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Study of the structure and rheological and mechanical properties of silicone rubber/montmorillonite nanocomposites

Summary — This work is dealing with preparation of nanocomposites based on silicone rubber *via: in situ* polymerization of octamethylcyclotetrasiloxane in the presence of nanofillers and *via* homogenization of silicone rubber α,ω -dihydroxypolydimethylsiloxane with nanofillers on three-roll mill. After the preparation, the rheological properties, especially viscosity of the mixtures, were measured and after curing the mechanical properties (tensile strength) were studied. The structure of nanocomposites was described using XRD, WAXS and TEM methods.

Key words: silicones, montmorillonite, nanocomposites, preparation, rheological properties, mechanical properties, structure.

BADANIE STRUKTURY ORAZ REOLOGICZNYCH I MECHANICZNYCH WŁAŚCIWOŚCI NANOKOMPOZYTÓW KAUCZUK SILIKONOWY/MONTMORYLONIT

Streszczenie — Przedstawiono ogólną charakterystykę i metody otrzymywania nanokompozytów polimer/krzemian warstwowy. Otrzymano szereg nanokompozytów typu polimer krzemooorganiczny/montmorylonit z matrycą polimerową stanowiącą bądź kauczuk silikonowy Lukopren N1000, bądź też polimer oktametylocyklotetrasiloksanu z montmorylonitem jako napełniaczem (wykorzystano 5 odmian handlowych montmorylonitowych). Nanokompozyty uzyskiwano w wyniku polimerizacji cyklicznego siloksanu w obecności napełniacza (metoda *in situ*) albo na drodze mechanicznego ujednolicenia w trójwałcowej mieszarce układów kauczuk silikonowy/montmorylonit. Zbadano wpływ sposobu syntezy nanokompozytu oraz rodzaju i zawartość napełniacza (3—10 phr) na właściwości reologiczne (tabela 1, 2, rys. 1) i mechaniczne przy rozciąganiu (tabela 3) produktów; metodami WAXS i TEM scharakteryzowano też ich strukturę (rys. 3).

Słowa kluczowe: polimery krzemooorganiczne, montmorylonit, nanokompozyty, otrzymywanie, właściwości reologiczne, właściwości mechaniczne, struktura.

POLYMER/LAYERED SILICATE NANOCOMPOSITES — GENERAL DESCRIPTION AND METHODS OF PREPARATION

Nanocomposites are a new class of materials, which differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase. The reinforcing material can be composed up of platelets (*e.g.* exfoliated clay particles), short fibers (*e.g.* carbon nanotubes), or long fibers (*e.g.* electrospun fibers) [1].

Recently, polymer/layered silicate (PLS) nanocomposites have attracted great interest, both in industry and in science, because they exhibit many advantages in comparison with traditional composites, namely increased modulus [2, 3] and strength [4, 5], decreased gas permeability [6, 7], better heat resistance [5] and decreased flammability [8, 9].

The layered silicates commonly used for the preparation of nanocomposites belong to the same general family of 2:1 layered or phyllosilicates. Their structures consist

of the layers built of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. The layer thickness is around 1 nm and the layers are bonded with van der Waals forces. Isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or Fe^{2+} or Mg^{2+} replaced by Li^+) generates negative charges that are counterbalanced by alkali or alkaline earth metals cations (Na^+ or K^+) situated inside the galleries [10]. The surface of these silicates is hydrophilic, therefore it must be changed to organophilic one to improve the miscibility with polymer matrix. Generally, this can be done by ion exchange reactions with cationic surfactants including primary, secondary, tertiary, or quaternary alkylammonium or alkylphosphonium cations, which makes intercalation of many engineering polymers possible [10].

Syntheses of PLS nanocomposites have typically involved either intercalation with a suitable monomer followed by *in situ* polymerization [11, 12], or intercalation in

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the solution [13, 14]. For some technological polymers, *in situ* polymerization and intercalation in the solution can not be used because neither a suitable monomer nor a compatible polymer-silicate solvent system are possible [15, 16]. Then the direct polymer melt intercalation occurs.

During *in situ* polymerization the layered silicate is swollen within the liquid monomer (or a monomer solution) and the polymer formation can occur between the plates of silicate [17].

When the intercalation with polymer in the solution occurs, the layered silicate is exfoliated into single layers using a solvent in which the polymer is soluble [17].

If the method of direct intercalation with polymer is applied, the layered silicate is mixed with the polymer matrix in the molten state at high shear stress so the polymer can go into the interlayer space [17].

Generally, different types of nanocomposites can be formed. In case that the polymer is unable to intercalate the silicate plates, a phase separated composite is obtained, with the similar properties as traditional microcomposites. In intercalated structure, polymer chains are placed among the silicate layers to form well ordered multilayer morphology where polymeric and inorganic layers are alternated. After the full dispersion of the silicate layers in a continuous polymer matrix, an exfoliated or delaminated structures are obtained [17].

This paper concerns nanocomposites based on silicone rubber prepared using five different types of layered silicates — montmorillonites. The preparation of the samples was carried out using two ways of preparation — polymerization *in situ* or homogenization of polymer with nanofiller. The rheological and mechanical properties of products were investigated and some analytical methods for description of the structures were applied.

EXPERIMENTAL

Materials

— Silicone rubber Lukopren N1000 [α,ω -dihydroxypoly(dimethylsiloxane), viscosity 2600 mPa·s];

— octamethylcyclotetrasiloxane (cyclic oligomer, melting point 17.5 °C, boiling point 175 °C, density 955.8 kg/m³);

— transferring agent of polymer chains [α,ω -dihydroxypoly(dimethylsiloxane), viscosity 50—100 mPa·s];

— thermolabile initiator TMAH (tetramethylammonium hydroxide, 33 % aqueous solution);

— C21 catalyst (solution of decaethoxytetrasiloxane/dibutyltindilaurate = 4/1 blend).

The supplier of all these materials: Lučebni Závody Kolin, Czech Republic.

Fillers based on montmorillonite

— Cloisite 15A [natural montmorillonite modified with quarternary ammonium salt (CH₃)₂(HT)₂N⁺, modi-

fier concentration 125 meq/100 g clay, producer: Southern Clay Products, Inc. USA];

— Cloisite 20A [natural montmorillonite modified with quarternary ammonium salt (CH₃)₂(HT)₂N⁺, modifier concentration 95 meq/100 g clay, producer: Southern Clay Products, Inc. USA];

— Cloisite 25A [natural montmorillonite modified with quarternary ammonium salt (CH₃)₂(HT)CH₂CH(C₂H₅)(C₄H₉)N⁺, modifier concentration 95 meq/100 g clay, producer: Southern Clay Products, Inc. USA];

— Dellite 72T [natural montmorillonite modified with quarternary ammonium salt (CH₃)₂T₂N⁺, modifier concentration not given, producer: Laviosa Chimica Mineraria S. p. A., Italy];

— Dellite 67G [natural montmorillonite modified with quarternary ammonium salt (CH₃)₂T₂N⁺, modifier concentration not given, producer: Laviosa Chimica Mineraria S. p. A., Italy];

(T = fatty acid — 65 % C18, 30 % C16 and 5 % C14, HT = hydrogenated fatty acid).

Preparation of uncured mixtures

The mixtures were prepared using two methods.

The first one was *in situ* polymerization of cyclic oligomer — octamethylcyclotetrasiloxane — in the presence of transferring agent, thermolabile initiator and one or two nanofillers based on montmorillonite in dosages of 3, 5 or 10 phr. The polymerization occurred in a bulk (250 ml) with stirring in oil bath at 100 °C for 2 hours; then thermolabile initiator TMAH was decomposed at 150 °C for 30 minutes.

The other type of nanocomposites was prepared classically — *via* homogenization of silicone rubber, *i.e.* α,ω -dihydroxypoly(dimethylsiloxane), with one or two nanofillers in dosages of 1, 2, 3, 4, 5 or 10 phr by mixing on an open three-roll mill which consisted of three rollers (23.5 cm across and 8 cm in diameter) rotating in opposite directions. For the preparation of nanocomposites in the presence of two nanofillers the ratio of them was 1:1.

Viscosity measurements

The apparent viscosity (η_a) dependent on shear rate (D) was measured immediately after mixture preparation at 30 ± 0.05 °C using a VT 550 Haake viscometer with the system of coaxial cylinders and again after 20 hours of maturing.

Vulcanization and mechanical properties measurement

The mixtures with known apparent viscosity were cured at room temperature during 24 hours, using C21 catalyst in amount of 4 phr. Test specimens for measure-

ments of mechanical properties were cut from cured plates (2 mm thick) with a sharp die in a shape of dumb-bell, and with the narrow section 10 mm. Tensile strength and elongation were measured according to ISO 37 using a tensile testing machine INSTRON 3365 (producer: INSTRON Ltd., Great Britain). The grips were power driven at 500 mm per minute.

Nanocomposite structure characterization

The structure of nanocomposites were measured by X-ray diffraction (XRD) using a diffractometer X'Pert PRO from the Netherlands company PANalytical [Cu K α radiation (1.5406 Å), 1° divergence slit, 0.2000 receiving slit, scan step time 0.3000 s, 25 °C].

Other method of the structure characterization was wide-angle X-ray scattering (WAXS). The measurements were carried out using a Japan instrument: Molecular Metrology SAXS/WAXS System of the company Rigaku, with BEDE Microsource® X-ray generator with Cu K α radiation ($\lambda = 1.542$ Å).

The nanocomposites structure were also examined by transmission electron microscopy (TEM). Ultrathin sections were prepared by ultramicrotome Leica UCT at -140 °C and images were taken using TEM microscope Tecnai G2 Twin 12 (FEI, Czech Republic) at 120 kV.

RESULTS AND DISCUSSION

Apparent viscosity

Mixtures with one nanofiller

The values of apparent viscosity of the mixtures containing one nanofiller differed, dependently on the method of preparation. The apparent viscosity of samples prepared *via* homogenization in *in situ* polymerization reached the values of the orders 10^4 — 10^5 mPa · s, that is about one order higher than for the compounds prepared *via* homogenization of Lukopren N1000 and nanofiller on three-roll mill (Table 1).

Table 1. Dependence of apparent viscosity (η_a) on shear rate (D) and on the method of preparation of mixtures of Lukopren N1000 containing 5 phr of Cloisite 25A

D , 1/s	<i>In situ</i>	Three-roll mill
	η_a , mPa · s	η_a , mPa · s
5	12 000	3600
10	11 200	3300
15	10 800	3200
20	10 700	3100
25	10 400	3100
30	10 300	3000
35	10 100	3000
40	10 000	3000

Mixtures prepared *via* homogenization of silicone rubber Lukopren N1000 and layered silicate on three-

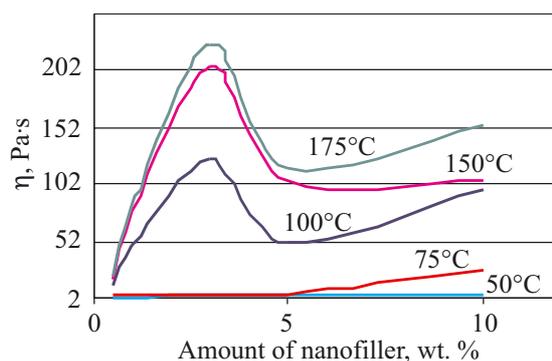


Fig. 1. Dependence of apparent viscosity on the concentration of nanofiller Cloisite 15A for different temperatures, at shear rate 5 s^{-1}

-roll mill were heated in a kiln for 8 hours at 50, 75, 100, 150 or 175 °C and η_a depended on shear rate was measured again. Fig. 1 illustrates a comparison of η_a at $D = 5 \text{ s}^{-1}$ for these various temperatures for the mixtures with different amounts of Cloisite 15A. The dependence shows maximum at 3 phr of nanofiller at 100 °C and higher temperatures. For the mixtures with 5 phr of nanofiller the curves show local minimum and the value of η_a increases with the increasing amount of nanofiller again, but linearly as for microcomposite. Apparent viscosity values measured at 30, 50 and 75 °C are of the same order (exception: the mixture with 10 phr of nanofiller heated at 75 °C for 8 hours — there is an increase of apparent viscosity about 1 order). Therefore it is possible to infer that up to 75 °C there is only a weak interaction, the filler behaves as non-active and the whole system as a microcomposite. But at 100 °C polymer and nanofiller interact intensively, viscosity increases swiftly as in *in situ* polymerization.

Such effect of increasing apparent viscosity about one order at temperature 100 °C and higher became evident only in case of the mixtures of Lukopren N1000 with Cloisite 15A. In an other mixtures the apparent viscosity increased linearly only a little, in the same order (Table 2).

Table 2. Dependence of apparent viscosity (η_a) on type and amount nanofiller of in the prepared *via* homogenization mixtures with Lukopren N1000 heated at 100 °C, at shear rate 5 s^{-1}

Filler	Apparent viscosity, mPa · s					
	Kind ^{*)}	15A	20A	25A	67G	72T
Content, phr		η_a , mPa · s				
1		7100	3100	2800	2200	2200
2		69 000	9600	2800	2900	2500
3		12 4000	3200	2900	2800	2500
4		74 000	3100	2900	3200	2500
5		49 000	3300	3600	3100	2800
10		95 000	4900	4000	3600	3200

^{*)} Symbol — see text.

Mixtures with two nanofillers

The values of η_a of the blends prepared *via in situ* polymerization of octamethyltetrasiloxane or by homo-

genization of silicone rubber Lukopren N1000 containing the combination of two nanofillers in the ratio 1:1 at three-roll mill were also measured. The mixtures with different values of viscosity were formed, dependently on the method of preparation. Namely, the apparent viscosity of the mixtures prepared *via in situ* polymerization reached the order 10^4 – 10^5 mPa · s, that is about 1 order higher than in case of the compounds prepared *via* homogenization of Lukopren N1000 and two nanofillers at three-roll mill. These results are similar to those obtained for the mixtures containing only one nanofiller, therefore it can be said that the effect of synergism of two nanofillers was not evident.

Mechanical properties

An attention was paid mainly to tensile strength of vulcanizates and their elongation at break. The values of tensile strength depended on the kind and content of fillers and on the method of mixtures' preparation. In the case of polymerization of octamethylcyclotetrasiloxane in the presence of one or two nanofillers, tensile strength showed higher values than for compounds prepared *via* homogenization at three-roll mill (see Table 3 for one nanofiller). As in the case of dependence of apparent viscosity, the effect of synergism of nanofillers was not evident.

Table 3. Tensile strength of mixtures of Lukopren N1000 with different fillers prepared *in situ* or at 3-roll mill (N = mixture was not prepared)

Kind ^{*)}	Content, phr	Tensile strength (MPa) and method of preparation					
		<i>In situ</i>			3-roll mill		
		3	5	10	3	5	10
15A		0.38	0.56	N	0.46	0.41	N
20A		0.54	0.62	0.71	0.32	0.33	0.5
25A		0.77	0.73	1.04	0.36	0.46	0.6
67G		0.65	0.81	0.98	0.38	0.42	0.59
72T		0.41	0.9	1.39	0.45	0.46	0.47
Lukopren N1000		0.3					

^{*)} Symbol — see text.

The mixtures prepared *via* homogenization of silicone rubber Lukopren N1000 and nanofiller were adjusted by the heating at 100 °C for 8 hours and after this time the mechanical properties were measured again. The values of tensile strength and elongation, kept the same level, so the heating at higher temperature did not influence them.

Structure

Prepared nanocomposites structure was described using XRD, WAXS and TEM methods. In Figure 2 which

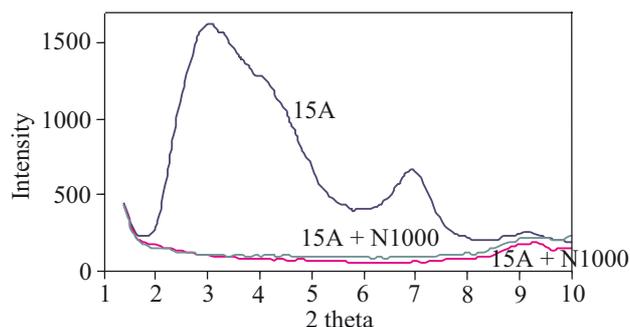


Fig. 2. WAXS spectra of montmorillonite Cloisite 15A and its mixture (5 phr) with silicone rubber Lukopren N1000 (at room temperature and at 100 °C)



Fig. 3. TEM image of the mixture of silicone rubber Lukopren N1000 + Cloisite 15A (5 phr)

illustrates the WAXS spectra, the Cloisite 15A and its mixture with silicone rubber Lukopren N1000 peaks corresponding to the layer spacing are visible. After the preparation of mixture and heating it, the peaks are more present because the layers were delayed on spacing, which could not be shown by these methods. In TEM image of this mixture the single plates of montmorillonite can be observed, but the filler still forms agglomerates (Fig. 3) — only partial exfoliation occurs.

CONCLUSION

The composites based on silicone rubber and different layered silicates were prepared either *via in situ* polymerization of octamethylcyclotetrasiloxane in the presence of montmorillonites or *via* homogenization of silicone rubber Lukopren N1000 with these fillers at three-roll mill. It was stated that apparent viscosity of the samples prepared *via* polymerization reached the values of the order 10^4 – 10^5 mPa · s, that is about 1 order higher than in the case of composites prepared *via* the latter method. The effect of synergism between two used fillers was not observed.

The viscosity of mixtures prepared *via* homogenization increased after heating at 100 °C and higher of about one order, but only in the case of Cloisite 15A as a filler, reaching η_a values as for the blends prepared *via in situ* polymerization of octamethylcyclotetrasiloxane, which occurred at 100 °C.

The structures of composites formed were determined using XRD, WAXS and TEM methods that showed partial exfoliation of nanofiller.

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