



POSS as promoters of self-healing process in silicone composites

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Abstract

This article focuses on the methods used to create self-healing silicone composites. It has been shown how incorporation of polyhedral oligomeric silsesquioxanes (POSS) molecules with acid and basic groups into silicone rubber affects the barrier properties, mechanical properties in room temperature or the influences on relaxation rates of the methylvinylsilicone rubber vulcanizates. Moreover, the presence of silsesquioxanes, their content and the way of composites preparation affect the amount of ionic bonds, as indicated by measurements of equilibrium swelling in toluene. The self-healing effect of preparing samples is best visualized by SEM images of samples after destruction and conditioning. Composites presented in this work based on the methylvinylsilicone rubber with fumed silica as the fillers were manufactured and studied. To obtain self-healing effect, various silsesquioxanes were used, such as amic acid-isobutyl POSS (AAIb-POSS), aminopropylisobutyl-POSS (APIb-POSS) and aminoethylaminopropylisobutyl-POSS (AEAPIb-POSS). Every tested sample demonstrated the ability to the self-treatment. The most significant effect was observed for system containing amic acid-isobutyl POSS/aminopropylisobutyl-POSS.

Introduction

Nowadays, it is a great technological challenge to design and manufacture multi-functional materials that are “smart” at the material level. The concept of smart material is based on the three fundamental principles: sensitivity to the environment changes, processing of the obtained information and response to the changes. The innovative features of smart materials are very often based on the observation of living organisms that constantly adapt to the continuous, dynamic changes of the

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environment. They adapt thanks to developing innate homeostatic abilities. Similarly, the self-healing mechanism of the discussed materials is analogous to the one that exists in nature (e.g., fusion of broken bones and wound healing) and is based on an immediate response to damage without (or minimal) human intervention [1].

The influence of thermal, chemical and environmental factors as well as cyclic material fatigue can damage the polymer. The inevitable exploitation of the structural elements requires innovative solutions that would prolong the life of materials [2]. The spread of cracks and the mechanics of damage aroused the interest of many researchers [3, 4]. When the polymer structure is damaged, the energy generated during a crack must be equal to or greater than the energy required to form a new surface on the material [5]. Although the new models of forming cracks are still being developed [6, 7], the most common mechanism is based on the parameter called K_I [8, 9], which is connected with the depth of a crack, geometry of the material, the crack as such and the applied stress.

The basic idea behind the design of self-healing materials is that after regeneration they should be able to regain their original mechanical properties or at least be able to reduce deterioration caused by micro-cracks [10]. “Self-healing” can be either automatic or activated by an external stimulus such as heat or radiation [1]. Autonomous self-healing materials do not need an external impulse, because the damage itself stimulates the repair process.

The first reports in the literature on self-healing materials come from the 1980s. Since then, we have been observing a rapid upward trend in the interest in this subject [11, 12].

Numerous strategies and approaches have been described which aimed to develop a variety of materials, including metals, ceramics and polymers capable of self-healing. Nevertheless, in all cases self-healing is based on the same general common principle and the identical basic concepts.

The ideal self-healing material is considered the one which is able to continuously detect and respond to damage as well as restore its quality without a negative impact on the original properties of the starting material. Furthermore, regeneration can contribute to regaining such properties as resistance to fracture, tensile strength, surface smoothness and barrier properties [13].

Conventional cross-linked rubbers generally consist of long polymer chains joined together by chemical bonds. However, Leibler et al. [14] synthesized elastomer-like self-healing networks from readily available small molecules of fatty acids. The ease of self-healing is the most interesting feature of this material. After cutting a sample into two parts, the fragments can regain their original strength by connecting the intersection surfaces [2, 15]. The unquestionable advantage of such self-healing mechanism is that the repair process can be repeated many times. Moreover, apart from the ability to self-heal, this property allows for complete recycling and any change in the shape of objects made of the supramolecular polymer. Unfortunately, due to the presence of hydrogen bonds only, rubber has a considerably lower strength compared to organic elastomers whose structure is based mainly on strong covalent bonds.

Using polymers with thermally reversible network bonds is another way of obtaining self-healing composites. The studies on networks with reversible cross-links for

self-healing purposes were initiated by Chen [16] who used the Diels–Alder reaction. It presents a simple and efficient way of obtaining new bonds using inter- and intramolecular cross-linking and involves cycloaddition of dienophile to conjugated diene [17, 18]. The main advantages of this phenomenon are complete reversibility, the possibility of multiple regeneration of damaged parts and the fact that the process does not require any additional components or especially modified surfaces [19]. Weiss et al. presented another approach to obtain reversing network bonds [20]. They postulated that simple three atomic molecules $X=Y=X$, where X atoms are more electronegative than Y atoms, can serve as a bridge connecting amino groups [21]. This method has a number of advantages such as the possibility to control a degree of cross-linking by using the proper quantity of amine functional groups contained in the polysiloxane, low cost, high speed of reaction, isothermality and above all reversibility [20]. In addition, such polysiloxanes subjected to the reaction of addition with three atomic particles obtain significantly higher viscosity and adhesiveness compared to the starting polymer [19].

The systems of ionomers are another group of polymers that use reactive bonds in the polymer medium. Ionomers are copolymers containing ions in the amount of about 15% moles [22, 23]. The properties of ion areas are determined by interactions between anionic and nonionic groups in the structure. Usually, acidic side groups in the polymer chain are ionic. They are neutralized by the metallic cation and form an ion pair. Their presence and properties give ionomers unusual and interesting microstructure [24]. Ion pairs are grouped in the areas called multiplets, where specific interactions cause that the polymer chains attached in their neighborhood have limited mobility [25, 26]. When the ion content increases, more multiplets gather and begin to form in the entire polymer structure a more continuous area of limited mobility. The glass transition temperature T_g of these rigid areas called ionic clusters is independent of the polymer [27, 28]. In this way, polymers having a low molecular weight can react with one another and form long chains connected with reversible ionic bonds [29].

The main objective of this paper was to obtain composites based on silicone rubber. The literature contains many examples of using the mechanisms of networks with reversible bonds [30–32], but they refer in large part to thermoplastic polymer media. Our idea was, however, to incorporate POSS functionalized by amino or acidic groups into rubber matrix. This led to the formation of thermoreversible network bonds capable of regeneration. The modifications that we suggested were carried out at the stage of preparing the rubber mixtures.

Experimental

Materials

The material used in this work was methylvinylsilicone rubber POLIMER MV 0.07, containing 0.07% of vinyl groups, purchased from Chemical Plant “Silikony

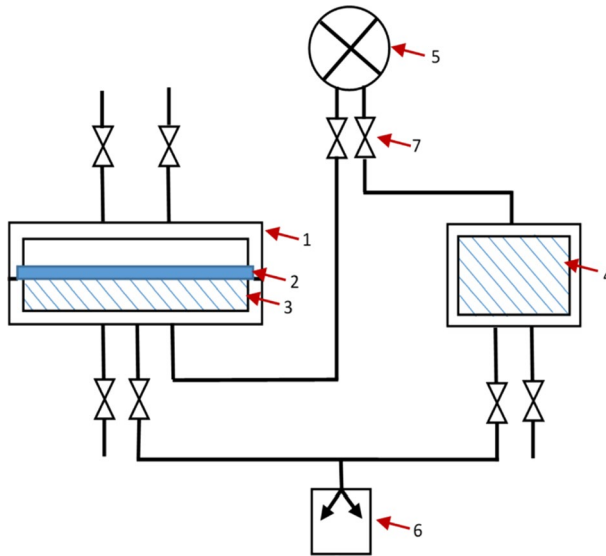


Fig. 1 Diagram of the apparatus for measuring gas permeability by a manometric method through a polymer sample (1. measuring cell, 2. sample, 3. chamber with low pressure, 4. reference chamber with low pressure, 5. differential transducer, 6. vacuum pump, 7. valves)

Table 1 Cross-link density of silicone rubber vulcanizates containing POSS molecules functionalized by amino or acidic groups

The applied POSS system	POSS (phr)	$\nu_{e\text{ tol}} \times 10^{-5}$ (mol/cm ³)	$\nu_{e\text{ NH}_3} \times 10^{-5}$ (mol/cm ³)	ν_{NH_3} (%)
Reference (with no POSS)	–	14.8	5.0	66
APIb-POSS + AAib-POSS	2	21.9	5.8	73
AEAPIb-POSS + AAib-POSS		18.2	5.3	71
APIb-POSS + AAib-POSS	5	24.0	6.4	73
AEAPIb-POSS + AAib-POSS		23.6	7.4	69
APIb-POSS + AAib-POSS	10	34.0	8.1	76
AEAPIb-POSS + AAib-POSS		27.7	8.3	70

$\nu_{e\text{ tol}}$, cross-link density in toluene; ν_{NH_3} , non-covalent cross-links concentration

Polskie” at Nowa Sarzyna, Poland. The elastomer was cross-linked with dicumyl peroxide (DCP) from Aldrich. The filler was fumed silica Aerosil 380 from Degussa, Germany. The POSS used in this study was aminopropylisobutyl-POSS (**APIb-POSS**), aminoethylaminopropylisobutyl-POSS (**AEAPIb-POSS**) and amic acid-isobutyl-POSS (**AAib-POSS**) (Fig. 1). They were in the form of white powders and were supplied by the Hybrid Plastics Company, Fountain Valley, California. The composition of a typical elastomer blend was: MV 0.07–100 phr

(Parts per Hundred Rubber), DCP—0.8 phr, A 380—30 phr, the total amount of POSS compounds—2, 5 or 10 phr (Table 1).

Methods

Methylvinylsilicone composites, containing polyhedral oligomeric silsesquioxanes, were obtained by the common manufacturing procedures of rubber. First, the masterbatches containing silicone rubber, fumed silica and POSS with amino or amic acid groups were prepared using two-roll mill at 30 °C. Blending two types of masterbatches: one with basic and the second with acid POSS were performed in Brabender measuring mixer N50 (temp. 70 °C, speed range 50 min⁻¹, time of the process 30 min). Finally, two-roll mill was used to mix the blends with the cross-linking agent (dicumyl peroxide). Then, the rubber compounds were vulcanized in a steel mold placed between electrically heated shelves of a hydraulic press. The vulcanization temperature and time were 160 °C and 30 min, respectively.

The cross-link density of vulcanizates was calculated from the measurements of equilibrium swelling in toluene, while the elastomer–filler interactions were estimated on the basis of vulcanizate swelling in toluene under ammonia-saturated atmosphere according to standard PN-74/C-04236. The samples of the composite material were subjected to equilibrium swelling in toluene for 48 h at room temperature. Then, the swollen samples were weighed on a torsion balance, next dried at a temperature of 50 °C to a constant weight and after 48 h they were reweighed. Based on the Flory–Rehner's equation [33], the cross-link density is determined using formula (1)

$$v = -\frac{1}{V_0} * \frac{\ln(1 - V_r) + V_r + \mu V_r^2}{V_r^{1/3} - \frac{V_r}{2}} \quad (1)$$

assuming the Huggins parameter (elastomer–solvent interactions parameter) at a temperature of 20 °C as $\mu = 0.45$ [34].

The tensile measurements were taken on dumbbell-shaped specimens by using a universal testing machine (Zwick Company, model 1435, Germany) according to ISO-37 at room temperature. The crosshead speed of testing was 500 mm/min. At least five different samples were tested from each rubber composite. The result was calculated as the average of measurements.

We have developed a method for testing the self-healing effect of elastomer composites, which is based on the measurement of gas permeability. After preparation, the vulcanizates were subjected to the measurement of barrier properties. Next, they were damaged and subjected to conditioning at the elevated temperature—the mechanisms of reactions which are used to obtain the self-healing effect of elastomer composites are usually initiated by the external thermal factor (temp. 70 °C, time 24 h). After conditioning, the samples were re-tested for gas permeability to verify the effect of composites regeneration.

The measurement of barrier properties was taken using a device for measuring the barrier properties testing the gas permeability by a manometric method. In the measuring apparatus, the measurement of barrier properties is based on a method that uses pressure differences in measuring chambers on both sides of the sample being tested—a polymer film. The measuring apparatus consists of a measuring cell between which a test sample (2) is placed in the holders. The measuring cell (1) is divided into two parts—a chamber with atmospheric pressure and a chamber with low pressure (3). Atmospheric gas (air) is supplied to the chamber at atmospheric pressure. The low-pressure chamber together with the reference chamber (4) is connected to a differential transducer (5) measuring pressure changes taking place in the measuring chamber as a result of permeation of gas molecules through the partition between the two chambers containing the sample of the test polymer. The low-pressure chamber is accompanied by a vacuum pump (6) that generates low pressure in the chambers (below 10 Pa). The diagram of the measuring apparatus is shown in Fig. 1.

On the basis of the obtained results, a graph of changes in pressure as a function of time was made and the slope of the rectilinear part of the graph was determined (dp/dt) (Pa/s). This allowed to calculate the gas transmission rate (GTR) and coefficient of gas permeability P using formulas (2, 3):

$$\text{GTR} = \frac{V_c}{R * T * P_u * A} * \left(\frac{dp}{dt} \right) \quad (2)$$

where GTR—gas transmission rate, V_c —volume of low-pressure chamber (l), T —measuring temperature (K), P_u —gas pressure in the high-pressure chamber (Pa), A —measuring area, area of gas penetration through the sample (m^2), R —gas constant ($= 8.31 * 10^3$) [(1 Pa)/(K mol)], dp/dt —pressure change per unit of time (Pa/s)

$$P = \text{GTR} * d \quad (3)$$

where GTR—gas transmission rate, d —sample thickness (m).

Visualization of the damage surface and after self-healing process was observed by scanning electron microscopy (SEM). The samples were covered with gold, followed by observation of the surface at 90–2500 magnifications. The tests were aimed at illustrating the damage and the changes occurring during the self-healing process.

Results and discussion

The idea of the self-healing mechanism presented by the authors consisted in the introduction of small-molecule compounds compatible with silicone rubber, functionalized with basic and acidic groups that interacting with each other would be able to create mobile network bonds capable of regeneration and reorganization in the elastomeric medium. The aim of the authors was to obtain polymeric materials

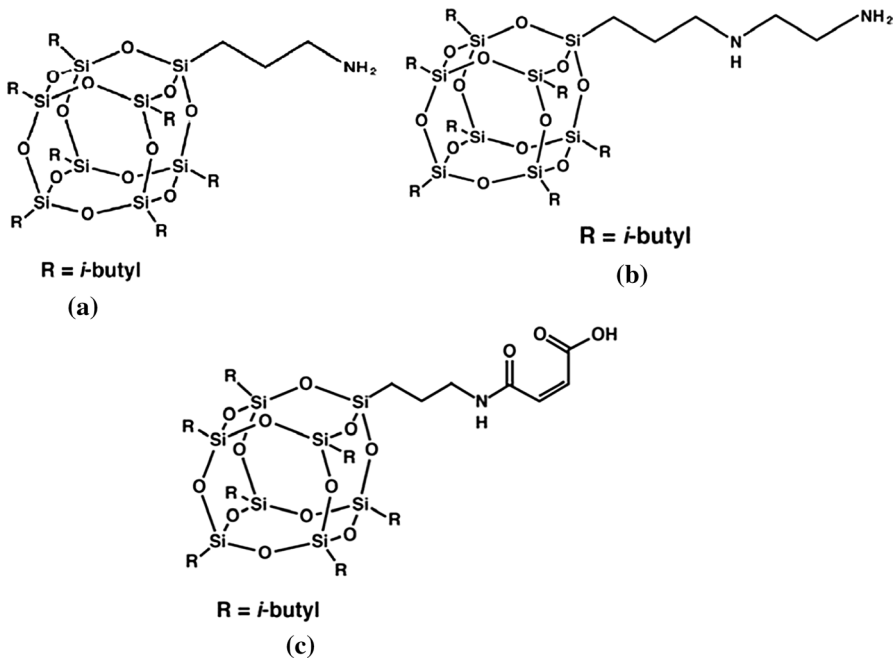


Fig. 2 Structure of POSS used for preparation self-healing silicone rubber (MVQ) composites. **a** Amino-propylisobutyl-POSS, **b** aminoethylaminopropylisobutyl-POSS, **c** amic acid-isobutyl-POSS

having reversible bonds, based mainly on internal interactions of functional groups of compounds introduced into the mixture at the stage of its preparation.

The most important aspect in obtaining self-healing elastomeric composites besides the used components has a way of preparing the mixture. As a consequence, the composition and method of combining the individual components were developed. Methods of premixes containing POSS with an acidic or basic group were used, which combine with each other in the next processing step. This solution promotes an even distribution of silsesquioxanes responsible for the formation of ionic bonds in the entire mass of the elastomer.

The obtained vulcanizates were first subjected to evaluation of mechanical behavior under load. Figures 2 and 3 show an influence of the type and quantity of POSS applied into a rubber on tensile strength and elongation at break of the tested elastomer composites. The results show that mechanical properties of the vulcanizates are determined by the type of functional group present in the POSS molecule. These vulcanizate samples which contain POSS functionalized by aminoethylaminopropylisobutyl groups (**AEAPIb-POSS**) revealed much better properties than the samples containing aminopropylisobutyl-POSS (**APIb-POSS**) or the reference sample. Depending on the amount of POSS, tensile strength of these vulcanizates was, respectively, 7.61; 8.27 and 7.05 MPa. That conclusion is particularly apparent in the composite obtained with the following system: AEAPIb-POSS + AAIb-POSS, applied in the amount of 5 phr. Larger amount of POSS influences increase in the cross-link density, so that the samples are more rigid, less elastic and cracked more

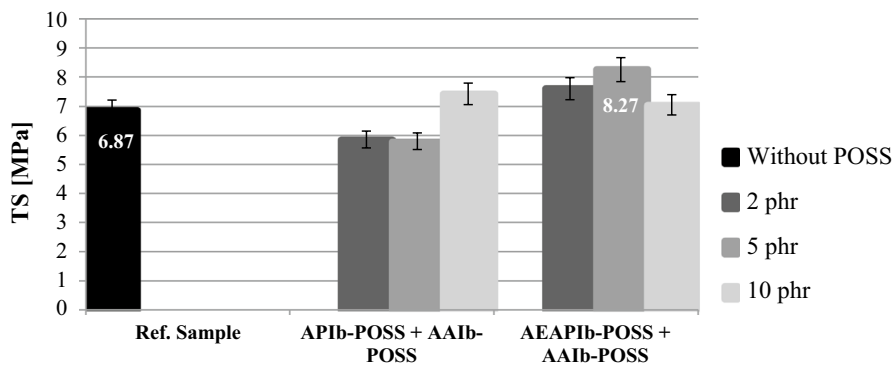


Fig. 3 Tensile strength of silicone rubber vulcanizates containing POSS molecules functionalized by amino or acidic groups

quickly when subjected to deformation. Of course, besides the cross-link density, many other parameters affect the properties of strength, such as good dispersion of the filler in the elastomer matrix and homogeneity of structure.

Despite the lower cross-link density of the reference vulcanization composites with the addition of 2 phr of POSS show a greater elongation at break. This is most likely due to the POSS additive, because the silicon cages dispersed in the elastomer have a plasticizing effect [35, 36]. With higher POSS content, the cross-link density is large and the effect is not noticeable. Such a relationship may result from the increase in cross-link density followed by the rise of stiffness. However, the amount of POSS affects not only the growing concentration of covalent bonds in the composite network, but first of all—the increase in ionic cross-links, proportional to the POSS quantity, what may be considered as evidently favorable phenomenon regarding the formation of material with self-healing properties.

In order to realize the object of the study which was the formation and then the evaluation of self-healing properties of the resulted rubber material, we developed a method for testing the self-healing effect of the composites, which was based on the measurement of gas permeability. In addition, the influence of conditioning at the elevated temperature (70 °C) on the cross-link density and the concentration of ionic cross-links in the vulcanizates network were investigated. The results are shown in Table 2 and in Figs. 4, 5, 6, 7, 8, 9, 10 and 11. In the first stage of the studies, concerning the barrier properties evaluation of the obtained vulcanizates, we observed that the presence of POSS functionalized with amino or acidic groups influences the increase in air permeability, with the growing amount of POSS compounds in the rubber. It is probably the result of POSS morphology, since silicon cages which are dispersed in the elastomer matrix are known from ability to increase free volume of the elastomer. Next, the damaged samples, after conditioning, were re-tested for gas permeability. The obtained results were positive and showed the regeneration effect of the composites formed with POSS. Moreover, after the conditioning at the elevated temperature, gas permeability results were much better in comparison with samples before damage. The best self-healing effect and improved barrier properties were observed for vulcanizates containing APIb-POSS + AAib-POSS, in the amount

Table 2 Barrier properties of silicone rubber vulcanizates containing POSS molecules functionalized by amino or acidic groups, before and after damage

The applied POSS system	POSS (phr)	$GTR \times 10^{-8}$ (mol/(m ² s Pa))		$P \times 10^{-11}$ (mol/(m s Pa))	
		Before damage	After damage	Before damage	After damage
Reference (with no POSS)	–	1.07	–	1.25	–
APIb-POSS + AAIB-POSS	2	1.74	1.35	1.90	1.52
AEAPIb-POSS + AAIB-POSS		1.35	1.29	1.70	1.49
APIb-POSS + AAIB-POSS	5	3.20	1.80	3.14	1.77
AEAPIb-POSS + AAIB-POSS		2.86	1.42	2.97	1.47
APIb-POSS + AAIB-POSS	10	5.01	1.29	5.76	1.49
AEAPIb-POSS + AAIB-POSS		9.43	8.34	9.90	8.93

GTR gas transmission rate, *P* gas permeation coefficient

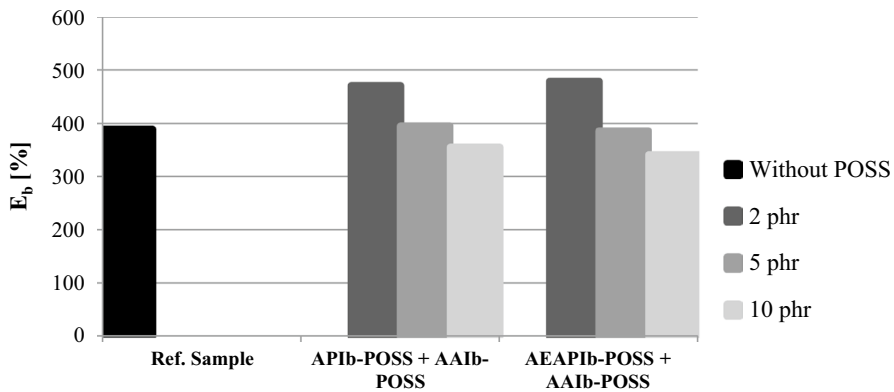


Fig. 4 Elongation at break of silicone rubber vulcanizates containing POSS molecules functionalized by amino or acidic groups

of 10 phr. The measurements showed that gas permeability coefficient decreased from 5.76 to 1.49 mol/m s Pa. Reduction of gas permeability arises probably from the increased ionic groups mobility induced by the elevated temperature of conditioning process of the samples, what positively influenced probability of the ionic groups encounter and then their interaction leading to self-healing phenomenon and increase in cross-link density inhibiting the air penetration through the sample.

The positive effect of increased concentration of ionic cross-links was confirmed by the same measurements taken on the vulcanizate formed without the POSS

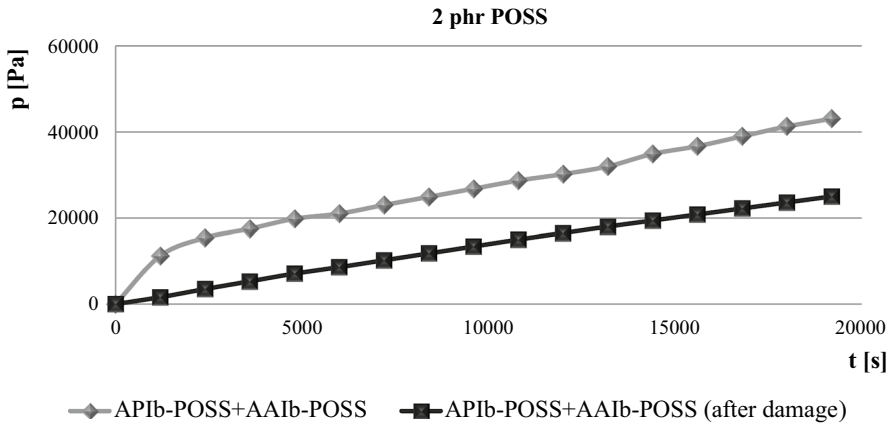


Fig. 5 Comparison of gas permeability rate for silicone rubber vulcanizates, before and after damage, containing: APIb-POSS + AAib-POSS, in the total amount of 2 phr

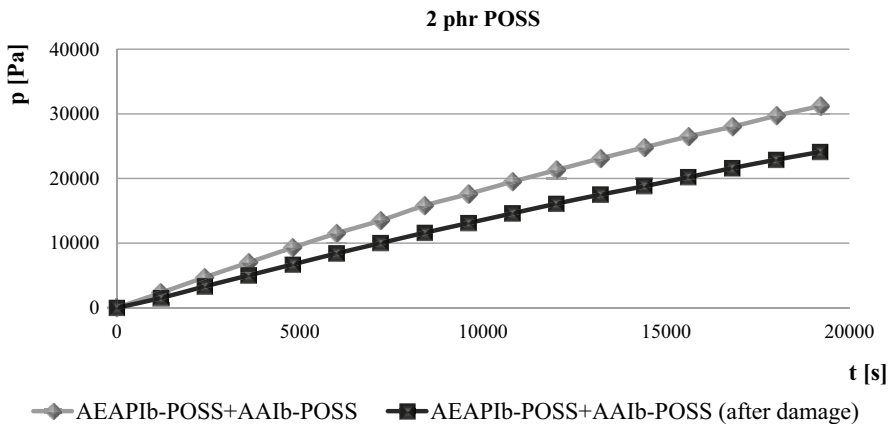


Fig. 6 Comparison of gas permeability rate for silicone rubber vulcanizates, before and after damage, containing: AEAPIb-POSS + AAib-POSS, in the total amount of 2 phr

addition. Then, after damage followed by conditioning, the regeneration of the tested sample was not observed. The vulcanizate did not reveal any barrier properties when used as a membrane during the test for gas permeability. Figures 4, 5, 6, 7, 8 and 9 show the changes of pressure in time for the samples before and after damage. The observed effect of self-healing was mostly developed by the increase in cross-link density in the network of vulcanized rubber composites, particularly by cross-links of ionic type, induced by conditioning. In particular, composites formed with APIb-POSS + AAib-POSS showed much higher concentration of mobile cross-links capable of reorganization and regeneration in comparison with the reference sample without the POSS presence. Figures 10 and 11 show it clearly (Fig. 12).

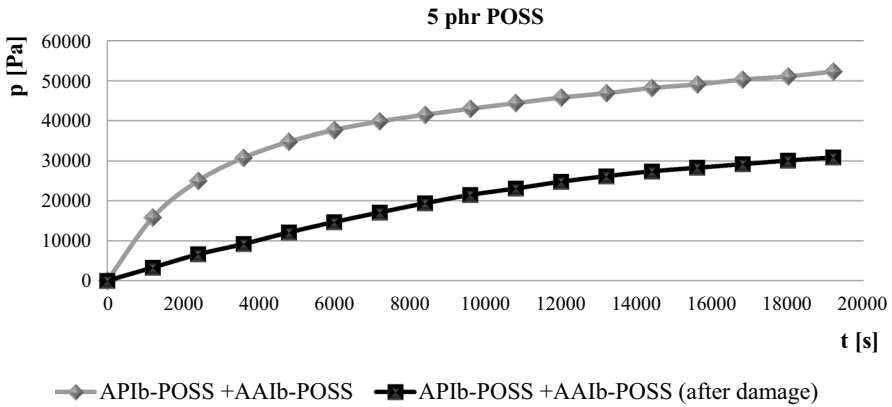


Fig. 7 Comparison of gas permeability rate for silicone rubber vulcanizates, before and after damage, containing: APIb-POSS + AAIb-POSS, in the total amount of 5 phr

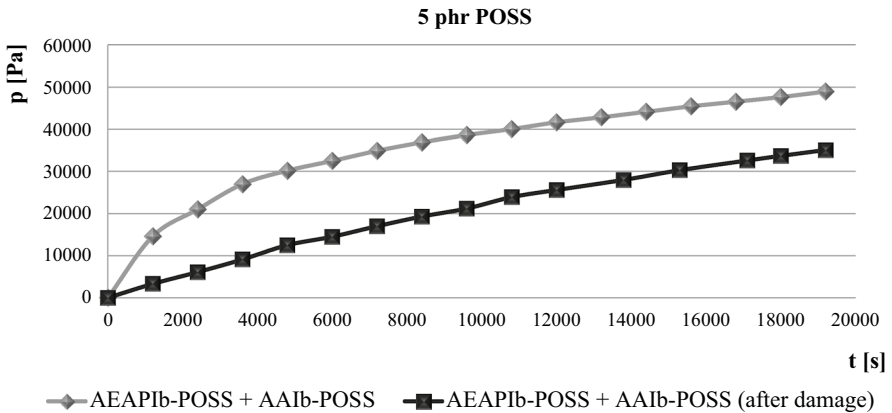


Fig. 8 Comparison of gas permeability rate for silicone rubber vulcanizates, before and after damage, containing: AEAPIb-POSS + AAIb-POSS, in the total amount of 5 phr

The best method confirming and illustrating the effectiveness of the self-repair process of composites is the analysis of the surface morphology by using scanning electron microscopy (SEM). It is not possible to present the surface of same sample which was obstructed and then healed because the procedure of sample preparation for photographs requires sticking the material to the tripod and then covered with gold, which makes it impossible to undergo conditioning and healing the once-tested sample. Therefore, the pictures present the damage as well as the place of healing done in other samples but the same vulcanizate. Figure 13a shows the surface visualization of an exemplary sample subjected to simulated failure conditions. Sample with micro-damage subjected to conditioning was self-healing, which is clearly visible in Fig. 13b. The place of puncture is vaulted and almost invisible. On the pictures below a sample containing 5 phr of

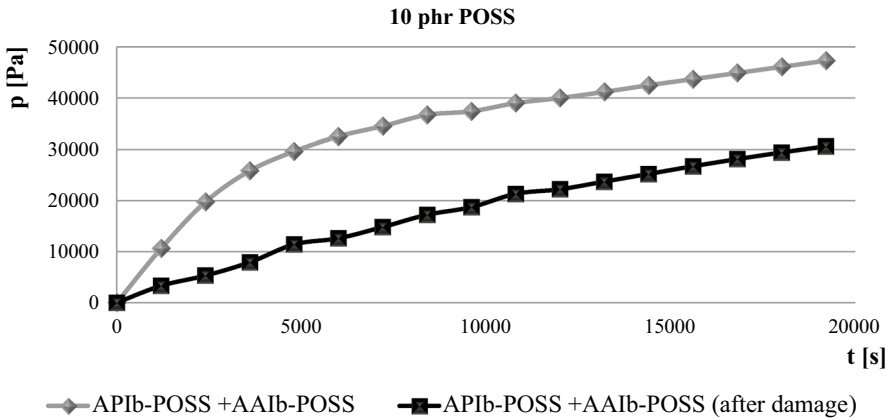


Fig. 9 Comparison of gas permeability rate for silicone rubber vulcanizates, before and after damage, containing: APIb-POSS + AAib-POSS, in the total amount of 10 phr

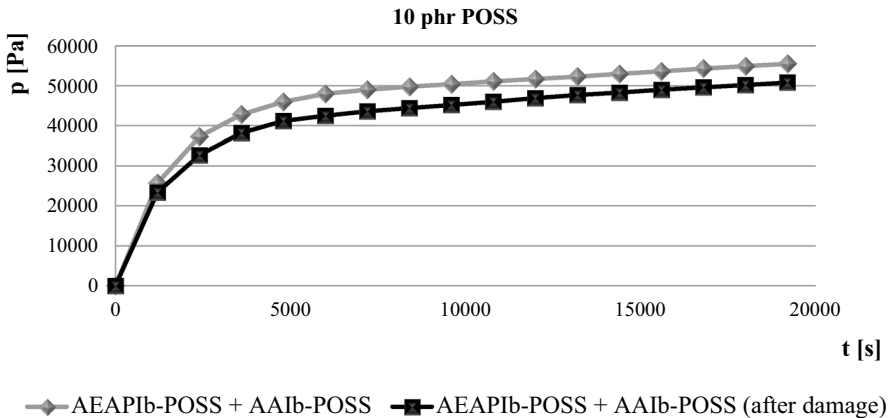


Fig. 10 Comparison of gas permeability rate for silicone rubber vulcanizates, before and after damage, containing: AEAPIb-POSS + AAib-POSS, in the total amount of 10 phr

AEAPIb-POSS + AAib-POSS was presented, but all the applied systems showed the same effect.

Conclusions

Self-healing composites of methylvinylsilicone rubber were formed with the use of POSS compounds which were selected regarding the choice of appropriate functional groups: basic or acidic, capable of interacting in order to form the labile ionic bonds in the elastomer.

The measurements of the behavior under load showed that the obtained composites reveal good mechanical properties and increased cross-link density, what may

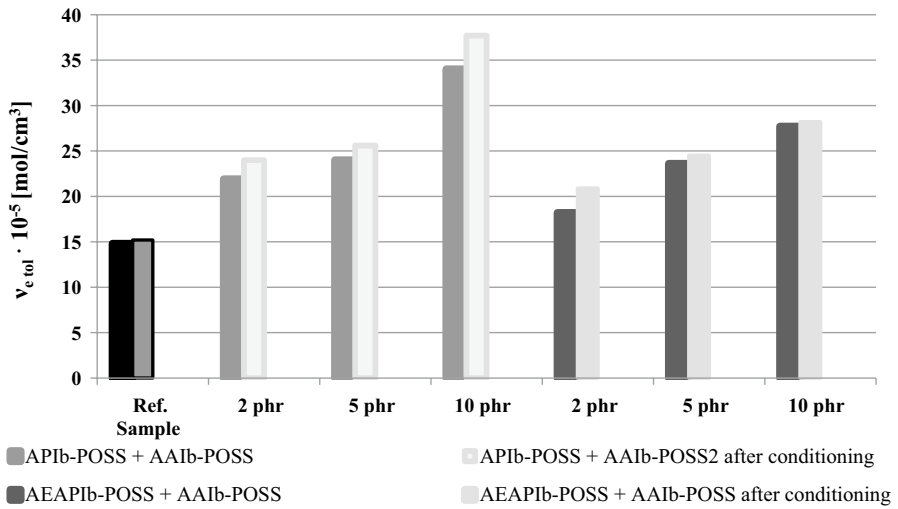


Fig. 11 Comparison of cross-link density of silicone rubber vulcanizates containing POSS molecules functionalized by amino or acidic groups, before and after conditioning

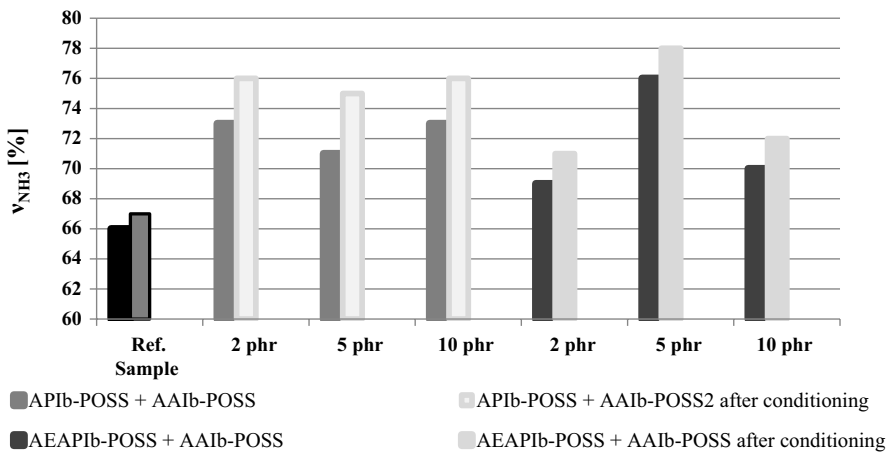
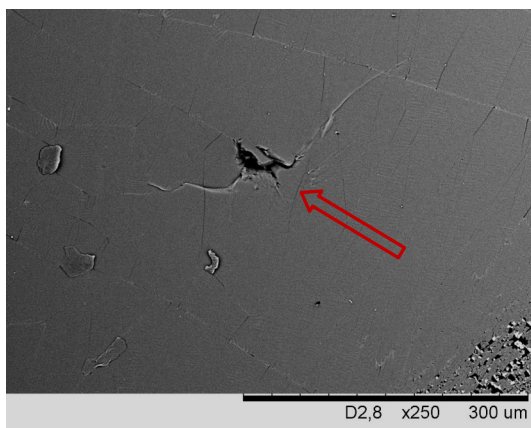


Fig. 12 Comparison of non-covalent cross-links concentration of silicone rubber vulcanizates containing POSS molecules functionalized by amino or acidic groups, before and after conditioning

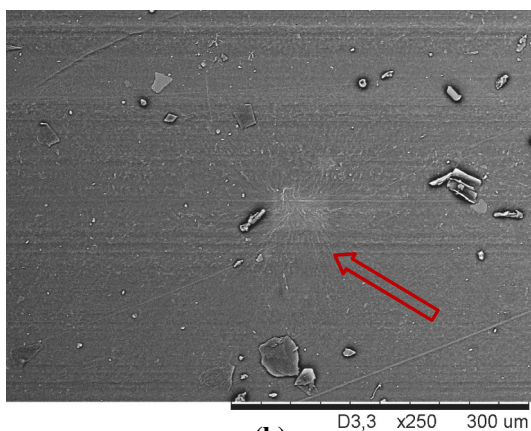
be considered as evidently favorable phenomenon regarding the capability of regeneration and self-healing effect of the rubber composites.

The process of conditioning at elevated temperature (70 °C) appeared to have significant effect on self-healing properties of the vulcanizates. In addition, the mode of the rubber compounds preparation, based on masterbatches containing suitably selected POSS compounds, was the essential factor as well, since it allows to combine the formed masterbatches and disperse POSS compounds homogeneously in the rubber matrix.

Fig. 13 **a** Surface morphology of silicone composites containing 5 phr of AEAPIb-POSS + AAIb-POSS subjected to simulated micro-damage. **b** Surface morphology of silicone composites containing 5 phr of AEAPIb-POSS + AAIb-POSS subjected to simulated micro-damage after the self-repair process



(a)



(b)

The ability of the resulted rubber composites to self-healing behavior was evaluated from the measurements of gas permeability. The obtained results were positive and showed the regeneration effect of the composites formed with POSS, after the process of conditioning carried out at elevated temperature during 24 h. Moreover, the conditioning favorably influenced barrier properties. Reduction of gas permeability arises probably from the increased concentration of ionic groups induced by the elevated temperature, leading to increase in cross-link density, inhibiting the air penetration through the obtained rubber composites.

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