fillers against electron structure the metal intercalated in the epoxysilicate matrix indicated that G-ESM increases the mechanical properties of the phe

nilone-based material; Co → ESM and Ni → ESM improve the triboengineering properties, while Fe → ESM and Co → ESM increase thermal stability. It was established that changes in the thermophysical properties of the materials correlates with the nucleus charge and atom's radius of the intercalated metal. The values of heat conduction examined over the test temperature range show that organosilica fillers raise heat conduction of base polymer by 14.7-20.8 %.

The efficiency of hybrid fillers grows with introduction of thermoexpanded graphite (TEG) in the composite; this is explained by synergistic effect that allows to vary widely the thermophysical, physicomechanical, as well as triboengineering properties of the material [9]. It was found that hybrid fillers are most efficient in increasing the performance characteristics of phenylone when used in combination with thermoexpanded graphite (Fig. 3).

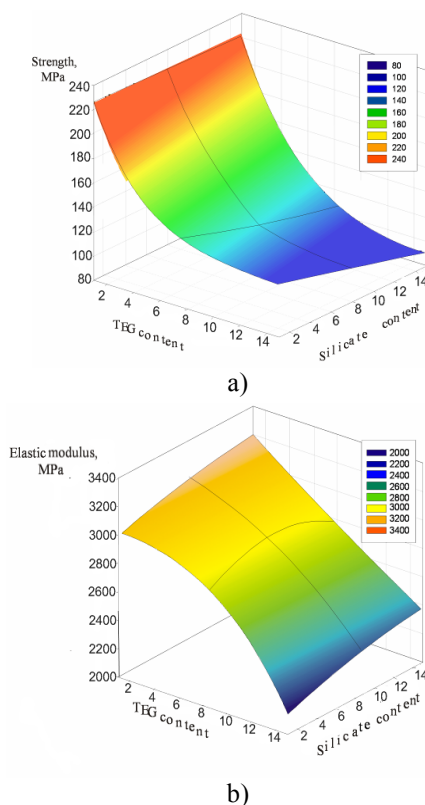


Fig. 3. Strength (a) and elastic modulus (b) dependence at compression versus composition of phenylone-based composite modified by TEG and (Co → ESM)

The analysis of operating conditions (pressure and sliding velocity) effect on triboengineering characteristics of the material (Fig. 4)

with an optimum filler (TEG/ (Co → ESM) = 1/1) concentration, that ensures a set of highest thermophysical and mechanical characteristics [7, 9] depicted in Figure 3, allows the following conclusion: wear and temperature in the contact zone vary proportionally; the friction coefficient vary inversely proportionally with pressure and sliding velocity; at similar PV-values, the contact temperature is lower at a higher velocity, i.e. when the friction contact time is shorter.

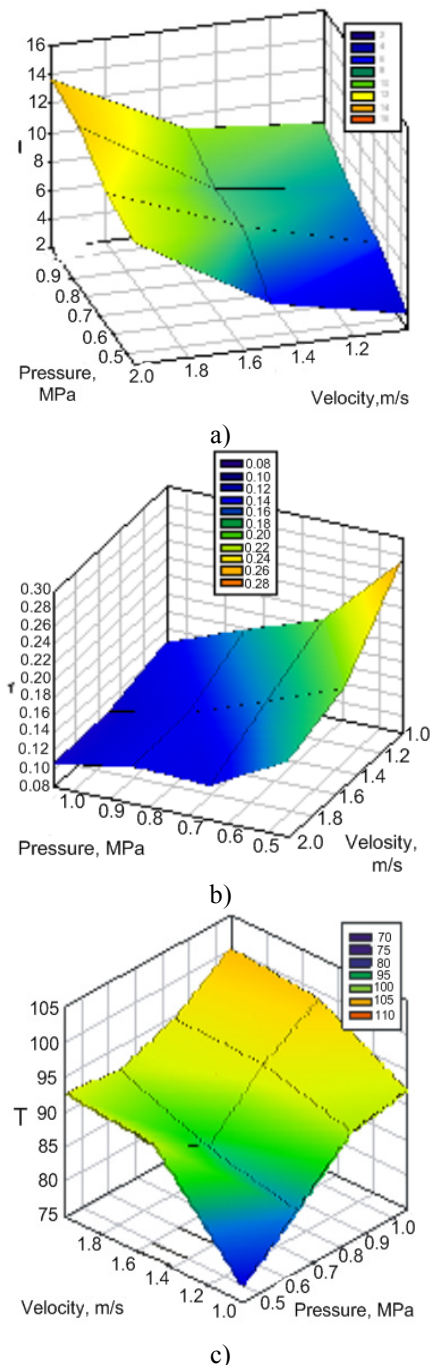


Fig. 4 – Linear wear rate (a), friction coefficient (b) and temperature (c) in the contact zone versus sliding velocity and pressure (steel 45, HRC 52,

$R_a = 0.17$) for phenylone-based composite with a hybrid filler ($TEG/(Co \rightarrow ESM) = 1/1$)

The surface of composition samples is glassy within the test load range, which is typical of fatigue wear. The results obtained showed that joint use of fillers causes mutual activation and synergistic effect that allows a wide variation in the thermophysical, physico-mechanical and triboengineering properties of the materials.

CONCLUSION

Thus, the held investigations showed that the structural organization and properties of metal-(epoxy)silicate nanocomposites is determined by the type of the intercalated transition metal which is introduced into the epoxy-silicate matrix and provides for the functional activity of the formed products that can be applied as functionally active fillers for thermoplastic polymers improving physico-mechanical properties.

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