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A Thermoplastic Rubber Composition for Medical Purposes

Oleg Olegovich Nikolaev¹, Vladislav Borisovich Urhanov¹, Vladislav Pavlovich Britov¹, Alexander Dmitrievich Babaev¹, Valeri Vladimirovich Bogdanov^{1(*)} and Hamid Mirzadeh²

(1) Saint-Petersburg State Institute of Technology, Saint-Petersburg, Russia

(2) Department of Polymeric Biomaterials, Iran Polymer Institute, Tehran, I.R. Iran

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ABSTRACT

The rheology, vulcanizational, and the physico-mechanical properties of a composition of siloxane rubber and ultra-high molecular weight polyethylene are discussed. It is shown that such materials combine elasticity and strength. Inclusions of ultra-high molecular weight polyethylene in siloxane matrix, with large-sized globular structure, imparts material a good impact resistance property. Compositions developed may be used as polymer inserts for new generation of endoprosthetic appliances for hip joints.

Key Words: siloxane-UHMWPE composite, rheological properties, vulcanization features, endoprosthetic appliances

INTRODUCTION

Development of artificial organs and different means for implanting is now one of the most urgent and rapidly developing branches of medicine. Therefore, a special place belongs to siloxane elastomers, which are physiologically inert, hydrophobic and have relatively good hemo- and tissue compatibility. The main advantage of siloxane elastomers compared to other highly inert implanted materials is in their consistency, which is nearly equal to the one of surrounding tissues [1–3]. High elasticity and chemical and thermal resistance are important as well, while the siloxane elastic materials are known to have low strength.

Among extensive investigations in this field the following may be mentioned: introduction of resins containing SiO₂ units into the silicones; development of block-copolymer compositions containing polycarbonate polysiloxane blocks; obtaining graft copolymer of polydimethylsiloxane with unsaturated monomer possessing high impact strength, light resistance, colour stability and lusting surface, etc. In this connection, mixtures of polyorganosiloxanes with UHMW polyethylene are of great interest. Such mixtures combine high elasticity with strength and they may be used for production of medical articles [4–7]. Both components are, however usual materials for medical purposes.

This investigation is aimed to find the main technological and physico-mechanical properties of the compositions developed.

EXPERIMENTAL

Materials

For the main purpose of the investigation the

following compounds were selected:

Siloxane rubber of CKTB-1111 grade (Russia); ultrahigh molecular weight polyethylene (UHMPE) with molecular mass M=2,000,000 (Russia) and M=5,600,000 ("GUR" Germany).

Colloid silicilic acid of A-175 grade (Russia) was used as filler for rubbers.

Silicon Composition

Siloxane rubber of CKTB-11II grade: 1000 (by mass). -Colloid silicilic acid of A-175 grade: 200 (by mass). -Silanediol: 80 (by mass).

--Benzoyl peroxide 40%+ silicone oil 60%: 12 (by mass).

Components: Siloxane composition (by mass) + ultrahigh molecular weight polyethylene (UHMPE); by mass %.

Equipment

Mixing was carried out by laboratory rolls L×B= 315×160, V=15 m/min, and h=1 mm.

Viscosity was measured by a viscosimeter Rheotest 1000, a capillary method.

Elastic-strength features were studied by a universal test instrument Zwick 1445 with microprocessor.

Hardness tests were held according to ASTM D 2240, Shore method scale A.

Electron microscopy was performed by a Zeica Cambridge S-360 scanning electronic microscope.

Preparation of Composition

Before vulcanization polysiloxane composition was prepared, and then the powder PE imported into it. After the mixing the composition was vulcanized.

Test samples were prepared by laboratory rolls with friction f=1.27 and temperature 20-50 °C.

Vulcanization of polysiloxane composition was performed in presence of benzoyl peroxide.

At the first stage of vulcanization the temperature was at 170 °C, the time taken was 10 min at the pressure of 10 MPa. The second stage involved the heat treatment with temperature of 175 °C; the time taken was 2 h at the pressure of 10 MPa.

Test samples were produced by pressing at

temperature 170 °C for 10 min followed by heat treatment at 175 °C for 2 h.

RESULTS AND DISCUSSION

Composition Features

Rheological tests of the produced mixtures are shown in Figure 1.

Behaviour of composition with polyethylene content from 0 to 60% at 170 °C fully corresponds to the following rheological model

$$\eta = (\mathbf{A} \cdot \mathbf{x} + \mathbf{B}) \cdot \dot{\gamma}^{\mathbf{k}} \tag{1}$$

where: η : viscosity, Pa·s; γ : shear rate, s⁻¹; A, B: coefficients, Pa·s^{k+1}; x: mass part of polyethylene; $k\approx$ -0.71.



 $-\diamond - 0; -\Box - 5; -\Delta - 15; -x - 30; -* - 45; -O - 55; -* - 70; -* - 100.$ Figure 1. Dependence of viscosity (a) shear stress (b) shear rate for composition of polysiloxane and UHMWPE at 170 °C. Numbers for curves in the footnote show UHMWPE concentration in mass percentage/.

When matrix viscosity, η_M (in this case polysiloxane part of composition is a matrix) is described as:

The equation may be written as:

$$\frac{\eta}{\eta_{M}} = 1 + \frac{A}{B} \cdot \mathbf{x}$$

The last equation is similar in form to the equation developed by Einstein for hard particles, which are small compared to the vessel size and large compared to the liquid molecules. However A/B ratio is in the range of 0.6–0.7 which is 2–3 times lower than that in Einstein equation. This fact may be explained by polyethylene particles plasticity at vulcanization temperatures.

For compositions containing over 60% (mass) of polyethylene a sudden transition from shift flow to wall sliding (plug flow) is observed. It is caused by the inversion of composition phases with the range of 60-70 mass %, which as a consequence causes changes in mode of flow.

Ultra-high molecular weight polyethylenes are known, however, of not having their shift flow independent from the molar mass.

Vulcanizing Features

Qualitative trend of vulcanizing curves of individual polymers and their mixtures is shown in Figure 2.

The sum of the curves shows the trend of dependence, which can be anticipated for the polymers under investigation.

The minimum value of torque on this curve corresponds to the time when melt viscosity becomes equal to the viscosity of polysiloxane.

Insignificant maximum is noticed before the curve becomes flat which corresponds to the time when vulcanization process is practically completed.

The particular form of the dependence for polysiloxane-polyethylene mixtures would depend on the component ratio.

Thermomechanical curves of polysiloxane-



Figure 2. Vulcanizing curves of individual polymers and their mixtures: (1) polysiloxane, (2) UHMWPE and (3) polymer mixtures.

polyethylene mixtures in wide range of component ratios are shown in Figure 3. It can be observed that the mixture viscosity increases significantly along with polyethylene content.

Decreasing of the torque after maximum is achieved and it is explained by the fact that polyethylene melting in mixtures may continue even after polysiloxane vulcanization is almost completed.



Figure 3. Thermomechanical curves of mixtures of UHMWPE and polysiloxane with different component ratios: (1) 20:80, (2) 50:50, (3) 60:40, (4) 70:30 and (5) initial polyethylene.

Feature	UHMPE content (by mass%)						
	10	20	30	40	50	60	70
M⊾ (N.m)	0.09	0.12	0.17	0.31	0.78	0.92	1.17
M ₉₀ (N.m)	0.78	1.02	1.33	1.96	2.68	3.21	3.90
M _{HR} (N.m)	0.80	1.01	1.32	1.67	2.18	2.57	3.12
t _s (min)	0.96	0.73	0.55	0.39	0.26	0,19	0.17
t _{c(90)} (min)	1.13	1.10	1.09	1.06	1.03	0.92	0.81

Table 1. Vulcanzing features of midures of UHMWPE and polysiloxane.

Note: M_- minimum twisting moment characterizing meological properties (viscosity) of non-vulcanized material; Mear-maximum twisting moment characterizing the

elasticity of the vulcanizate t_e- time of commencing vulcanization, t_{ereor} optimal time of vulcanization, when M=Mao, Mao=MeR+0.9 (MeR+ML).

Numerical values of vulcanizing features of mixtures are shown in Table 1.

Composition and Structure Analysis

According to the results of electronic and optical microscopy tests it was established that the composition has macro-heterogenous structure.

In Figure 4, a micrograph of surface composition with magnification ×150 is shown. Polyethylene particles dimensions of about 5 to 7.10^{-2} mm (GUR, Germany) and $1-2\times10^{-2}$ mm (Russia), do not differ significantly from the grains of initial polyethylene.

At the same time the boundary layer at its surface is well developed. It gives evidence that shear stress during composition prepared is enough to "unroll" the polysiloxane molecules at the ultra-high molecular weight polyethylene surface but does not overcome the values leading to its dispersion.



Figure 4. Microstructure of polyethylene-polysiloxane composition of the ratio 50/50.

The Effect of Size and Particles Distributionn

As it was expected, reinforcing effect is noticed when particles dispersity increases, although it is not significant. When particle size decreases to half, the strength features increases insignificantly at the most interesting ranges of component ratio.

Elastic-strength Features

Dependence of strength and relative elongation versus polyethylene content are shown Figure 5. As it was expected, tension strength depends on the filling content and polyethylene type. For samples with polyethylene base, having more developed surface strength along with higher polyethylene content is being relatively dependent on additive character.

Simultaneously an abrupt drop of relative elongation occurs, which is practically independent from polyethylene type.



-A~ UHMPE (Russia); - X- UHMPE (GUR)

Figure 5. Dependence of tension strength and relative elongation for polyethylene-polysiloxane compositions v. polyethylene content. WWW.SID.U'



Figure 6. Dependence of Shore hardness (A) of compositions v. filling content.

Hardness

Dependencies of Shore hardness versus polyethylene content are shown in Figure 5. It is seen that samples hardness grows along with polyethylene content.

Comparison of polysiloxane mixture with an abrasive filler (quartz) and mixture with polyethylene base makes it possible to see more intensive growth of samples hardness at the polyethylene content range some 20–60 % (mass). This fact may be explained by formation of interpenetrating three-dimensional



Figure 7. Endoprosthetic appliance for hip joint: (1) hip joint parts, (2) insert from polymeric material.

networks of polyethylene and polysiloxane.

Hardness of the samples depends significantly on the size and form of polyethylene particles. The larger specific surface of polyethylene particle gives higher increase of hardness.

Thus mixtures of polyorganosiloxanes with UHMWPE combine high resiliency and strength. As the compositions are described by the large value of destructive work at tension and considering that ultrahigh molecular weight polyethylene inclusions have large-sized globular structure, therefore, these classes of materials possess good impact resistance.

The following possible areas of using of such materials for medical purposes may be discussed.

For example when hip joint prosthetics are produced, the inserts of bioinert and insulating materials are used (Figure 7).

Formerly medical grades of high-density polyethylene were used for these purposes. However, the working life of such articles counts 10–15 years and complicated surgical operation is needed for substitution. Development of friction pairs with the longer working life with polyamide and fluoride base plastics has failed.

Nowadays, ultra-high molecular weight polyethylene is used for these purposes making articles of working life nearly equal to human life.

However, this material is highly rigid making it inconvenient at work. Using of polyethylene-polysiloxane composition opens the possibility to develop new generation of endoprosthetic appliances.

CONCLUSION

New polymeric composite material with polysiloxane base and ultra-high molecular weight polyethylene is developed.

Rheological and vulcanization behaviour of composition with a wide range of component concentrations is investigated.

Elastic-strength and hardness properties of vulcanizates are studied.

Possible fields of applying the composites for development are proposed as well.

REFERENCES hive of SID

- Mirzadeh H. and Khorasani M.T., Polydimethylsiloxane surface modification by laser irradiation, a novel technique for the preparation of blood compatible materials, in "Surface Modification Technology X", The Institute of Material, London, T.S. Sundrashan (Ed.), p 499-507, 1997.
- Mirzadeh H., Khorasani M.T. and Sammes P., "Laser surface modification of polymers: a novel technique for the preparation of blood compatible materials-(ii) in vitro assay", *Iran. Polym. J.*, 7, 1, 5-13, 1998.
- Fallahi D., Mirzadeh H., Khorasani M.T. and Mehrabzadeh M., "Biocompatibility evaluation of hydrophobic silicone rubbers", Proceedings of Iran. 5th Sem. on Polym. Sci. & Technol., 335– 342, 12–14 September 2000.
- 4. Ugelevsky U.A. et al., Rubber, 4, 6-8, 1984.
- Andreiva I.N. et al., High-density super high molecular polyethylene, Leningrad: Chemistry, 80, 1982.
- 6. Biomedical Polymers, Plastverarbeiter, 46, 2, 110, 1995.
- Zulkaneev R.A., Aulkaneev R.R., Artificial materials and their influence on repair of skeleton bone structure defects (Review), Plastic, masses, 5, 51-53, 1995.

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