

Properties of Polyphenylsilsesquioxane-Polydimethylsiloxane Block Copolymer and Its Filled Vulcanizates

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Abstract

The aim of this work was to obtain the siloxane-polyphenylsilsesquioxane block copolymer and its vulcanizate by standard methods. Polyphenylsilsesquioxane-polydimethylsiloxane block copolymer was obtained by hydrolytic polycondensation of polydimethylsiloxane with phenyltrichlorosilane, followed by condensation of the hydrolyzate. It represents a material with uniform distribution of the silicon organic and inorganic phases at the molecular level, filled by non-condensed polyphenylsilsesquioxanes. A high temperature resistance of new block copolymer was shown by thermogravimetric analysis. The experimental test on mechanical properties such as tensile strength, elongation at break, hardness and compression set carried out on the vulcanizates of new rubber produced showed an increase in the tensile strength, elongation, hardness and heat resistance.

Keywords

Polyphenylsilsesquioxane-Polydimethylsiloxane Block Copolymer, Hydrolytic Polycondensation, Filled Vulcanizate, Heat Resistance

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1. Introduction

Organic-inorganic hybrid materials have been opening a new field of materials science because of a wide range of possible applications. Among a variety of organic-inorganic hybrid materials, hybrid materials based on a siloxane network are very attractive due to the robust nature of the siloxane bond [1] and thus are studied intensively.

From the viewpoints of synthetic approach and the resulting materials structure, the siloxane-based hybrid materials can be divided into two classes. Class I corresponds to nanocomposite materials, which are synthesized by an inorganic hydrolytic polycondensation (sol-gel reaction) of tetraalkoxysilane monomer in the presence of low molecular weight organic compounds as dopants. In this class of hybrid materials, the organic dopants are just embedded in the

inorganic matrix and are likely to be isolated due to phase separation.

Class II corresponds to nanostructured hybrid materials prepared from a sol-gel reaction of trialkoxysilane-based precursor monomers having organic substituents in the molecular chains. The resulting network polymers are called polysilsesquioxanes (PSSQ), where the organic substituents bound covalently to the siloxane network are fixed strongly and homogeneously in the polymer bulk. For example, when the sol-gel reaction occurs on the surface of glass, terminal silanol groups of PSSQ react with hydroxy groups of the surface, so that the organic functional groups can be fixed on the substrates through the siloxane network in PSSQ. PSSQ have been used as novel high-performance materials such as water-repellent agents for automobiles, catalyst supports, adsorbents, optics, and biosensors.

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As well known, PSSQ is a product of hydrolytic polycondensation of alkyltrichlorosilane with the empirical formula $[RSiO_{1.5}]$ [2, 3]. PSSQ are incompletely condensed T-resins of irregular, ladder and cage structures with high level of hydroxy-groups [4]. PSSQ are intermediate between SiO_2 and (R_2SiO) since silicon is bonded with three oxygen atoms and hydrocarbon substituent (e.g., phenyl, cyclopentyl, can contain the various functional groups as side-chains) promoting the compatibility of the filler and the polymer matrix in the filled material. PSSQ, referred to as T_n , have been the focus of considerable experimental and theoretical interest because of their wide variety of practical uses for many years. Among a huge number of investigations for these diverse polyhedral compounds, the approach to make use of their cavity for various purposes, such as a container of atomic or molecular species, medical supplies, molecular sieves, or a reaction filed for H_2 formation, is one of the extremely attractive research areas of the PSSQ chemistry. In addition to many interesting experimental observations, theoretical studies have been making considerable contributions in this area. For example, there are systematic and comprehensive studies for the encapsulation of various atomic or ionic species into T_8 and T_{10} .

In particular, much interest has been paid to cubic T_8 silsesquioxane $(R-SiO_{1.5})_8$, consisting of a rigid, crystalline silica-like core that is perfectly defined spatially (0.5–0.7 nm) and that can be linked covalently to eight R groups, because of their possible applications in optics, electronics, engineering, and biosciences [5]. PSSQ have attracted much attention in the research fields of organic-inorganic hybrid materials for academic and application reasons, exhibiting superior thermal, mechanical, and chemical stabilities derived from siloxane (Si–O–Si) bond frameworks with high bond energy compared with C–C bonds [6]. These studies must give useful information for the future design of the molecular sieve or better drug delivery.

The silsesquioxane family is now recognized to have an enormous potential as a building block for various advanced materials, and their applications can be found in the areas of catalysis, coordination chemistry, and material science. PSSQ is useful as a framework in organic - inorganic polymer hybrid material because of its high heat resistivity, high mechanical properties, and easy introduction of functional groups in the side chain [7 - 9].

We wonder that in the world a little research is deal with silsesquioxane - polysiloxane polymer composites [10]. A lot of investigations are devoted to the synthesis of polyhydrocarbon-, polyepoxy-, polythiophene-[1], polyketone [1, 11, 12], fluorine-containing polymers [13] or phosphor-containing polymer [1, 14] with PSSQ as a hard block.

Currently it is known a polyphenylsilsesquioxane-polydimethylsiloxane block copolymer brand Lestosyl obtained by a homofunctional polycondensation polydimethylsiloxane with a chain length of 200 ± 20 units and phenyltrichlorosilane. This polymer consists of "hard" block - polyphenylsilsesquioxane (PSSQ) and "flexible" polydimethylsiloxane block [15].

Lestosyl used as a solution for filled and unfilled protective and anti-adhesive elastic hydrophobic non-toxic coatings for a variety of structures, pipes, devices and components stably working in a wide temperature range from - 60 to + 250°C. Lestosyl is a solid amorphous crumb, it's impossible to mill it.

It was shown that this block copolymer consists of two fractions by fractional analysis [16]. Macromolecular fractions part (40%) has a wide distribution of molecular weight $M_n = 1,0 \div 7,0 \cdot 10^4$ and consists of branched polyfunctional macromolecule, wherein the hard blocks are randomly connected by flexible siloxane chains. The second part of the fraction (60%) is a low molecular weight block polyphenylsilsesquioxanes (PSSQ) with high level hydroxy-groups.

Consequently, this polymer can be considered as a nanocomposite in which polyphenylsilsesquioxane-polydimethylsiloxane block copolymer highly filled by "full condensed" polyhedral silsesquioxanes and "incompletely condensed" T-resin. Properties and reproducibility of the properties of these materials are very dependent on the nature of the interaction between the phases, phase compatibility / incompatibility and structure of interfacial areas.

One of the promising directions in materials science of recent years is the creation of polymer nanocomposites, in which inorganic and organic components are combined in one molecule in such a way that the hard segments in principle can't form a separate phase. It is expected that, compared with traditional, in these composite materials internal defects will not appear in the hard reinforcing elements, and this will provide a significant improvement in mechanical and thermal properties of composites.

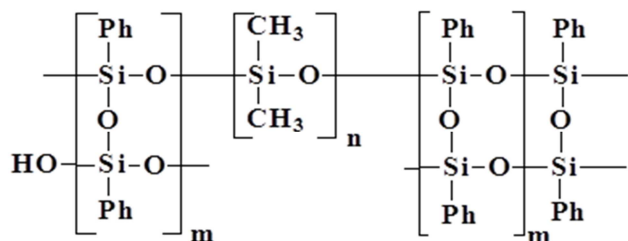
One of problems in creating composites is phase separation of the components. There are several ways to suppress the phase separation, but the most promising of which is the synthesis of polymers in which the rigid and flexible segments are chemically linked. Such materials are called molecular composites [5].

2. Research Significance

The aim of this work is the synthesis of siloxane block copolymers suitable for the vulcanization by standard

methods for silicone rubber and studies the properties of the filled vulcanizate.

To create a rubber to mill it was obtained polyphenylsilsesquioxane-polydimethylsiloxane block copolymer of the general formula:



As we said above there is a widespread method for producing organic-inorganic composites by creating terminal trifunctional triethoxysiloxy-units in that the organic polymer, followed by the sol-gel polymerization in the presence of tetraethoxysilane. In our case this method is unacceptable because of uncontrolled formation of filler in the polymer matrix during the sol-gel polymerization. This method is applicable to the production of gels in general, but for elastomers, curable by conventional methods, it is impossible.

The said block copolymer is prepared in two steps:

1. a silylation of polydimethylsiloxane with a chain length of 300 units by phenyltrichlorosilane in an organic solvent in the presence of an amine compound, α, ω - bis-(dichlorophenylsilyl) polydimethylsiloxane is obtained,
2. a hydrolytic polycondensation α, ω - bis-(dichlorophenylsilyl) polydimethylsiloxane and phenyltrichlorosilane in an organic solvent in the presence of an amine compound, a subsequent condensation of the resulting hydrolyzate and isolating the desired product.

It was shown by fractional analysis that new block copolymer consists of two fractions. Macromolecular fractions part (60%) has a narrow distribution of molecular weight $M_n = 4,0 \div 7,0 \cdot 10^4$ and consists of polyphenylsilsesquioxane-polydimethylsiloxane macromolecule. The second part of the fraction (40%) is a low molecular weight block PSSQ with high level hydroxy- groups.

The formation of a substantially larger proportion of high molecular weight fractions takes place most likely due to (dichlorophenylsilyl) siloxy- groups which allow to zoom its reactivity in the reactions of a hydrolytic polycondensation to phenyltrichlorosilane's reactivity and, thereby, to provide chemical bonding flexible and rigid blocks.

Thus, both the produced block copolymer can be considered as nanocomposite materials, in which polyphenylsilsesquioxane-polydimethylsiloxane is filled by incompletely condensed

PSSQ directly in the synthesis process. In different block-copolymers the proportions of filling are different.

We have studied the temperature resistance of the obtained polymer by TGA (thermogravimetric analysis) in an inert atmosphere (GTA-6000 «Perkin Elmer», heating range of 40 to 600°C at a speed of 10°C / min).

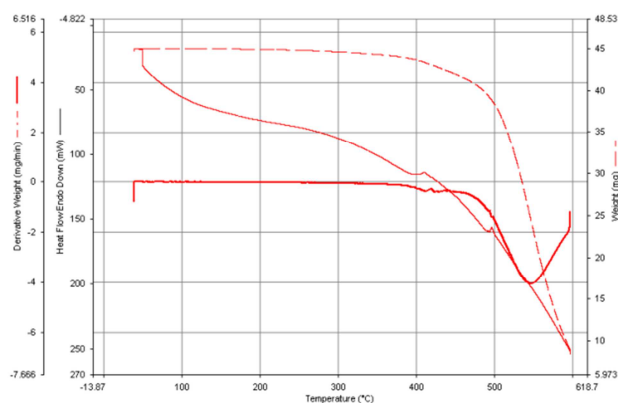


Fig. 1. Thermogravimetric differential thermal analysis of new polyphenylsilsesquioxane-polydimethylsiloxane.

The data obtained are presented in Table 1 compared with the data on Lestosyl, polydimethylsiloxane (PDMS) and polydimethylmethylphenylsiloxane (PDMPHS-50).

Table 1. Thermostability.

Block copolymer	τ_0	τ_5	τ_{10}	τ_{20}	τ_{30}	τ_{40}	τ_{50}
A new polyphenylsilsesquioxane-polydimethylsiloxane block copolymer	407	426	485	495	525	550	585
Lestosyl	400	428	479	505	520	530	551
PDMS	300	390	420	430	440	440	450
PDMPHS-50	353	365	384	412	430	440	450

τ - a temperature at which to start weight loss (τ_0) or reaches a certain magnitude of these losses: 10% (τ_{10}), 20% (τ_{20}) etc.,

Lestosyl SM – a well-known polyphenylsilsesquioxane-polydimethylsiloxane block copolymer,

PDMS – polydimethylsiloxane,

PDMPHS-50 – polydimethylmethylphenylsiloxane containing 50% (mol.) methylphenylsiloxy- units.

Comparative analysis of this data shows that the heat-resistant of new block copolymer is not inferior to Lestosyl, and the both of block copolymers are much superior linear siloxanes: polydimethylsiloxane and polydimethylmethylphenylsiloxane.

The glass transition temperature of the test sample was determined by the DSC 8500 (differential scanning calorimetry). The sample weight is of 12-20 mg, heating rate of 10°C / min, the minimum cooling temperature is -80°C. In the temperature range from -75 to 0°C a glass transition of new block copolymer could not fixed, which gives reason to

assume that its glass transition is below.

On the basis of these both block copolymers were prepared non-filled films whose properties are shown in table 2.

Table 2. Physical and mechanical properties of films.

Block copolymer	D/T	the flexible block's length	f_p	δ
Lestosyl	2,1	180 - 240	10,0	130
Lestosyl	3,3	80 - 120	4,0 - 6,0	250
A new block copolymer	4,0	300	4,0	500

D/T - the ratio of D- and T- links, *the flexible block's length* – number of D-units in polydimethylsiloxane block,

f_p - tensile strength, MPa,

δ - elongation at break, %.

The data show that the growth of the flexible block's length (300 units D-) leads to an increase an elasticity of the film and a share growth of the trifunctional units' part (T- units) leads to increased strength.

A filled vulcanizates were obtained on the basis of the new block copolymer by standard methods.

Obviously, the ability to mill is associated with the greater elasticity of the material due to the greater length of the rigid block than in Lestosyl.

Physical and mechanical properties of this vulcanizates are shown in Table 2. As we said above to get a Lestosyl' vulcanizates was not possible.

Table 3. Physical and mechanical properties of vulcanizates of new polyphenylsilsesquioxane-polydimethylsiloxane block copolymer.

Indicator	Value
f_p	4,3 - 4,7
δ	130 - 170
Shore A Hardness	61-66
K_b A coefficient of recoverability at -60°C	0,6
C_B	49
f_p (after 300°C, 336 h)	4,0 - 4,2
δ (after 300°C, 336 h)	80 - 100
f_p (after 350°C, 24 h)	4,1 - 4,3
δ (after 350°C, 24 h)	70 - 90
f_p (after 350°C, 72 h)	4,2 - 4,4
δ (after 350°C, 72 h)	20 - 30

f_p - tensile strength, MPa,

δ - elongation at break, %,

C_B – compression set (250°C / 24 h.), 20% compression, %,

K_b - coefficient of recoverability at -60°C.

The data show that the vulcanizates of a new block copolymer has good physical and mechanical properties and high heat resistance.

3. Conclusion

We've succeed in synthesis of new polyphenylsilsesquioxane-

polydimethylsiloxane block copolymer. Investigations by various methods have shown its high temperature resistance and low glass temperature. Films from this block copolymer demonstrate high tensile strength and elasticity. Rubbers have high physical and mechanical properties and heat resistance.

Thus, the new polyphenylsilsesquioxane-polydimethylsiloxane block copolymer has got a processability in comparison with its predecessor - Lestosyl while maintaining high heat resistance.

References

- [1] Ichiro Imae, Shotaro Takayama, Daisuke Tokita, Yousuke Ooyama, Kenji Komaguchi, Joji Ohshita, Yutaka Harima "Synthesis of a Novel Family of Polysilsesquioxanes Having Oligothiophenes with Well-Defined Structures", International Journal of Polymer Science V. 2012, Article ID 484523, 10 page.
- [2] H. Endo, N. Takeda, M. Unno "Synthesis and Properties of Phenylsilsesquioxanes with Ladder and Double-Decker Structures", Organometallics, 33 (15), 4148–4151.
- [3] G. Kickelbick "Silsesquioxanes", Functional Molecular Silicon Compounds I, 155, 1-28 (2013).
- [4] R. Duchateau "Incompletely Condensed Silsesquioxanes: Versatile Tools in Developing Silica-Supported Olefin Polymerization Catalysts", Chem. Rev., 102, 3525.
- [5] H. Baney, M. Itoh, A. Sakakibara, T. Suzuki "Silsesquioxanes", Chem. Rev., 95, 1409.
- [6] D. Chen, Y. Liu, C. Huang "Synergetic effect between POSS and fumed silica on thermal stabilities and mechanical properties", Polymer degradation and stability, 97, 308.
- [7] D. Gnanasekaran, K. Madhavan, B.S. Reddy "Developments of polyhedral oligomeric silsesquioxanes (POSS), POSS nanocomposites and their applications", J. Scientific & Industrial Research, 68, 437.
- [8] K. Pielichowski, J. Njuguna, B. Janowski, J. Pielichowski "Polyhedral oligomeric silsesquioxanes (POSS)-containing nanohybrid polymers", Adv. Polym. Sci., 225, 201 (2006).
- [9] A. Lou Douglas and J.S. Kennet, "Bridged polysilsesquioxanes. Highly Porous hybrid organic-inorganic materials", Chem. Rev., 95 (5), 1431.
- [10] M. Handke, B. Handke, A. Kowalewska, W. Jastrzebski New polysiloxane materials of ladder-like structure, J. Mol. Structure, 254 (2009).
- [11] X. Li, Y. Song, M. Zhu, B. Liu, and Z. Jiang, "Preparation and properties of the POSS-containing composites as proton exchange membranes," Gaodeng Xuexiao Huaxue Xuebao, vol.32, № 8, pp. 1670–1672 (2011).
- [12] S. H. Pezzin, N. Stock, S. Shishatskiy, and S. P. Nunes, "Modification of proton conductive polymer membranes with phosphonated polysilsesquioxanes," Journal of Membrane Science, vol. 325, № 2, pp. 559–569 (2008).

- [13] C. Chanthad, K. Xu, H. Huang, and Q. Wang, "Protonconductive polymer nanocomposite membranes prepared from telechelic fluorinated polymers containing perfluorosulfonic acid side chains," *Journal of Polymer Science, Part A*, vol. 48, № 21, pp. 4800–4810 (2010).
- [14] B. J. Liu, X. F. Li, M. M. Guo, C. Liu, L. Li, and Z. H. Jiang, "Synthesis and hybrid of a(4-phosphonic acid) phenylated poly (aryleneether sulfone)," *Gaodeng Xuexiao Huaxue Xuebao*, vol. 31, № 6, pp. 1081–1083 (2010).
- [15] Pat. Russian Federation 2 142 478: MCI 08 C 77 G, C 08 F 283/12, C 08 G 77/06.
- [16] E.G. Ehrenburg, S.B. Dolgoplosk, L.M. Terentyeva *Vysokomolekulyarnye soedineniya. Serie B.*, 33 (8), 586.