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Viscoelastic Behavior, Curing and Reinforcement Mechanism of Various Silica and POSS Filled Methyl-Vinyl Polysiloxane MVQ Rubber

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Abstract

The role of Aerosil silicas, A90, R812, R812s on the complex dynamic viscosity η^* of methyl-vinyl polysiloxane MVQ at processing temperature 80°C was analyzed based on experiments with a torsional rheometer Rubber Process Analyzer RPA. The influence of surface area and surface activity on the Payne's effect was determined by oscillating rheometer Ares G2. The decrease in complex modulus G^* by increasing strain for silicas R812, R812s was mostly due to the breaking down of filler-filler networking, the modification of surface led to better processability resulting in the increase of tensile strength TS, from 0.42 MPa unfilled silicone to 9.31 MPa MVQ containing R812. Higher surface activity of silica A90 caused a decrease in filler networking due to a better filler-polymer interactions, which resulted in the increase of the percentage of non-covalent crosslinks determined for samples treated with ammonia. The decrease of static water contact angle θ of silicone rubber after incorporation of A90 was observed. Influence of allylisobutylPOSS on curing, crosslink density, static and dynamic behavior of silicone rubber was considered.

1 Introduction

Polysiloxane "silicone" rubber is an elastomer containing siloxane bond of (Si-O) molecular structure as the main chains [1]. Polysiloxane elastomers with a structure $[Si(R)(R')-O]_x$, where R, R' are methyl, vinyl or phenyl groups, have been widely used in industry because of their interesting properties: low toxicity, good thermal oxidative and mechanical stabilities over a wide range of temperature and humidity. Main applications of polysiloxane elastomers include aerospace and medical application, sealants and other materials for automotive industry, packaging and baking pans for the food industry, connectors and cables for telecommunications appliances, protective functional coatings [2]. Generally, polysiloxane elastomers are reinforced with relatively large amount of filler to increase their stiffness, tensile and compressive strength. Among these fillers, due to

remarkable physical and chemical properties, fumed silica particles have been commonly applied as a reinforcing filler for polysiloxane rubber. Silica particles are usually rich in residual silanol groups on surface (Si-OH). The primary particles can form aggregates and agglomerates via hydrogen bonds and van der Waals forces due to presence on surface Si-OH groups [3]. One of the goals in this area is to modify the surface of silica particles to improve compatibility with polymer, to increase the wettability, to prevent the agglomeration and to achieve better dispersion of filler in polysiloxane matrix. For this purpose the hexamethyldisilazane (HDMS) is chosen as a preferred modifier [4]. A better miscibility and compatibility with silicone rubber after the modification resulting in the increase of the tensile strength and tear strength of vulcanizates [5]. To achieve efficient reinforcing effect both the uniform dispersion in the rubber matrix and the strong polymer-filler interactions are necessary. The type and number of adsorption sites on filler surface determine the possibility of the polymer-filler interactions. These factors are highly dependent on the surface modification. After treated with HDMS fumed silica exhibits tri-methylsilyl groups on the surface. It was found that the amount of bound silicone rubber, defined as polymer chains adsorbed on filler surface having restricted mobility, is slightly affected by filler's

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dispersion but mainly affected by filler's concentration, specific surface area and surface chemistry. Experimental results showed that modification with HDMS reduced the amount of occluded rubber for silicas with the same surface area indicating lower polymer-filler interactions due to the change of surface characteristics [3]. Various nanoparticles were applied to improve the properties of polysiloxane elastomers among them very promising are POSS particles [6]. Polyhedral oligomeric silsesquioxanes (POSS) can be considered as the smallest silica particles, they contain an inorganic cage-like silicon-oxygen structure surrounded by organic substituents. The most common structure has eight silicon atoms, each carrying an organic group. POSS molecules with one reactive groups can be grafted to a polymer as a side chain [7], with two or more reactive substituents can be incorporated into polymer backbones by copolymerization or can form crosslinks in polymer network [8, 9]. POSS are known to enhance the fire retardancy of polymer materials [10]. The chemical incorporation of POSS into polydimethylsiloxane PDMS chains increased thermo-oxidative stability [11], and the mechanical properties of RTV silicone rubber [8, 12]. The synergistic effect between divinyl-hexa[(trimethoxysilyl)ethyl]-POSS and fumed silica on thermal stabilities and mechanical properties of room temperature vulcanized (RTV) silicone rubbers was observed [13]. The chemical, physical and mechanical properties are strongly affected not only by presence of active fillers but also by the cure behavior. The vulcanization process has a crucial influence on the performance and quality of the final silicone rubber products. For curing of silicone rubber peroxide and platinum catalysis are commonly used [14]. In this paper commercially available fumed silicas with different surface characteristics and surface area were selected as reinforcing fillers. Allylisobutyl-POSS with one active allyl group was used as a novel ingredient in methyl-vinyl silicone rubber MVQ. Three types of chemical reactions are possibly during peroxide curing, the crosslinking of methyl-vinyl silicone rubber MVQ, the polymerization of POSS molecules containing unsaturated >C=C< functional groups, the grafting reaction between POSS and polymer. According to the literature the allylisobutyl-POSS, because of the steric hindrance of the molecule, mainly participate in grafting reaction [15]. The current methods to investigate the curing of a silicone materials are differential scanning calorimetry (DSC), an oscillating disc rheometer (ODR) and a moving die rheometer (MDR) [14]. A parameter known as the cure degree (cure rate) is defined and plotted versus time to describe the temporal behavior of the curing reactions [16]. In this work, a rubber process analyzer RPA was used to determine the changes occurring in viscosity, processability and vulcanization characteristic of various MVQ silicone rubber formulations. In particular the influence of silica properties such as surface area, structure and surface activity and POSS grafting on the reinforcement mechanism, and Payne's effect

[17] were analyzed. The influence of production method, rubber type and the presence of additives such as solid particles on the hydrophobic properties and water contact angles of room temperature vulcanizing RTV silicone was observed [18], coatings containing silica filler indicated lower water contact angles. The effect of silica surface modification on the hydrophobic performance and air permeability of MVQ methyl-vinyl silicone elastomer was evaluated.

2 Experimental

2.1 Materials and Preparation of Silicone Mixtures

The rubber mixtures were prepared using methyl-vinyl silicone rubber (MVQ), Polymer MV 007 with vinyl units content of 0.05-0.09 mol%, supplied by Silikony Polskie Chemical Company. Silicone rubber were crosslinked with (bis(1-methyl-1-phenyl-ethyl) peroxide, DCP. Fumed silicas (Evonik) were used as reinforcing filler: hydrophilic Aerosil A90), hydrophobic, modified by hexadimetylsilazane (HDMS) Aerosil R812s, organic phase C content 3-4%) and Aerosil R812, organic phase C content 2-3%). Polyhedral oligomeric silsesquioxane POSS was obtained from Hybrid Plastics (allylisobutylPOSS, OL118) containing one allyl group and seven isobutyl groups. Rubber compounds with the formulation given: MVQ (100phr), SiO_2 (40phr), POSS (3 phr), DCP (2 phr) were prepared using two steps method. In first step silicone rubber was mixed with silica using Brabender Measuring Mixer N50. The rubber compounds were processed using 50 rpm (revolution per minute) rotor speed at the initial temperature 40°C. After 2 minutes of rubber mastication silica was added and mixed for 15 minutes, for the formulations modified by addition of POSS after the silica mixing the POSS was added and mixed for additional 5 minutes. The compounded rubbers were homogenized with peroxide curing system in a laboratory two-roll mill (temperature 40°C, friction ratio 1:1.2, dimension of rolls, diameter 200 mm, length 450 mm) during 15 minutes. The compounded rubbers were cured at 160°C using electrically heated hydraulic press under a pressure of 5 MPa at their optimum curing time. Cured sheets were conditioned before testing (24 h maturation at room temperature).

2.2 Characterization of Silica

The oil absorption parameter OAP of fillers was measured according to ASTM D2414 using Absorptometer C equipment connected with Brabender station. The process parameters were: sample weight 20 g, titration rate 4.0 mL/min. The oil used in this study was dibutyl phthalate (DBP). Specific surface area SA_{N2} was measured based on nitrogen adsorption

using a Gemini 2360 V2.01 porosimeter (Micrometrics,USA). Measurements were performed according to the Brunauer-Emmett-Teller (BET) nitrogen adsorption method.

2.3 Analysis of Viscoelastic Properties and Curing Characteristics of Uncured Silicone Rubber

The Rubber Process Analyzer RPA 3000 MonTech with the lower die of the chamber oscillated sinusoidally at a fixed angle and frequency was used to characterize viscoelastic properties and curing of rubber mixtures. Uncured silicone behavior was studied according to ASTM D6204 Part A (low strain) and Part B (high strain) standards. The dynamic viscosity measurements were made based on a frequency sweep in which the frequency was programmed to change in range 0.5 – 400 rad/s under constant strain amplitude 7% or 100%, the temperature of measurements was 80°C. Before every measurement at 80°C the conditioning step at frequency 3 rad/s and strain 2% was carried out. The curing studies were done at 160°C according to ASTM D5289. The parameters: the optimum cure time (τ_{90}), scorch time ($t_{\Delta2}$), minimum elastic torque ($S_L^{'}$), maximum elastic torque ($S_H^{'}$) and increment of elastic torque ($\Delta S^{'} = S_H^{'} - S_L^{'}$) were calculated based on the curing curves.

2.4 Analysis of Payne's Effect and Viscoelastic Properties of Cured Silicone Rubber

Dynamic rheological measurements of cured vulcanizates were carried out using an oscillation rotational rheometer Ares G2, TA Instruments (USA), plate-plate geometry with two parallel plates with a diameter of 25 mm was used during measurements. The rheological tests were performed in oscillation strain amplitude sweep mode (constant angular frequency 10 rad/s, oscillation strain range 0.01-100%) at room temperature 25°C and 100°C.

2.5 Measurement of Cross-Link Density

The network structure was analyzed according to ASTM D6814-02 standard. Weighted rubber samples were swollen at 25°C in solvent (reagent grade purity toluene) for the time necessary to achieve weight balance of swollen samples. The solvent was replaced with fresh toluene every 12h. After swelling the excess liquid was removed from the surface of the samples with a soft paper towel and the samples were weighted. In the next step the specimens were dried at 50°C in a forced-ventilating air oven for 24 h until constant mass. The dried samples were cooled down to room temperature (25°C) using a desiccator and weighted again. To determine the content of non-covalent crosslinks in the elastomer network samples were swollen in toluene in a desiccator with saturated ammonia vapor (25% aqueous solution).

2.6 Stress-Strain Behavior

Stress-strain behavior was characterized using Zwick 1435 tensile machine. The moduli at 100% elongation (SE_{100}), tensile strength (TS) and elongation at break (E_B) were measured at 25°C with crosshead speed of 500 mm/min for testing type 1 dumb-bell specimens preparing according to ISO-37-2005 standard. Five different specimens were tested and the average value for each formulation was reported.

2.7 Wettability Measurements

The water contact angles θ were measured using OCA 15EC data physics video based optical contact angle measuring instrument using parameters: the dosing volume of water 1.2μL, dosing rate 0.50μL/s. Ten measurements points for every sample were taken to calculate the water contact angle θ.

2.8 Air Permeability Measurements

The permeability of silicone samples for atmospheric air at room temperature 25°C was determined by the manometric method using equipment working according to ISO 15105. A sample of vulcanizate in the shape of a disc with diameter of 30 mm and thickness of about 1 mm was placed and sealed in the measuring chamber. The sample was a barrier separating the chamber into two parts. On one side of the tested sample, the air was pumped out using a vacuum pump, so that the pressure was less than 10 Pa, while on the other side of the chamber the atmospheric pressure prevailed. After reducing the pressure difference to zero, the measurement of the pressure increase due to air transfer through the vulcanizate in the vacuum chamber was initiated. The pressure increase was measured during a period of about 4 hours. By obtaining a series of measurements points, the pressure change diagrams as a function of time were made. Gas permeability P_{AIR} was determined as volume of gas passing through a membrane of unit thickness, per unit area and unit time, under unit partial – pressure difference between the two sides of the material.

3 Results and Discussion

3.1 Influence of POSS and Various Silicas on the Properties of Uncured Silicone Mixtures

In practice silicone elastomers are filled to increase their stiffness. In this case the mechanical and viscoelastic response of rubber composition is complicated, exhibiting numerous phenomena e.g. filler-filler and filler-rubber interactions. In our work three various fumed nanometric silicas Aerosil A90, Aerosil R812, Aerosil R812s were applied as a filler for

silicone rubber MVQ. Aerosil A90 is hydrophilic silica with the surface area SA_{N2} 87 m^2/g, as measured by BET method, Aerosil R812 (274 m^2/g) and Aerosil R812s (215 m^2/g) are silicas after treated with HMDS and demonstrated improved hydrophobicity. Surface area, particles size, the size of formed aggregates and surface energy are the key factors influencing the behavior of filler during processing with rubber. The presence of nanostructures with high surface area resulting in enhancement of the interphase contact between solid surface and elastomer chains and thus has strong impact on the viscoelastic behavior, viscosity and the reinforcing effect. One of the filler characteristics contributed to reinforcing effect is the tendency to create "filler particles structure" as a result of particle/particle interactions. This tendency can be estimated on the basis of the oil absorption parameters (OAP). The empty space (void volume) between aggregates and agglomerates linked together through physical interactions and creating network can be expressed as the volume of dibuthyl phthalate (DBP) absorbed by a given amount of filler (g DBP/100g filler). Ability of silica to create network structure in elastomer matrix via hydrogen bonds between silanol groups present on the silica surface is well known, the values of oil absorption parameter for silica Aerosil 90 (A90) was 285.1 g DBP/100 g filler. However silica A90 characterizes lower surface area, the tendency to form particle/particle interactions is stronger than for hydrophobic silicas Aerosil R812 (OAP = 228.6 g DBP/100g filler) and Aerosil R812s, (OAP = 219.7 g DBP/100g filler). Surface covering with hexadimethylsilazane (HDMS) reduced the amount of silanol groups on the silica surface causing the decrease of the oil absorption parameter (OAP) for both hydrophobic silicas.

The testing, how the additives to rubber formulation such as fillers influence on compound processing characteristics and mechanical properties, is very important for a manufacturing of rubber stuff with high quality. Uncured rubber behaves as a viscoelastic fluid during mixing and processing. Various test methods are useful to determine and control the rubber compound processability and achieve better processing conditions. We have adopted the "Rubber Process Analyzer" (RPA) - oscillating rheometers technique. This type of analyzer allows to study both elastic and viscous properties of elastomers through the application of a sinusoidal strain to an uncured rubber mixture molded in a sealed, pressurized cavity cone-cone shape. The RPA torsion-rheometer strains a sample in shear by oscillating the lower die sinusoidally. The upper die is fixed and connected with a measuring device, which records the applied bending moment S^*. After the application of sinusoidal strain to molded rubber test sample the complex torque response S^* is out-of-phase with the applied strain, this out-of-phase response is quantified by the phase angle δ. The elastic torque S' (in-phase with the applied strain), the viscous torque S'' (90° out-of-phase with the applied strain) are derived from the complex torque S^* and the phase angle δ. The storage shear modulus (G'), the loss shear modulus (G'') and the complex shear modulus (G^*) are calculated from [19–21]:

$$G' = k \cdot S'/strain \qquad (1)$$

$$G'' = k \cdot S''/strain \qquad (2)$$

Where k is a constant connected with the geometry of the die cavity.

$$G^* = \left[(G')^2 + (G'')^2 \right]^{1/2} \qquad (3)$$

The complex dynamic viscosity η* is calculated as follows:

$$\eta^* = G^*/\omega \qquad (4)$$

Where ω is the frequency of the sinusoidal strain in radians/second.

The results of RPA experiment are the shear storage and the shear loss modulus (G', G'') and the complex dynamic viscosity η* for one specified angular frequency. During one experiment more than one frequency can be investigated. Additionally this analyzer allows to study the cure behavior of rubber similar as ODR and MDR rheometers commonly used in rubber industry.

Viscosity is an important parameter in the evolution of the rheological behavior of filled silicone rubber. Rubber compositions are non-Newtonian fluids and show shear thinning characteristics, the reduction in measured viscosity with an increase in applied shear rate is observed. For processing of filled systems it is important to know how fast viscosity is reduced with increasing shear rate. In RPA analyzer the increasing of shear rate is done by increasing the frequency of the sinusoidal strain. Plotting the log of the complex dynamic viscosity against the log of frequency in radians/second usually gives a straight line, viscosity decreases according to the power law model. Rubber formulations containing various reinforcing fillers have different log-log slopes.

Figure 1 shows the results of RPA experiments at 80°C for the MVQ silicone rubber formulations filled with silicas. The high strain 100% was applied during the measurement. Application of higher strain more rapidly and effectively destroys silica aggregate-aggregate network which is formed in the rubber mixture during storage. As it can be seen at Fig. 1 the addition of silicas changed the viscosity profile of uncured silicone elastomer, the molded filled rubber behaved according to power law model in range of investigated frequency. The type of silica and their tendency to form aggregate-aggregate network influenced on the shear thinning characteristic of silicone rubber mixtures. The higher values of dynamic viscosity η* were observed for silicone rubbers modified by addition of 40 wt% of silica A90 and R812 although no
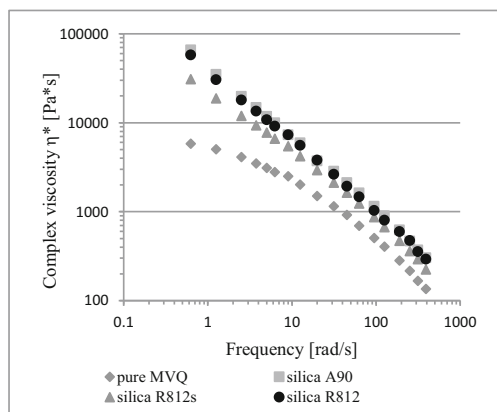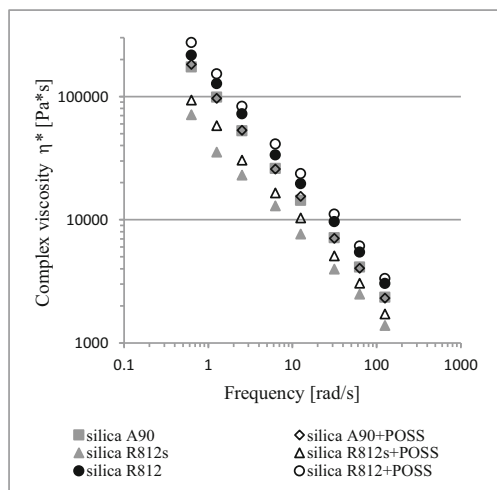
Fig. 1 Log-log plots of complex viscosity η^* (Pas) at 80°C in function of frequency ω (rad/s) for high strain (100%) RPA measurements

meaningful differences in shear thinning profiles between both appeared. The more fluid consistency of molded rubber for the same amount of filler and lower changes in dynamic viscosity η^* with increasing frequency occurred for silicone rubber containing silica R812s.
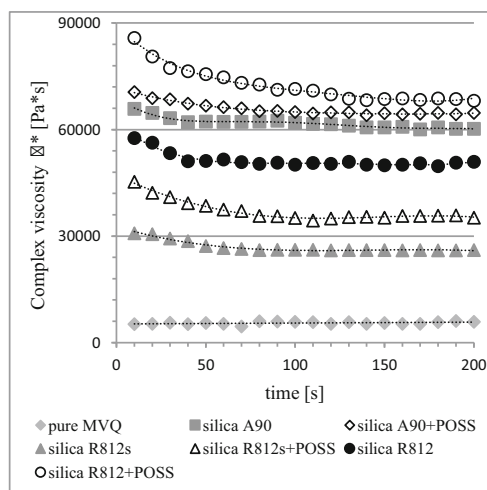
Figure 2 shows the results of RPA experiments at 80°C for the rubber formulations modified by the addition of allylisobutyl-POSS. The measurements were done at low strain 7% to avoid fast breaking of formed aggregate-aggregate network. The obtained results clearly illustrate that the addition of a small amount (3 wt.%) of nanometric POSS can significantly change the viscosity and the shear thinning characteristic of rubber formulation and hence the processing of the silicone rubber. The weakest influence on the dynamic viscosity η^* of silica filled MVQ rubber was observed after the addition of POSS particles to silicone rubber containing hydrophilic silica Aerosil A90. Among the silicone formulations containing only silica the highest values of complex viscosity η^* for studied frequency range were observed for MVQ mixed

with hydrophobic Aerosil R812 (measurement at low strain 7%, Fig. 2) and hydrophilic Aerosil A90 (measurement at high strain 100%, Fig. 1). Different tendency of silicas to create agglomerate-agglomerate network, the size of formed aggregates, their stability and time necessary to break the structure during application of strain are responsible for disparity in tendencies for A90 and R812 formulations measured at high (100%) and low (7%) strain.

To estimate the influence of tendency to create the agglomerate-agglomerate network and the actual structure of the applied fillers inside silicone rubber the measurements of complex viscosity η^* at constant oscillation frequency 0.1 rad/s and high strain (100%) during 200 seconds were carried out. The curves at Fig. 3 illustrate the changes in values of complex dynamic viscosity η^* for the same shear rate (constant values of frequency and strain) during time. The results indicated that the POSS moieties participated in filler-filler interactions. The addition of POSS to silica filled MVQ rubber caused a formation of the inter-aggregate associations, these aggregates formed by physical interactions were loosely linked together and the decrease of complex dynamic viscosity η^* due to the breakdown of agglomerate-agglomerate network after 100 seconds was observed. The stronger decrease of complex dynamic viscosity η^* during first 100 seconds of measurement was noted in case of silicone rubber containing hydrophobic silicas R812 and R812s indicating the presence of structure formed by easily destroyable aggregates at high strain. The nanometric primary particles of fumed silicas during the initial filler formation stage fuse together building up three dimensional branched clusters called aggregates. The amount of primary particles per aggregate may vary depending on surface activity of primary particles. These aggregates again may form loose or strong bonded agglomerates. It is assumed that the volume of dibutylphthalate DBP absorbed by a given

Fig. 2 Log-log plots of complex viscosity η^* (Pas) at 80°C in function of frequency ω (rad/s) for low strain (7%) RPA measurements

Fig. 3 The changes in values of complex dynamic viscosity η^* (Pa*s) for silicone formulations in function of time for the same shear rate RPA measurements (80°C, frequency 0.1 rad/s, strain 100%)

amount of filler, the oil absorption parameter (OAP) reflects structure as a whole, both aggregates and agglomerates. This parameter can be measured very precisely, but do not give any information about the changes in shape of the aggregates, which may influence the viscosity, furthermore it does not reflect the actual structure of filler inside rubber, medium with different surface energy and viscosity than DBP oil. The agglomerates may change their shape during mixing and preparation of filled rubber. It was not surprising that the measured OAP values did not correlate well in case of hydrophobic silicas R812, R812s with the tendency to form aggregate-aggregate association observed for the dynamic measurements (Fig. 3).

Rubber is viscoelastic material characterized by both viscous and elastic behavior in the uncured as well as in cured state. The elasticity of uncured rubber is mainly the result of chain entanglements. Tan δ defined as a ratio of loss modulus G'' to storage modulus G' has been found as a sensitive parameter indicating the differences in processing for rubber [20]. At a defined temperature, frequency and strain the uncured rubber with similar viscosity, but with higher values of storage modulus G' indicating higher elasticity and with the lower ratio of viscous component to the elastic one characterizes worse processability for the same processing conditions. As our measurements showed the applied silicas and POSS formed structured associations in silicone and influenced the complex viscosity. The storage shear modulus G' and loss shear modulus G'' for MVQ rubbers were measured at 160°C (temperature of curing), frequency 10 rad/s and low strain 7% using Rubber Process Analyzer RPA, tan δ was calculated (Table 1), the measurements were done during incubation time t_i, before the curing reactions started. Although the effect of the addition of active fillers as silicas on the storage shear modulus G' is well-recognized phenomena, still it is essential to study how changes in rubber formulation will influence the processability of rubber, its curing and the performance of the final product. The addition of silica to MVQ rubber causes the increase of complex shear modulus G^* and the storage shear modulus G' mainly as a result of three phenomenons: hydrodynamic effect resulting from the fact that filler is the rigid phase; occlusion of rubber on the filler surface (occluded rubber is shielded from deformation and therefore increases the effective filler content); formed filler network. The presence of these phenomenons depends on the nature of the filler, the factors such as: the primary particle size, specific surface area, surface activity and tendency to form aggregate-aggregate associations are important. Although the specific surface area of Aerosil A90 is lower than Aerosil R812s, the values of storage shear modulus G' of A90 filled MVQ rubber are significantly higher for the same filler loading. It should be kept in mind that measured surface area does not have to correlate exactly with the area actually occupied on filler surface by silicone in a mixture. The surface activity plays also very important role in filler-polymer interactions and formation of occluded rubber. These interactions can be attributed to physical (van der Waals, hydrogen bonds) as well as to chemical linkages or mixture of both. The surface of silicas R812 and R812s is modified by HDMS, the presence of different chemical groups on surface has a significant effect on viscoelastic properties of silicone. For both hydrophobic silicas values of tan δ at 160°C are higher than for MVQ containing Aerosil A90 indicating higher viscous quality and better processability. The mixtures containing Aerosil R812s, silica with higher organic phase (C) content on surface (4%) characterized the values of tan δ about 0.9 what confirms that on the viscoelastic behavior stronger influenced the surface activity of applied silica than its surface area. The addition of POSS caused additional increase of storage shear modulus G' and decrease of tan δ comparing to silicone mixtures containing only silica.

The influence of silicas and POSS on curing behavior of silicone rubber at 160°C were analyzed (Table 1). The scorch time $t_{\Delta 2}$ is the time required at a specified temperature for a rubber mixture to form initial stage of crosslinks. Usually peroxide crosslinked rubber has short scorch time $t_{\Delta 2}$. The peroxide curing reactions at given temperature 160°C started very fast and with short incubation time t_i (17 seconds). Application of fillers reduced scorch time of silicone rubber. The addition of POSS to the mixture caused further decrease of this parameter. Mixtures containing both hydrophobic silicas characterized slightly longer scorch time $t_{\Delta 2}$. The cure time is second very important parameter because a high cure time basically means lower profits. Parameter τ_{90} is the time necessary to reach a 90% state of cure. However applied silicas increased the τ_{90} parameter, from practical point of view it is advantage, too short cure time for thick rubber articles may cause the differences in cure state between the center and the surface of rubber articles resulting from a variable temperature heat history. The incorporation of POSS to silicone

Table 1 The values of shear storage modulus G' and tan delta δ, the minimum S_L' and maximum S_H' values of elastic torque, scorch time $t_{\Delta 2}$ and cure time τ_{90} for silicone formulations measured by RPA

	G' * kPa	Tan δ* -	S_L' dNm	S_H' dNm	$t_{\Delta 2}$ min	τ_{90} min	G' ** kPa
MVQ	12.0	1.24	0.15	2.94	0.89	2.38	75.2
A90	156.6	0.44	1.99	11.03	0.60	5.83	566.5
A90 POSS	171.9	0.41	1.75	10.95	0.48	7.06	720.5
R812s	53.5	0.92	0.80	8.51	0.69	5.24	520.1
R812s POSS	89.9	0.94	0.53	7.77	0.57	8.34	766.9
R812	215.3	0.58	2.69	13.10	0.69	4.55	674.6
R812 POSS	208.4	0.53	2.61	13.90	0.57	8.34	757.3

* measured before curing at 160°C (6.28 rad/s, 7%); ** measured after curing at 80°C (6.28 rad/s, 0.1%)

mixtures led to further increase of τ_{90} parameter. When discussing processability the ultimate state of cure is measured as the maximum of elastic torque ($S_H^{'}$). All investigated silicone mixtures reached a plateau of elastic torque $S^{'}$ during cure, the maximum values of elastic torque $S_H^{'}$ and the highest increment of elastic modulus during curing were noted for the silicone rubber filled with Aerosil R812.

In our work, POSS was incorporated into MVQ rubber together with silica, at 3 wt% loading. POSS molecules with reactive group such as allyl group containing unsaturated >C=C< bond are able to be bonded to the backbone of the polymer acting as side chains. Grafted particles acting as nano-reinforcement strongly influenced the properties of silicone even at low concentration. Strong increase of the storage shear modulus $G^{'}$ for formulations containing POSS after rubber curing was observed indicating that the grafting reactions occurred.

To estimate the influence of POSS addition on curing reactions of silicone rubber the first derivative of elastic torque $dS^{'}/dt$ versus reaction time was analyzed. The first derivative gives us information about how whether a function is increasing or decreasing, and by how much it is increasing or decreasing. With respect to the reaction speed which is given by the curves of first derivative of the elastic torque $dS^{'}/dt$ versus reaction time (Fig. 4) the addition of POSS to rubber mixtures significantly affected speed of curing particularly when POSS was added together with hydrophobic silicas R812, R812s. In

the presence of POSS the local maximum of the first derivative $dS^{'}/dt$ was achieved during shorter time indicating influence on the cure rate (the speed of cure), although the ultimate state of cure (the maximum value of the first derivative $dS^{'}/dt$) in every case was lower comparing to the mixtures containing only silica. After the maximum of the cure rate the further differences in the speed of the curing for the mixtures containing silica and POSS occurred. The faster speed of curing was recorded for the rubber containing POSS and hydrophilic silica A90 than for these containing POSS and hydrophobic silicas R812 and R812s. Differences in the cure rate between pure MVQ and filled MVQ also have been recorded. Comparing applied silicas, the slower cure rate during first minute of curing was noted for silicone rubber containing the hydrophobic silicas R812, R812s.

3.2 Crosslink-Density, Mechanical Properties and Payne's Effect of Cured Silicone Rubber

The crosslink density of cured elastomer can be estimated based on the swelling measurements. Crosslinked rubber absorbs solvent until the balance between the retractive forces in the extended molecular strands and the forces tending to swell the network is achieved. The Flory-Rehner's equation [22] is commonly used to determine the crosslink density based on the amount of swelling in toluene. The volume fraction V_R of

Fig. 4 Cure rate $dS^{'}/dt$ (dNm/min) for silicone formulations measured by RPA at 160°C (**a-d**)
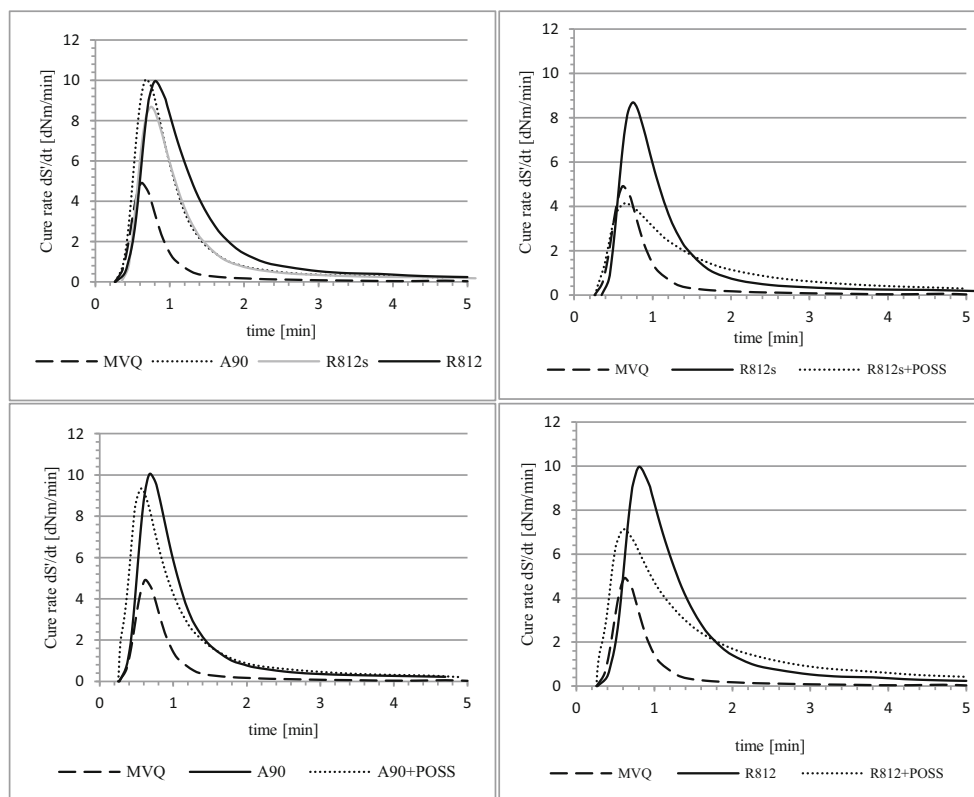
rubber in the swollen gel was calculated from the equation as follows:

$$V_R = \frac{(D-FH)/\rho_R}{\frac{D-FH}{\rho_R} + A_0/\rho_S} \qquad (5)$$

where H is initial weight of rubber sample, D is constant weight of deswollen specimen, F is weight fraction of insoluble additives such as fillers, A_0 is weight of the absorbed solvent (A_0 – immediate weight after removing from solvent minus initial weight of rubber sample H), ρ_R is rubber density, ρ_S is density of the solvent. The classical Flory-Rehner equation at swelling equilibrium condition is expressed by:

$$-\left[\ln(1-V_R) + V_R + \chi V_R^2\right] = \frac{\rho_R}{M_C}V_S\left(V_R^{\frac{1}{3}} - \frac{2V_R}{f}\right) \qquad (6)$$

where f is cross-linking functionality. Swollen network can be described by phantom network model as follows:

$$-\left[\ln(1-V_R) + V_R + \chi V_R^2\right] = \frac{\rho_R}{M_C}V_S\left(1 - \frac{2}{f}\right)V_R^{\frac{1}{3}} \qquad (7)$$

According to the model expressed by above equation the crosslink density ν_T can be calculated from:

$$\nu_T = \frac{1}{2M_C} = -\frac{\ln(1-V_R) + V_R + \chi V_R^2}{V_S \rho_R \left(V_R^{\frac{1}{3}} - \frac{V_R}{2}\right)} \qquad (8)$$

where V_R is the volume fraction of rubber in the swollen samples, χ is the Flory-Huggins polymer solvent interaction parameter for MVQ rubber [23], M_C is the molecular weight between cross-links, V_S is the molar volume of the solvent.

The percentage of non-covalent crosslinks present in cured rubber was determined by decomposition of present ionic crosslinks under the ammonia vapor treatment (ν^*) and was calculated according to the equation [23]:

$$\nu^* = \frac{\nu_T - \nu_A}{\nu_T} \cdot 100\% \qquad (9)$$

where ν_A is the crosslink density determined for samples treated with ammonia, ν_T is the crosslink density determined for samples swollen in toluene.

Calculated values of crosslink density are compiled in Table 2. The conclusions from analysis of the Fig. 4 are confirmed by the results of crosslink density measurements. The differences in curing behavior was observed between the silicone mixtures containing hydrophobic silicas R812, R812s and this containing hydrophilic silica A90, resulting in changes in the crosslinks network structure of vulcanizates. The crosslink density of vulcanizates calculated from the equilibrium swelling in toluene is almost 200% higher after incorporation of the same amount of silica A90 than silicas R812s and R812. The calculated percentages of non-covalent crosslinks which are destroyed after ammonia treatment in the total amount of crosslinks are more than 50% for vulcanizates containing silica A90 and between 25 – 30% for these containing hydrophobic silicas. The modification of silica surface with HDMS influences the surface activity of silica, the polar –OH groups present on silica surface which are able to form physical interactions with polymer are blocked resulting in smaller amount of non-covalent crosslinks. From the other hand also observed changes in peroxide curing profile affected the total amount of crosslinks ν_T and the crosslink density determined for samples treated with ammonia ν_A, the values of both parameters indicated that in case of silicone filled by hydrophobic silicas R812 and R812s the lower amount of covalent bonds in cured network is formed. The incorporation of POSS to R812 and R812s filled silicone rubber increased the total amount of crosslinks ν_T.

Table 2 Crosslink density calculated from the swelling measurements in toluene ν_T and determined for samples treated with ammonia ν_{NH3}, the percentage of non-covalent crosslinks ν^* and mechanical properties of silicone rubber

	$\nu_T *10^{-5}$ mole/cm^3	$\nu_{NH3}*10^{-5}$ mole/cm^3	ν^* %	SE_{100} MPa	TS MPa	E_B %	RI_{TS}
MVQ	9.2±0.1	8.1±0.1	11.9	0.25±0.01	0.42±0.04	285±57	-
A90	30.2±0.2	14.4±0.3	52.3	1.67±0.10	4.59±0.28	303±107	4.37
A90 POSS	26.6±0.2	13.2±0.2	50.4	1.71±0.05	5.95±0.34	285±18	6.09
R812s	13.3±0.1	9.7±0.3	27.1	0.73±0.04	8.35±0.33	821±20	7.95
R812s POSS	14.4±0.1	10.1±0.1	29,9	0.75±0.04	7.90±0.29	729±16	8.09
R812	15.3±0.2	11.0±0.1	28.1	0.93±0.04	9.31±0.43	701±23	8.87
R812 POSS	17.8±0.1	13.3±0.1	25.3	1.06±0.09	9.56±0.38	617±38	9.79

Having established the influence of various silicas on the vulcanization process and crosslink density of cured rubber, we then examined their mechanical properties (Table 2). For rubber as a parameter estimating the reinforcing effect of various fillers and their mixtures the reinforcing index RI (equation 10) proposed by S. Kohijya and Y. Ikeda [24] can be used.

$$RI = \frac{N}{N_0} \cdot \frac{m_F}{100} \tag{10}$$

Where N, N_0 are values of selected mechanical parameters for vulcanizates filled and without fillers adequately, m_F is mass of fillers added.

It can be clearly observed that the incorporation of hydrophobic silicas R812 and R812s had stronger impact on the tensile strength TS of cured silicon, the values of RI_{TS} increased indicating stronger reinforcing effect. Dispersion of the filler is one of the parameters which strongly influences on the tensile strength TS of cured rubber. The mixing and dispersing of both hydrophobic silicas in silicone rubber was easier, as we described above these silicone mixtures characterized better processability parameters, the facilitated dispersion is responsible for higher values of tensile strength. The significant increase of modulus at 100% elongation for silicon rubber containing Aerosil A90 resulting from the increase of crosslink density. As it was expected the modification of silicas with HDMS led to obtain vulcanizates with different static stress-strain behavior (low values of modulus at 100%, higher values of tensile strength, higher values of elongation at break E_B) comparing to silicone rubber containing unmodified silica A90 (high value of modulus at 100%, lower values of tensile strength, value of elongation at break E_B similar to unfilled silicone). The incorporation and grafting of small quantities of POSS restricted motion of elastomer chains under strain causing decrease of elongation at break E_B comparing to vulcanizates without POSS. The reinforcing indexes RI_{TS} increased.

Concisely it can be stated that the "reinforcing effect" means significant enhancement of tensile strength, abrasion resistance, tear resistance and modulus more than the values resulted from hydrodynamic effect (the effect caused by colloidal spherical particles). The addition of chosen silicas and POSS had a strong impact on the static behavior of cured silicone elastomer. In real conditions the rubber components are deformed dynamically, therefore the effect of strain amplitude on the dynamic modulus should be analyzed to estimate the influence of filler on cured rubber. The reinforcing effect of various fillers on rubber properties can be also estimated based on the analysis of Payne's effect [17]. The Payne's effect is directly related to the dynamic properties of the cured rubber, this phenomena is difficult to measure in tension, useful mode to study the Payne's effect are measurements in shear

as it is possible using oscillation rotational rheometer Ares G2. A.R. Payne defined the Payne's effect as the difference between the estimated values of shear modulus G_0 at 0% of oscillation strain and the values of shear modulus G_∞ at infinite strain, in practice to measure the Payne's effect in cured rubbers the differences (decrease of the value) between shear modulus G^* at 0.01% and 50% under dynamic shear deformation can be used in comparative studies of cured rubbers reinforced with various fillers. The strain dependence of the complex shear modulus G^* and the loss factor tan δ for silicone rubbers are shown at Figs. 5 and 6. Similar to the Payne's model the strain-independent part of the complex modulus G^* at low oscillation strain is observed. Higher values of complex modulus comparing to pure silicone resulting from: the combination of the polymer network which depends on the crosslink density of cured rubber; the hydrodynamic effect; and the contribution from "the effect of the structure" which is attributed to a combination of the structure formed between the filler particles and the filler-rubber interactions (the occluded rubber). The adsorbed and physically bonded on filler surface rubber is shielded from deformation and thus increases the effective filler content. Possible mechanisms for the decrease of complex shear modulus G^* as the deformation increases are: the destruction of a filler associations forming network structure; adsorption-desorption of elastomer chains occurring at the filler interface; disentanglement of bulk polymer from the rubber bonded to the surface of filler; strain-softening of the polymer shell surrounding the particles surface. The unfilled rubber shows no indication of non-linearity up to 9% of oscillation strain. Addition of fillers led to the increase of complex shear G^* modulus due to the mechanisms described by us above.

The comparison of the curves of the filled vulcanizates displays the differences in values of G^* for three silica grades with varied surface characteristics and surface area. However the surface area of R812 and R812s silicas was higher than hydrophilic Aerosil A90, the values of G^* modulus at low
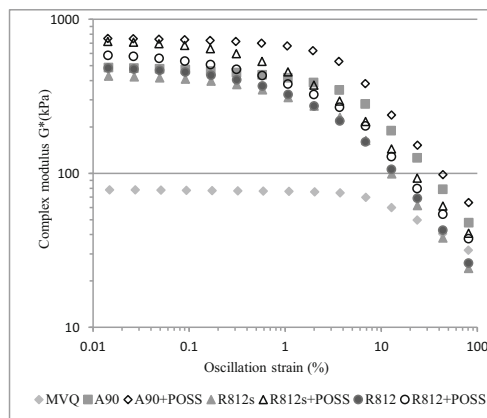
Fig. 5 The complex shear modulus G^* (kPa) as a function of oscillation strain (%) measured for cured silicone at 25°C, frequency 10 rad/s

Fig. 6 a-d Tan δ as a function of oscillation strain measured at 25° and 100°C for silicone rubber
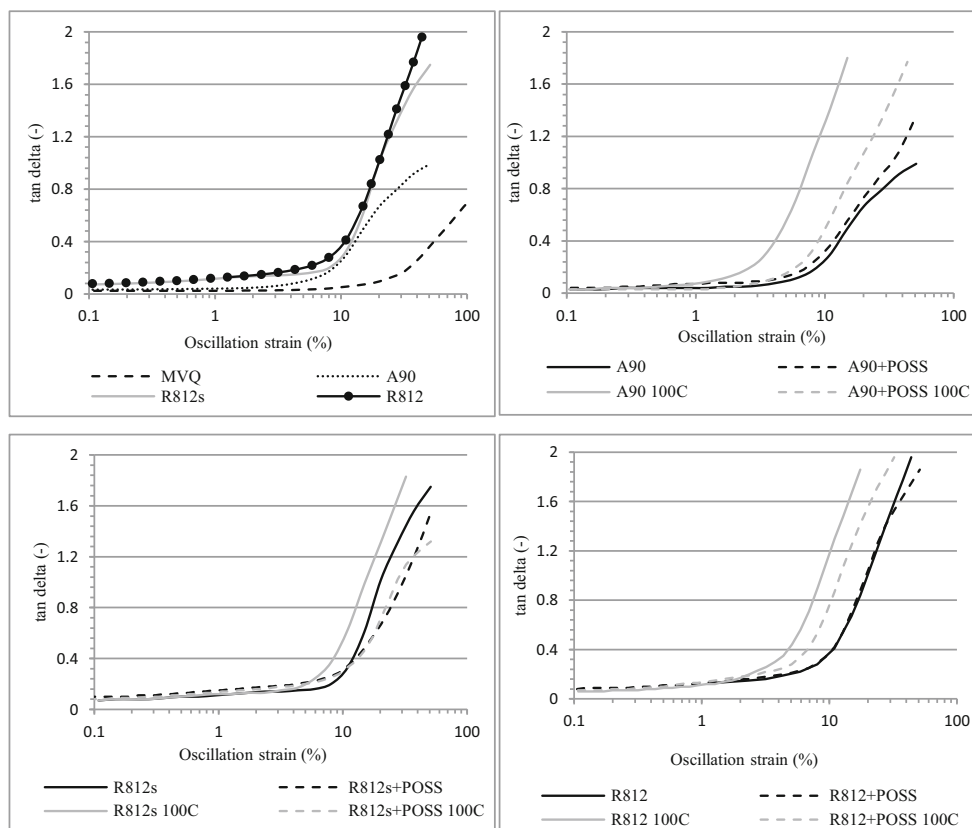
strain (0.01%) for silicone rubber containing R812s were lower and for silicone rubber containing R812 were almost similar to this observed for A90 (Table 3), as we described earlier, the measured surface area do not have to correlate exactly with the surface occupied by rubber chains and the amount of occluded rubber. Certainly, the extent of filler network is more pronounced, when the surface area rises but the probability for the formation of a filler-filler network and filler-polymer interactions is significantly influenced by the presence of chemical groups able to form the physical or chemical bonds on the filler surface. Analyzing the linear part of complex modulus G^* and the decrease in values of G^* modulus occurring for the

1% and 10% of strain (Table 3) it can be stated that the reduction in complex modulus G^* level at low strain due to the breakdown of the continuous filler network into subnetwork occurred in higher extent for the hydrophobic silicas. Additionally the polymer chains movement upon straining was facilitated. It can be understood that filler-filler and filler-polymer interactions are competitive in certain way. Increase of surface activity can lead to facilitation of occluded rubber formation during mixing with rubber phase preventing the filler-filler network formation. The crosslink density of A90 reinforced silicone rubber was higher due to higher amount of non-covalent, ionic crosslinks, in this case the

Table 3 Values of complex shear modulus G^* at 0.01 and 100% of strain and decrease of complex shear modulus ΔG^* for 1, 10 and 50% of strain

	$G^*_{0.01\%}$ at 25°C kPa	$G^*_{100\%}$ at 25°C kPa	$G^*_{100\%}$ at 100°C kPa	(A) ΔG^* at 25°C kPa	(B) ΔG^* at 25°C kPa	(C) ΔG^* at 25°C kPa
MVQ	78.3	29.7	24.3	0.6	15.6	39.9
A90	486.3	43.3	16.9	70.0	275.3	417.7
A90 POSS	754.7	58.0	39.1	82.1	487.2	666.5
R812s	428.9	21.6	13.0	118.9	315.6	395.0
R812s POSS	721.6	36.7	30.3	265.2	561.0	666.2
R812	485.3	23.1	14.2	160.9	367.2	447.6
R812 POSS	587.2	34.3	26.1	207.4	440.6	537.5

Measurements were done at 25°C and 100°C using 10 rad/s frequency

(A) $\Delta G^* = G^*_{0.01\%} - G^*_{1\%}$; (B) $\Delta G^* = G^*_{0.01\%} - G^*_{10\%}$; (C) $\Delta G^* = G^*_{0.01\%} - G^*_{50\%}$

polymer network contribution and "in-rubber" structure resulting from the filler-polymer interactions in complex modulus G^* were more pronounced than for hydrophobic silicas. This is confirmed by the final values of the complex modulus G^* at high 100% strain and the tan δ curve versus strain (Fig. 6). The lower values for tan δ, the lower energy dissipation for all deformation is a consequence of the stronger physicochemical interactions occurring between Aerosil A90 and silicone rubber than for hydrophobic silicas R812, R812s.

As expected grafting of allyl-POSS led to meaningful enhancement of the complex modulus G^* level, these changes in complex modulus behavior can be attributed to increased interactions with the rubber phase. The dynamic studies confirmed that the POSS moieties can act as a nano-reinforcement, which significantly influences the dynamic properties of silicone rubber.

The linkage between filler and polymer, the presence of grafted nanostructures with bonding of chemical nature can restrict the mobility of polymer chains, therefore polymer segments cannot undergo surface displacements by molecular slippages. The higher the temperature the higher the mobility of the polymer chains and as a consequence the faster desorption of polymer chains from filler surface under strain. In order to study the influence of silicas and POSS on silicone rubber the values of complex modulus G^* at high strain (100%) at 100°C were measured. The complex modulus at high strain indicates the real "In-rubber" structure which can be understood as the extent of filler-polymer interactions. As can be seen in Table 3 only the silicone rubber with POSS shows at 100°C the enhancement of the complex modulus G^* at 100% strain comparing to pure MVQ. The decrease of the G^* values at 100°C comparing to room temperature, with particularly strong decline in value observed for A90 reinforced silicone, indicated the higher desorption rate of polymer segments from silica surface caused by temperature. The enhancement of the high strain modulus G^* by incorporating POSS into rubber is attributed to the formation of stronger "in-rubber" structure, the presence of chemical bonds between POSS and silicone chains instead of physical bonds restricted the mobility of the polymer chains and prevented their desorption at higher temperature. The tan δ measured for temperature 100°C in function of oscillation strain were analyzed. As it can be seen at Fig. 6 the behavior of filled rubber modified by POSS at 100°C varied comparing to silicone reinforced only with silicas. As expected the tan δ curve versus strain gave for all deformations distinctly lower values for formulations containing POSS as a consequence of the strong physicochemical interactions with the polymer resulting from the grafting of nanofillers particles into rubber network. However silicas (especially Aerosil 90) as a filler itself showed a very strong filler networking and ability to form the physical interactions with the polymer at higher temperature 100°C the breakdown of

the inter-aggregate bonding of the silica and the desorption of silicone chains from the surface occurred faster and at lower values of strain. The higher values of tan δ versus strain curves at 100°C were observed indicating stronger energy dissipation for silicone rubber reinforced only with silica.

3.3 Wettability and Air Permeability Characteristic of Cured Silicone Rubber

The addition of second inorganic phase into homopolymer changes the bulk properties of material but also influences the surface properties such as the surface wettability. The surface behavior of the samples was investigated through measurements of contact angles against water and the results are presented in Table 4. The basic Young's equation relating the surface free energy of solid (γ_S) and that of the liquid in contact with the solid (γ_L), the interfacial free energy between the solid and the liquid (γ_{SL}), and the contact angle (θ) is given by [25]:

$$cos\theta_{\gamma_L} = \gamma_S - \gamma_{SL} \tag{11}$$

The larger the water contact angle, more is hydrophobic surface. It was observed that the silicone formulation containing hydrophilic silica Aerosil A90 characterized significantly lower water contact angles indicating better wettability (Table 4). No significant differences in contact angles of water for pure silicone and that containing hydrophobic silicas R812 and R812s were noted. Also the incorporation of POSS into silicone rubber formulation did not affected the surface wettability, the static water contact angles for samples containing POSS were similar to these containing only silica.

Gas permeability is a measure of the ease with which gas can penetrate through the polymer sample. Permeability is the amount of gas which, under steady conditions, crosses unit area and unit thickness of the sample in unit time under unit pressure difference and at constant temperature.

Table 4 Static water contact angle θ and the gas permeability coefficient P_{AIR} for silicone rubber

	Static water contact angle θ °	P_{air} mole/(m*s*Pa)
MVQ	120.0±0.8	$1.5*10^{-11}$
A90	113.8±0.7	$6.6*10^{-12}$
A90 POSS	113.4±1.3	$7,3*10^{-12}$
R812s	121.3±0.8	$8,4*10^{-12}$
R812s POSS	121.3±2.3	$8,3*10^{-12}$
R812	120.2±0.8	$8,1*10^{-12}$
R812 POSS	121.0±0.3	$7,5*10^{-12}$

For one-dimensional steady-state mass transfer the permeability coefficient (P) is related to the quantity of permeate transferred through the membrane [26] as follows:

$$P = \frac{Qx}{At\Delta p} \tag{12}$$

where, Q – amount of permeate passing through the material, x is thickness of polymer film, A is surface area available for mass transfer, t is time and Δp is the change in permeate partial pressure across the film. The gas permeability coefficient of filled silicone rubber was calculated according to [27]:

$$P_{AIR} = GTR \cdot x = \frac{V_C}{RTP_{UA}} \cdot \left(\frac{dp}{dt}\right) \cdot x \tag{13}$$

where x is the thickness of sample, GTR is the gas transmission rate, V_C is the volume of low pressure chamber, R is the gas constant, T is temperature of measurement (K), P_U is the pressure of gas in high pressure chamber (atmospheric pressure chamber), A is area of disc-shaped sample forming a barrier to air, dp/dt is the rate of pressure rise in low pressure chamber.

Calculated air permeability coefficients for silicone rubber are compiled in Table 4. As it was expected permeability analysis indicated that the addition of filler decreased the constant rate of gas diffusion and gas permeability coefficient P_{AIR} comparing with the reference sample pure silicone rubber. The best barrier properties are observed for silicone rubber containing Aerosil A90. The tendency of air permeability coefficients decrease is in accordance with the crosslink density of rubber, the higher crosslink density of cured rubber the lower P_{AIR} coefficients, indicating that the effect of permeability decrease is connected not only with the presence of the solid particles but also with their tendency to form strong interactions with polymer.

4 Conclusions

For determination of the viscoelastic properties of rubber mixtures, torsional rheometers are required. Rubber Process Analyzer RPA allows to study the viscoelastic properties in uncured as well as in cured state. In this paper three different silicas varied in surface area and surface characteristics were applied as reinforcement for peroxide cured silicone rubber MVQ. Surface modification of silica influenced shear thinning characteristics, complex viscosity η^* and processability of uncured reinforced silicone rubber at 80°C. The presence of structure formed by more easily destroyable at high strain aggregates was indicated for modified, hydrophobic silicas Aerosil R812 and R812s comparing to hydrophilic Aerosil

A90. The results clearly indicated that the addition of POSS led to increase of the complex viscosity of silicone rubber. Additionally the curing behavior of silicone rubber was influenced by the presence of POSS molecules, the mixtures characterized reduced scorch time $t_{\Delta 2}$, longer optimum cure time τ_{90}. The analysis of cure rate showed that the POSS molecules and type of silica used significantly affected speed of curing, the faster speed of curing was recorded for silicone rubber containing hydrophilic silica A90 and POSS. Significant increase of the complex modulus G^* can be attributed to the formation of chemical linkage between POSS and silicone chains. The modification of silica and lower amount of the polar –OH groups on surface caused the changes in network structure of silicone vulcanizates, smaller amount of non-covalent crosslinks was formed. Meaningful enhancement of tensile strength TS after incorporation of Aerosil R812 was observed. The analysis of Payne's effect revealed that the decrease of complex modulus G^* values at low strain due to the breakdown of the filler network occurred in higher extent for the hydrophobic silicas, for the silicone rubber reinforced by hydrophilic silica A90 more predominant were the filler-polymer interactions and occluded rubber formation. Significant increase of complex modulus G^* attributed to formation of chemical linkage between POSS and silicone chains was observed. Grafting of POSS influenced the dynamic behavior of rubber at higher temperature (100°C). The chemical bonds restricted the mobility of the polymer chains and prevented their desorption from filler surface. Lower values of the tan δ at 100°C for all deformation for formulation containing POSS compared to the formulations reinforced only by silica were observed.

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