

Reinforcement of Rubber by In-situ Formed Silica

Magdalena Lipińska¹, Marian Zaborski²

¹Institute of Polymer and Dye Technology, Lodz University of Technology, Lodz, 90-924, Poland, magdalena.lipinska@p.lodz.pl

²Institute of Polymer and Dye Technology, Lodz University of Technology, Lodz, Poland, 90-924

Abstract— Silica with various surface morphology was synthesized by sol-gel reactions, tetraethoxysilane TEOS was used as a precursor of silica synthesis. To influence on morphology and surface characteristics the sol-gel reactions were modified by the presence of dispersing agents, anionic, cationic and non-ionic surfactants. Application of surfactants had an effect on the shape, morphology and size of synthesized silica particles. The reaction was conducted in decade (non-polar medium chosen as an elastomer model) and “in-situ” in two differ in polarity elastomers, ethylene-propylene rubber EPM, and hydrogenated butadiene-acrylonitrile rubber HNBR. The sol-gel reactions in elastomeric matrix were catalyzed by swelling the elastomers containing various amount of tetraethoxysilane TEOS in carbon dioxide or by the influence of the atmosphere of high moisture 70% or ammonia vapor. Silica particles formed in-situ in rubber matrix resulted in increase of tensile strength TS of rubber vulcanizates.

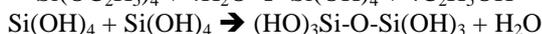
Keywords— Sol-gel reactions, rubber, nanocomposites, nanometric fillers, silica, tetraethoxysilane.

I. INTRODUCTION

The properties of various polymers and elastomers usually are modified and improved by the presence of an inorganic fillers. Investigation of many researchers has been focused on the synthesis of the reinforcing nanoparticles directly in various polymer matrices [1-6]. These hybrid inorganic-organic materials belong to nanocomposites because of the small size of formed inorganic structures within an organic polymer matrix. In situ synthesis of the nanometric filler is a novel way to obtain nanocomposite with a specific degree of filler dispersion. Formation of nanoparticles directly in matrix allows to overcome the problems with the poor compatibility of filler with polymer during mixing in molten state causing the agglomeration of nanoparticles and the deterioration of composite properties. In sol-gel processes as a precursors able to undergo the hydrolysis and condensation reactions resulting in an inorganic phase formation the alkoxy derivatives of metals are applied [7]. The metal alkoxides $M(OR)_n$ in presence of a small amount of acid or base catalyst are hydrolysed and metal hydroxides $M(OH)_n$ are formed according to the reaction [3]:



where $M = Na, Ba, Cu, Al, Si, Ti, Ge, V, W, etc., R = CH_3, C_2H_5, C_3H_7, C_4H_9, etc.$ Formed $M(OH)_n$ undergoes condensation reactions with $M(OR)_n$ or $M(OH)_n$ forming reactive, three-dimensional network containing $-O-M-O-M$ linkages. Depending on the nature and reactivity of the inorganic precursors and process parameters such as: the type of catalyst, presence of water, pH, temperature different fillers with various morphology and functionality can be created [6]. The most common precursor for silica particles in-situ formation is tetraethoxysilane TEOS [6-9]. The formation of silica particles involves the catalytic hydrolysis and condensation of tetraethoxysilane also known as tetraethylorthosilicate TEOS according to reaction [9], [10]:



The aim of the present investigation was to carry out the in-situ synthesis of silica particles via sol-gel reactions in two

elastomers differ in polarity ethylene-propylene elastomer EPM and hydrogenated butadiene-acrylonitrile rubber HNBR. It should be taken into consideration that many factors can influence on sol-gel chemistry and the silica formation in molten polymers and elastomers, among them the dispersion of inorganic precursors in matrix, their thermal stability, the effect of polymer crystallization on the final nanocomposite morphology. Two methods of in-situ silica synthesis in elastomers are reported in literature [10], in first method the filler is created before the curing of elastomer, in second method the sol-gel reaction are carried out in crosslinked elastomer. In second method the rubber sample is placed in solution of inorganic precursor and catalyst until the swelling equilibrium is reached, then the swollen sample is placed in an aqueous environment at higher temperature. This method was applied by Dewimille et al. [11] to create in-situ silica particles in poly (dimethylsiloxane) PDMS, the applied catalysts (tin catalysts, DEA) influenced the morphology of formed silica particles. It was found that the use of the pre-hydrolyzed TEOS facilitated the silica formation in crosslinked poly (dimethylsiloxane) PDMS and resulted in higher thermal stability and mechanical properties of PDMS composites [12]. Size of formed silica domains was 200 nm. The two-step method, first swelling uncured natural rubber NR sheet in TEOS, then swelling NR sheet in the aqueous solution of n-butylamine was reported [13]. The presence of in-situ generated in NR rubber silica particles was confirmed by transmission electron microscope TEM [13]. The filling of styrene graft natural rubber with in-situ formed nanosilica particles (40 nm) was obtained using the latex solution method in which the high ammonia NR latex containing 60% of dry rubber content was used. TEOS together with the styrene monomer was added to rubber latex and the graft copolymerization and sol-gel reaction were proceeded simultaneously [14]. Additionally the sol-gel process in solid rubber was performed in which the uncured rubber sheets were immersed in TEOS and in an aqueous solution of n-hexylamine at 40°C. The mechanical properties of the nanocomposites prepared using latex and solid rubber were comparable [14]. According to Ikeda and Kohjia studies [15]

in-situ silica filling of sulfur-cured butadiene rubber BR using the swelling in TEOS method improved the mechanical properties. The tensile and dynamic behavior of in-situ filled BR samples were better comparing to conventional BR vulcanizates prepared by mechanical mixing of the filler particles and having the same amount of silica. Authors [15] reported that size of obtained silica particles was influenced by the crosslink density of rubber network in which they were formed. Silica filled ethylene-propylene-diene EPDM nanocomposites were prepared via reactive batch mixing in mixer and reactive extrusion [16], in both methods TEOS and catalyst solution were added during rubber mixture processing after the plasticization of rubber at higher temperature and the mixture was subjected to homogenization until the stable values of torque were achieved. The sol-gel reaction were carried out during processing of rubber using longer time of mixing and 80°C temperature. Materials obtained via reactive batch mixing showed a significantly higher silica content for a similar reaction time as compared to composites prepared using a diffusion process (swelling method) under static conditions [16]. The dispersion of in-situ formed silica (3.2 wt%) in reactive extrusion characterized uniform distribution of silica particles, the mechanical properties of nanocomposites were similar to properties of conventional EPDM rubber containing 10wt% of added during extrusion silica [16]. Pietrasik et al. [17] investigated the molecular dynamics of carboxylated acrylonitrile-butadiene rubber-silica hybrid synthesized using as a silica precursor varied amount of N-(2-aminoethyl)-3-aminopropyl-trimethoxysilane DAMS, serving also as a cross-linker. It was found that silane influenced the crosslink density of rubber, the cross-links had ionic nature, filler-filler and filler-rubber interactions were present, due to the specific nature of obtained materials [17]. According to authors mentioned above the few key issue are important when preparing in-situ silica filled nanocomposites, among them are: controlling of alkoxyane precursor amount in order to obtain the desired silica content and the type of catalyst which strong influences the size and morphology of in-situ generated silica particles. The aim of our studies was to synthesize using TEOS as a precursor the well-dispersed silica filler in two elastomers differ in polarity ethylene-propylene copolymer EPM and hydrogenated butadiene-acrylonitrile rubber HNBR. Furthermore various stabilizers and dispersing agents were applied to develop the sol-gel reactions and to change the size and morphology of formed silica. To catalyze the sol-gel reaction the rubber mixtures were swelled in carbon dioxide atmosphere and immersed in atmosphere with high moisture 70% or ammonia vapor. The decane was chosen as a model solvent in which additionally the sol-gel reaction were conducted in presence of various stabilizers. The morphology of obtained silica fillers and influence of nanofillers on the properties of rubbers were studied.

II. EXPERIMENTAL

A. Materials

As a precursor in in-situ synthesis of silica tetraethoxysilane TEOS (Sigma-Aldrich) was used. The

morphology and size of formed silica particles were modified by use of various catalysts and chemicals.

Alkyl ammonium chloride and bromide salts as follows:

- trimethylhexadecylammonium bromide,
- trimethyldodecylammonium bromide,
- dimethyldidodecylammonium bromide,
- benzylododecyltrimethylammonium bromide,
- trimethyldodecylammonium chloride,
- tetradodecylammonium chloride

produced by Sigma-Aldrich.

Cationic, anionic, non-ionic dispersants as follows:

- triethanolamine,
- octadecylamine,
- magnesium stearate,
- zinc stearate,
- 4-nonylphenyl-polyethylene glycol

produced by Sigma-Aldrich.

Hydrogenated acrylonitrile-butadiene rubber HNBR (Therban 3407, Arlanxeo) containing 34 ± 1.0 wt.% acrylonitrile (ISO 24698-1) and $\leq 0.9\%$ of residual double bonds after hydrogenation was obtained from Arlanxeo, ethylene-propylene copolymer EPM (Dutral CO 054) containing 41 wt.% propylene was produced by Versalis Sp.A. Composites were crosslinked with 3 phr of (bis(1-methyl-1-phenyl-ethyl) peroxide) DCP (Sigma-Aldrich).

B. Synthesis of Silica Particles in Decane

Synthesis of silica particles in the decane, being a model of the elastomer environment, was carried out using traditional sol-gel catalyst, ammonia and autocatalysed with various types of chemicals (described in section materials) in presence of moisture. For this purpose in a 500 ml flask, 50 ml of decane, 25 ml of tetraethoxysilane (TEOS) and 1.75 g of various dispersants were placed. The process of mixing was carried out in an oil bath using a reflux condenser at 160°C for 30 minutes (the parameters of temperature and time usually used during peroxide curing of elastomers). The emulsion obtained was allowed to stand in open flask for two weeks to precipitate the silica, during this time was mixed. After two weeks the obtained solid was filtered and dried in an oven at 100°C during 24h.

C. Synthesis of Silica Particles in Rubber Matrix

The rubber mixtures containing various amount of tetraethoxysilane TEOS were prepared using laboratory two-roll mill (temperature 40°C, friction ratio 1:1.2, dimension of rolls- diameter 200 mm, length 450 mm) during 20 minutes. The composition of rubber mixtures was as follows: HNBR or EPM 100 phr, TEOS 0, 5, 10, 15, 20 phr, dicumyl peroxide DCP 3 phr, Prepared rubber mixtures were swelled in supercritical carbon dioxide during 5h or they were immersed in ammonia saturated atmosphere 24h or in atmosphere with 70% of moisture at 40°C during 14 days. After the swelling rubber mixtures were dried and cured at 160°C for time necessary for a torque increase of rheometric moment by 90% (τ_{90}).

D. Characterization

The size of synthesized in decane silica was determined using a Zeta Sizer Nano Series S90 (Malvern Instruments). The measurements were based on the DLS (Dynamic Light Scattering) method for the dispersion of silica in decane. The measurements were done for the sample taken from reaction flask for silicas obtained after 72h and after 14 days.

The zeta potential in function of pH for the silica water dispersion (1g/L) was determined by Zetasizer 2000 (Malvern Instruments) equipment. The pH was changed by addition of HCl and NaOH solution.

Rheological properties of silica suspension in paraffin oil (concentration 2g SiO₂/100ml oil) were studied using rotational viscometer RM 500 (Rheometric Scientific), concentric cylinder measuring geometry (CC25) was used, the range of applied shear rate was: 0.1 – 120s⁻¹, time of measurement 600s, temperature 20°C.

Morphology of silica particles and their surface structure were examined using scanning electron microscope LEO 1530 (Zeiss), samples with graphite coated surface were used in these investigation. In case of vulcanizates the surfaces formed after liquid-nitrogen fracture was examined.

The ODR rheometer W2 (Metalchem) was used to characterize curing of EPM, HNBR composites. The curing studies were done at 160°C according to ASTM D5289. The optimum cure time (τ_{90}), minimum torque (M_{min}), maximum torque (M_{max}) were calculated based on the curing curves. The compounded blends were molded and vulcanized 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).

The network structure was analyzed according to ASTM D 6814-02 standard. Weighed rubber samples were swollen at room temperature (25°C) in solvent (reagent grade purity toluene) for the time necessary to achieve weight balance of swelled samples (48h). The solvent were replaced with fresh toluene from time to time. After swelling the excess liquid was removed from the surface of the specimens with a soft paper towel and the samples were weighed. 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 weighed again.

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 prepared according to ISO-37-2005 standard. Five different specimens were tested and the average value for each formulation was reported. The tearing behavior was determined according to PN-ISO 34-1:2007 standard.

III. RESULTS AND DISCUSSION

A. Properties of Silica Synthesized in Decane

The particle size of the synthesized silica in decane (as an elastomer model) was determined after 72 hours (3 days) from

the beginning of sol-gel reactions. Synthesis of silica using silane precursor (TEOS) was catalyzed with ammonia and autocatalysed with dispersants. After 72 hours from the start of the sol-gel reaction, a sample was taken from the decane suspension and for the mixture the particle size was measured. In Fig. 1 is shown the number percentage in function of size of particles for silicas obtained in presence of various alkyl ammonium chloride and bromide salts. The character and structure of dispersants had an effect on the size of silica particles. Addition of trimethyldodecyl ammonium chloride and tetradodecyl ammonium chloride led to slowing down sol-gel reaction, silica particles obtained after 72 hour characterized the smallest particles size, for tetradodecyl ammonium chloride 50% by number of silica particles had diameter of 2 nm, for trimethyldodecyl ammonium chloride 50% by number of silica particles had diameter of 5 nm. We observed the influence of alkyl ammonium bromide salts structure on formation of silica particles in sol-gel reaction in decane. The length of alkyl chains and the amount of long alkyl chains present in salts had an effect on the TEOS/decane emulsion formation, its structure and the size of TEOS droplets in which the sol-gel reaction proceeded. The presence of benzyl group together with long dodecyl chain hindered the formation of larger TEOS droplets in first stage of sol-gel reactions what caused the formation of smaller silica particles, for benzyl dodecyl dimethyl ammonium bromide 42% by number of silica particles had diameter of 52 nm, for trimethylhexyl ammonium bromide 36% by number of silica particles had diameter of 92 nm. The higher amount of long alkyl chains (dodecyl group) resulted in larger diameter of synthesized silica particles, for trimethyldodecyl ammonium bromide 48% by number of silica particles had diameter of 147 nm, for dimethyldodecyl ammonium bromide 44% by number of silica particles had diameter of 234 nm.

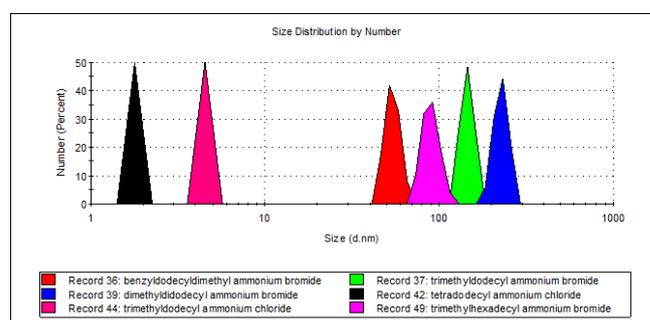


Fig. 1. Size distribution by number after 72h for the silica synthesized in decane in presence of alkyl ammonium salts.

Size of silica particles synthesized after 72h in presence of octadecylamine was in range 36 – 58 nm and in presence of triethanolamine in range 82 – 208 nm (Fig. 2). The largest diameter of silica particles obtained after 72h of sol-gel reaction was observed for the use of ammonia as a catalyst, the particles size was in range 165 – 372 nm. Ammonia is one of the typical catalyst used in synthesis of silica by sol-gel reactions. No particles were observed after 72h in TEOS/decane mixture containing magnesium stearate, zinc stearate and 4-nonylphenyl-polyethylene glycol.

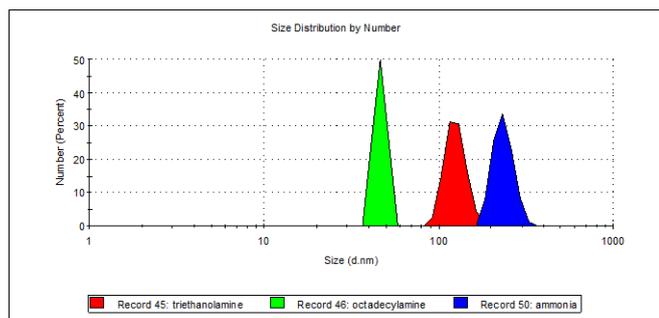


Fig. 2. Size distribution by number after 72h for the silica synthesized in decane in presence of ammoniam, octadecylamine, triethanolamine.

TABLE I. Size distribution by number after 14 day for SiO₂ obtained by sol-gel reactions in presence of various modifying substances. Measurements were done for a silica dispersion in decane.

Modifying substance used in sol-gel reactions	Size distribution by number for SiO ₂ after 14 days
ammonia	0.6 – 3 μm
trimethylheksadecylammonium bromide	1.4 – 1.8 μm
trimethyldodecylammonium bromide	0.8 – 1.5 μm
dimethyldidodecylammonium bromide	0.4 – 1.0 μm
benzylododecyldimethylammonium bromide	0.4 – 1.0 μm
trimethyldodecylammonium chloride	1.0 – 2.0 μm
tetradodecylammonium chloride	1.0 – 2.0 μm
triethanolamine	0.8 – 1.5 μm
octadecylamine	0.8 – 1.5 μm
magnesium stearate	0.6 – 2 μm
zinc stearate	0.8 – 2.2 μm
4-nonylphenyl-polyethylene glycol	1.0 – 1.3 μm

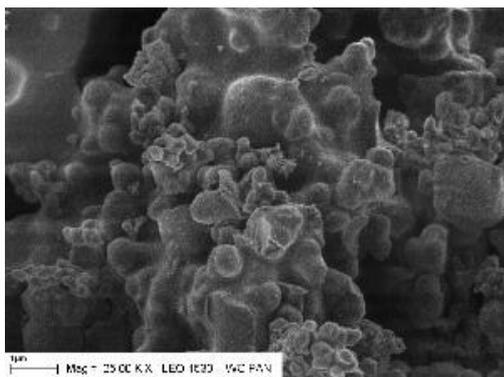


Fig. 3. SEM image of silica obtained by sol-gel reaction, catalyst ammonia.

In Table I are compiled the results of particle size measurements for silica obtained after 14 days of sol-gel reactions. No significant differences are observed in silica particles size obtained from TEOS in presence of alkylammonium bromide salts, triethanolamine and octadecylamine. Precipitated silicas characterized micrometric size, with a wide spread of aggregates size. Although the silica particles obtained in presence of alkylammonium chloride salts characterized the smallest size after 72h, longer time of reaction (14 days) led to synthesis of silica particles with larger diameter comparing to these obtained in presence of alkylammonium bromide salts. Synthesis in presence of stearates and non-ionic dispersant 4-nonylphenyl-polyethylene glycol required a longer time, and resulted after 14 days in

precipitated silica particles with size more than 2 μm for stearates and 1 μm for non-ionic dispersant. The largest silica particles were synthesized in presence of ammonia, up to 3 μm.

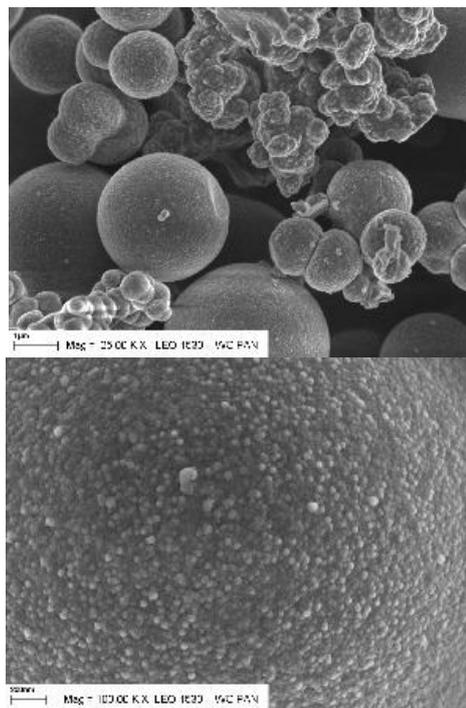


Fig. 4. SEM images of silica obtained by sol-gel reaction, catalyst triethanolamine.

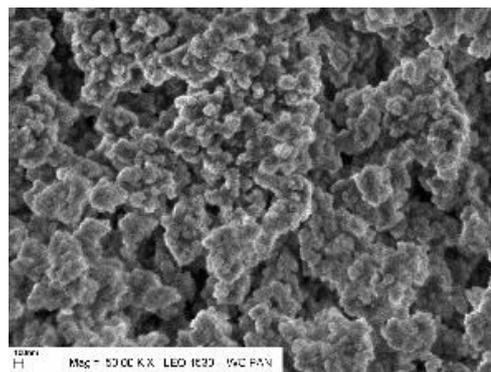


Fig. 5. SEM image of silica obtained by sol-gel reaction, catalyst octadecylamine.

Moreover, the shape and morphology of synthesized silicas were strongly connected with the type of dispersant used during sol-gel reactions. Silicas obtained from TEOS in decane in presence of ammonia (Fig. 3), triethanolamine (Fig. 4) and octadecylamine (Fig. 5) were characterized by globular structure. The higher tendency to agglomeration and irregular shape of formed structures was observed in case of silica synthesized using ammonia. Application of triethanolamine led to precipitation of large ball-shaped particles of silica consisting of small spherical nanometer particles as shown in higher magnification SEM picture (Fig. 4). Octadecylamine caused precipitation of small spherical particles which opposite to triethanolamine formed grain structure instead of ball-shaped (Fig. 5). Non-ionic dispersant 4-nonylphenyl-

polyethylene glycol promoted formation of spherical silica particles with narrow size distribution (Fig. 6).

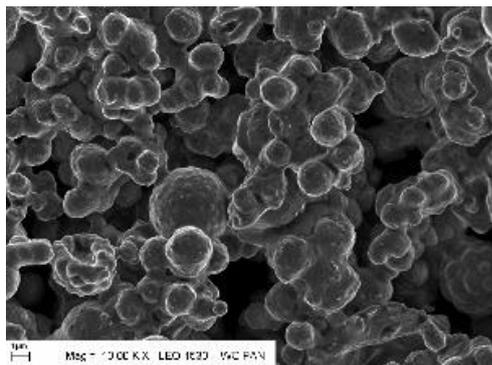


Fig. 6. SEM image of silica obtained by sol-gel reaction in presence of 4-nonylphenyl-polyethylene glycol.

The substances as alkylammonium bromide and chloride salts led to obtain silica with highly aggregated structure with dense and cohesive particles, as was shown for selected silicas obtained in presence of dimethyldidodecylammonium bromide (Fig. 7) and tetradodecylammonium chloride (Fig. 8).

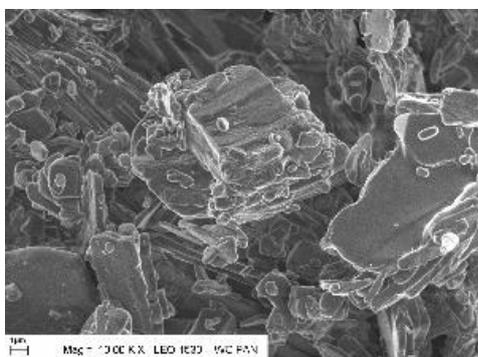


Fig. 7. SEM image of silica obtained by sol-gel reaction in presence of dimethyldidodecylammonium bromide.

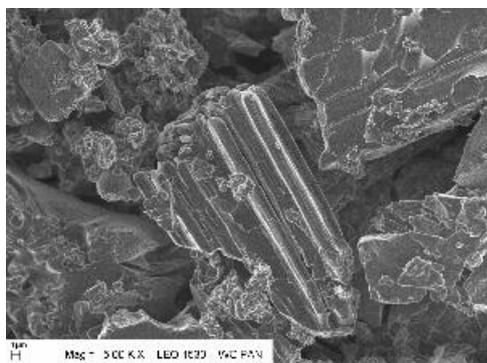


Fig. 8. SEM image of silica obtained by sol-gel reaction in presence of tetradodecylammonium chloride.

The plate-like shape of particles, the more layered morphology of aggregates with a high degree of surface development characterized particles obtained in presence of magnesium (Fig. 9) and zinc stearates (Fig. 10). Probably the magnesium and zinc ions participated in formation of crystalline solid Si-O- network.

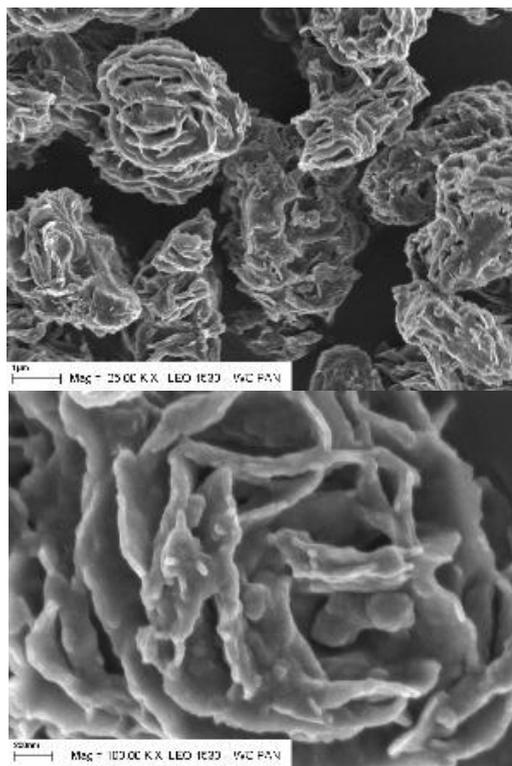


Fig. 9. SEM images of silica obtained by sol-gel reaction in presence of magnesium stearate.

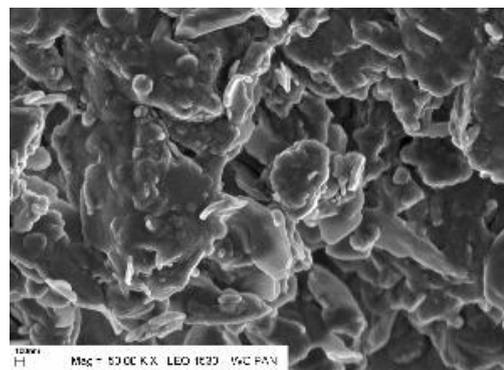


Fig. 10. SEM image of silica obtained by sol-gel reaction in presence of zinc stearate.

The ζ potential of silica water dispersion in a function of pH was examined. The values of this parameter for commercially available silicas take negative values in a wide range of pH with the isoelectric point (pH value for the ζ potential zero value) occurring at about pH = 2 [18]. Introduction of dispersants to the sol-gel synthesis caused the changes in the nature of the SiO₂ surface depending on the type of substance used. Two effects were observed. First, the curves of ζ potential in a function of pH characterized same tendency as observed for conventional silicas, the values of ζ potential decreased as pH became more basic but the isoelectric point was shifted towards higher values of pH. This behavior showed the suspension of silica obtained in presence of ammonia, triethanolamine, magnesium and zinc stearate, 4-nonylphenyl-polyethylene glycol, benzyl-dodecyl-dimethyl-ammonium bromide, trimethyldodecylammonium chloride. In

second type of ζ potential curves no isoelectric point was appeared, the ζ potential received positive values in the entire range of pH. This behavior showed the suspension of silica obtained in presence of octadecylamine, trimethylhexadecylammonium bromide, trimethyldodecylammonium bromide, dimethyldidodecylammonium bromide, tetradodecylammonium chloride. Silicas obtained in sol-gel reactions characterized different surface characteristics and surface charge. Alkylammonium bromide and chloride salts having long hydrocarbon chains caused the isolation of silica particles, influenced on the silica surface energy and increased the stability of silica suspension in larger or even in entire range of pH. The ζ potential curves for selected silicas are shown in Fig. 11, in table II are compiled pH of isoelectric point. The pH of isoelectric point for silica synthesized in presence of ammonia, magnesium and zinc stearate, triethanolamine and non-ionic dispersant 4-nonylphenyl-polyethylene glycol appeared at 5-7 pH. The pH of isoelectric point of silica obtained in presence of alkylammonium bromide and chloride salts appeared at 7-10 pH or the values of ζ potential were positive in entire range of pH indicated that this type of modifying substance had stronger impact on surface energy of synthesized silicas.

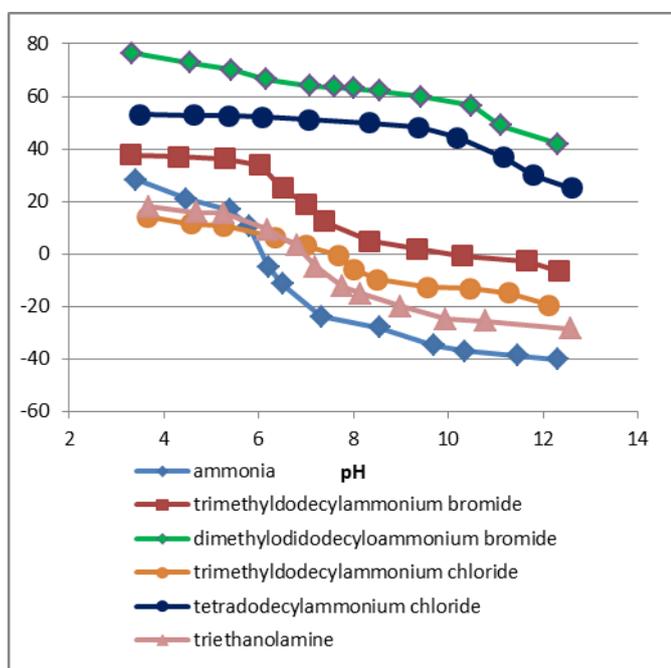


Fig. 11. The ζ potential [mV] in function of pH for silica suspension obtained in sol-gel reaction in presence of selected dispersants.

TABLE II. pH for the isoelectric point for the suspension of silica obtained by sol-gel reactions in presence of various substances.

Modifying substance used in sol-gel reactions	pH of isoelectric point
ammonia	6.10
benzylododecyltrimethylammonium bromide	7.50
trimethyldodecylammonium bromide	10.0
trimethyldodecylammonium chloride	7.60
triethanolamine	6.95
magnesium stearate	7.20
zinc stearate	5.20
4-nonylphenyl-polyethylene glycol	6.85

Determination of rheological properties of suspensions in paraffin oil allows to evaluate the behavior of the filler in the elastomeric medium. The formation of the filler structure affects the rheological properties of the dispersion. The volume fraction of filler units in oil ϕ , the ratio of the volume fraction of aggregates to the mass percentage of filler ϕ / ϕ_0 and the limit viscosity η_∞ are shown in Table III and were calculated according to the Mooney equation [19]:

$$\eta = \eta_0 \exp(2.5\phi/1-k\phi) \quad (1)$$

where η - relative viscosity, η_0 - viscosity of paraffin oil, ϕ - the volume fraction of filler aggregates in oil, $k = 1.63$ constant, the self-crowding factor.

The silicas synthesized in the presence of various dispersants do not significantly increased the viscosity of the suspensions. The highest viscosity as well as the tendency to form the structure were reported for suspended silica slurries obtained using in sol-gel reactions triethanolamine as a catalyst. In this case the highest volume fraction of fillers in oil ϕ occurred, the smallest value of this parameter was reported for silica obtained in a reaction catalyzed with trimethyldodecyl-ammonium chloride. For the other synthesized silicas, the volume fraction of aggregates ranges from 1.86-3.38; the viscosity of suspensions ranges from 192 to 200 mPa·s.

TABLE III. Rheological properties, the viscosity of paraffin oil suspensions η_∞ , volume fraction of filler in oil ϕ , the ratio of the volume fraction of aggregates to the mass percentage of filler ϕ/ϕ_0 .

Modifying substance used in sol-gel reactions	η_∞ mPas	ϕ	ϕ/ϕ_0
paraffin oil	183	---	---
ammonia	199	3.18	1.31
trimethylhexadecylammonium bromide	200	3.31	1.37
trimethyldodecylammonium bromide	192	1.86	0.77
dimethyldidodecylammonium bromide	194	2.25	0.93
benzylododecyltrimethylammonium bromide	199	3.16	1.31
trimethyldodecylammonium chloride	187	0.85	0.35
tetradodecylammonium chloride	200	3.36	1.39
triethanolamine	204	4.06	1.68
octadecylamine	199	3.11	1.31
magnesium stearate	198	2.99	1.24
zinc stearate	200	3.34	1.38
4-nonylphenyl-polyethylene glycol	200	3.38	1.40

B. Synthesis of Silica by Sol-Gel Reactions in Rubber Matrix.

In order to synthesize silica in-situ in the elastomeric medium, rubber mixtures containing a various amount (5, 10, 15, 20 phr) of tetraethoxysilane TEOS were prepared. Additionally the properties of rubber mixtures containing 10 phr of TEOS and 1 phr of modifying substances triethanolamine, zinc or magnesium stearate and 4-nonylphenyl-polyethylene glycol were studied. Mixtures containing various amount of TEOS were left for 14 days in a chamber of high humidity 70% and in a desiccator containing ammonia vapors (24h) to initiate the sol-gel reaction in-situ. Part of the mixtures before vulcanization was subjected to swelling in supercritical CO₂ for 5 hours.

The influence of TEOS addition on the peroxide curing of ethylene-propylene copolymer EPM and hydrogenated butadiene-acrylonitrile rubber HNBR was investigated. ODR rheometer was used to follow the reaction stages in

vulcanization of both rubbers. The curing characteristics at 160°C for ethylene-propylene rubber EPM and calculated rheometric parameter as: the optimum cure time τ_{90} revealed that the addition of TEOS or TEOS in a presence of modifying substances did not change significantly the values of τ_{90} parameters, time of curing for unfilled EPM and filled with TEOS was in range 28-30 min. The introduction of the TEOS compound into the EPM blends resulted in the reduction of the minimum torque value M_{min} , from 26,3 dNm (unfilled EPM) to 17,7 dNm (EPM filled with 20 phr of TEOS). Delta torque ΔM calculated as:

$$\Delta M = M_{max} - M_{min} \quad (2)$$

where M_{max} is maximum torque, M_{min} is minimum torque decreased for the mixtures containing TEOS from the value of 76,4 dNm (unfilled EPM) to the value of 35 dNm (EPM containing 20 phr of TEOS). The changes in values of ΔM parameter indicated that the incorporation of TEOS and its residue after in-situ silica synthesis led to decrease of peroxide curing efficiency. Opposite influence of TEOS addition on the optimum cure time τ_{90} and delta torque ΔM was reported for hydrogenated butadiene-acrylonitrile rubber HNBR. The addition of silane shortened the vulcanization time of the HNBR blends from 33 min (unfilled HNBR) to 19 min (HNBR mixtures filled with 20 phr of TEOS). The increase of the ΔM parameter from the value of 50.7 dNm (pure HNBR) to value of 73.8 dNm (HNBR mixtures containing silane) indicated that incorporation of TEOS enhanced the cure rate of HNBR rubber. Similar effect, lower values of minimum torque M_{min} were reported, for both rubber the addition of TEOS reduced the viscosity of rubber mixtures.

The crosslink density of cured elastomer can be determined from swelling measurements. Crosslinked elastomers absorb solvent, swelling continues until the retractive forces in the extended molecular strands in the network balance the forces tending to swell the network. The Flory-Rehner's equation [20] (3) is widely used to determine the crosslinking density related to the amount of swelling in toluene according to equation:

$$v_T = - \frac{\ln(1 - v_p) + v_p + \chi v_p^2}{v_s(v_p^{1/3} - \frac{v_p}{2})} \quad (3)$$

where v_T is crosslink density, V_p is the volume fraction of elastomer in the swollen gel and V_s is the molar volume of solvent (mole/cm³). The Huggins parameter (χ) for elastomer-solvent interaction are given by the following equations [21-22]:

$$\chi = 0.501 + 0.273 V_p \text{ (HNBR)} \quad (4)$$

$$\chi = 0.425 + 0.34 V_p \text{ (EPM)} \quad (5)$$

In every case, the addition of TEOS reduced the crosslinking density of EPM and HNBR vulcanizates, as presented in Fig. 12 and in Table IV. Treatment of EPM blends before the vulcanization with ammonia vapor resulted in higher values of crosslink density comparing with these immersed in chamber of high moisture. Dispersants such as triethanolamine, 4-nonylphenyl-polyethylene glycol and zinc stearate had a negative impact on crosslinking of EPM rubber, strong decrease in crosslink density was reported. Significant

deterioration in amount of formed crosslinks was noted for every HNBR vulcanizates containing TEOS (Table IV).

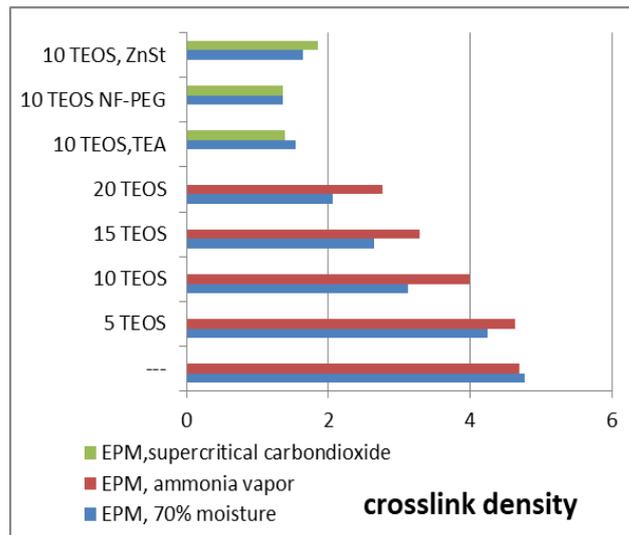


Fig. 12. Crosslink density $v_T \cdot 10^5$ (mole/cm³) calculated from equilibrium swelling in toluene for EPM vulcanizates. TEA – triethanolamine, NF-PEG – 4-nonylphenyl-polyethylene glycol, ZnSt – zinc stearate

TABLE IV. Values of crosslink density v_T , modulus at 100% elongation SE_{100} , tensile strength TS, elongation at break E_B for HNBR vulcanizates. The dispersants added to HNBR rubber mixtures: TEA – triethanolamine, NF-PEG – 4-nonylphenyl-polyethylene glycol, Mg,ZnSt – magnesium and zinc stearate.

HNBR 100 phr	$v_T \cdot 10^5$ mole/cm ³	SE_{100}	TS MPa	E_B %
---	6.18	0.94	7.65	617
rubber mixtures immersed in 70% moisture before curing				
TEOS 5 phr	2.83	0.67	5.60	627
TEOS 10 phr	2.62	0.65	6.23	650
TEOS 15 phr	2.92	0.74	7.94	640
TEOS 20 phr	3.12	0.73	9.59	656
TEOS, TEA 1 phr	2.50	0.97	7.39	505
TEOS, NF-PEG 1 phr	2.10	0.96	7.23	496
TEOS, MgSt 1 phr	4.90	1.17	11.53	458
rubber mixtures treated with ammonia vapor before curing				
TEOS 5 phr	2.74	0.58	10.96	897
TEOS 10 phr	2.54	0.53	10.00	920
TEOS 15 phr	2.13	0.56	11.46	987
TEOS 20 phr	1.85	0.59	12.89	997
rubber mixtures swelled in supercritical CO₂ before curing				
TEOS, TEA 1 phr	2.20	0.61	1.41	1202
TEOS, NF-PEG 1 phr	2.40	0.64	1.72	1187
TEOS, ZnSt 1 phr	5.20	0.68	1.90	997

Having established the influence of TEOS on the vulcanization process and crosslink density of rubbers we then examined their mechanical properties, the results are given in Table IV and Table V. From the values presented in Table IV, it can be clearly observed that the way of rubber mixtures treatment before the vulcanization had the influence on occurrence of reinforcing effect and the enhancement of mechanical properties. Our investigation showed that for the HNBR rubber mixtures immersed in chamber with higher moisture the higher values of tensile strength are observed for vulcanizates containing 15 phr of TEOS and more. The addition of the lower amount of TEOS did not lead to precipitation on silica in elastomer and it caused the

deterioration of mechanical properties. The incorporation of 10 phr of TEOS together with selected modifying substances had an impact on the values of mechanical parameters, the increase in the values of modulus at 100% elongation SE_{100} and tensile strength TS were noted. As we expected the treatment of HNBR rubber mixtures with ammonia vapor before the vulcanization led to stronger increase in the values of tensile strength TS. However the greater changes were noted in values of modulus at 100% elongation SE_{100} and the elongation at break E_B . Effect was caused by lower crosslink density of vulcanizates. Additionally the ammonia treatment could cause the damage of uncured elastomer. Swelling in supercritical carbon dioxide led to the deterioration of mechanical properties indicating that the destruction of elastomer during treatment occurred.

TABLE V. Values of modulus at 100% elongation SE_{100} , tensile strength TS, elongation at break E_B for EPM vulcanizates. The dispersants added to HNBR rubber mixtures: TEA – triethanolamine, NF-PEG - 4-nonylphenyl-polyethylene glycol, ZnSt – zinc stearate.

	SE_{100}	TS MPa	E_B %
---	0.85	1.20	422
rubber mixtures immersed in 70% moisture before curing			
TEOS 5 phr	0.67	3.20	788
TEOS 10 phr	0.61	2.88	753
TEOS 15 phr	0.57	2.84	796
TEOS 20 phr	0.54	2.52	832
TEOS 10 phr, TEA 1 phr	0.51	2.74	936
TEOS 10 phr, NF-PEG 1 phr	0.57	1.07	876
TEOS 10 phr, ZnSt 1 phr	0.69	1.80	890
rubber mixtures treated with ammonia vapor before curing			
TEOS 5 phr	0.44	2.29	886
TEOS 10 phr	0.22	3.09	1399
TEOS 15 phr	0.22	3.46	1073
TEOS 20 phr	0.24	3.48	1099
rubber mixtures swelled in supercritical CO₂ before curing			
TEOS 10 phr, TEA 1 phr	0.72	3.15	1100
TEOS 10 phr, NF-PEG 1 phr	0.54	1.09	1078
TEOS 10 phr, ZnSt 1 phr	0.67	1.87	908

The tensile strength TS of the EPM vulcanizates containing TEOS increased as a result of strengthening effect caused by the formation of silica particles in EPM matrix (Table V). Furthermore it was found that the observed improvement, the higher values of tensile strength TS comparing to unfilled EPM rubber occurred for every type of EPM rubber mixtures treatment. As it was observed for the HNBR rubber the values of modulus at elongation of 100% decreased and the values of elongation at break increased after ammonia treatment.

We observed the effect of introducing TEOS on the tear strength of EPM vulcanizates (Fig. 13). Tear strength of EPM vulcanizates obtained from rubber mixtures exposed to water and ammonia vapor and containing various amount of TEOS increased with increasing silane content. The increase in tear strength Rr was another factor suggesting that the precipitation of silica occurred.

To confirm the presence of silica particles synthesized in situ in rubber matrix the SEM image of selected vulcanizates were analyzed. The analysis of SEM images proved that it is possible to obtain silica particles directly in elastomer matrix

using TEOS as a precursor or TEOS in presence of dispersants.

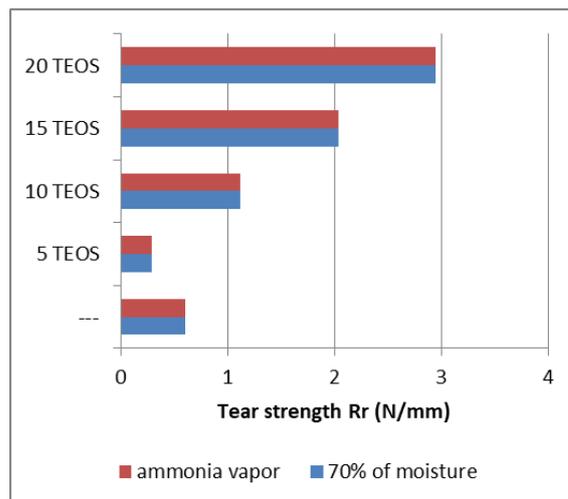


Fig. 13. Tear strength Rr of EPM vulcanizates containing TEOS.

The silica particles formed in situ in ethylene-propylene copolymer using ammonia and high moisture treatment were a micrometric size (Fig. 14-15). The lack of homogeneity of rubber matrix, the areas in which the small bubbles were present, probably containing the residue of TEOS and products of sol-gel reactions as water, were observed for the rubber mixtures treated with ammonia vapor (Fig. 14).

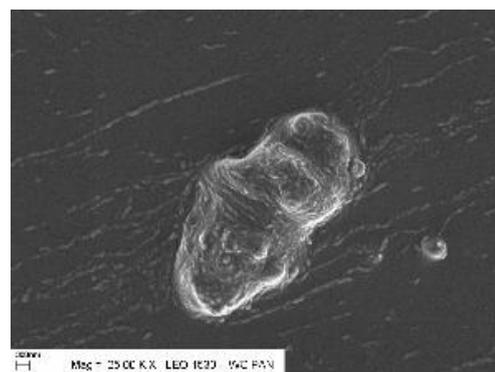


Fig. 14. SEM image of EPM vulcanizate obtained from rubber mixture containing 20 phr of TEOS. Rubber mixture was treated with ammonia vapor before the vulcanization.

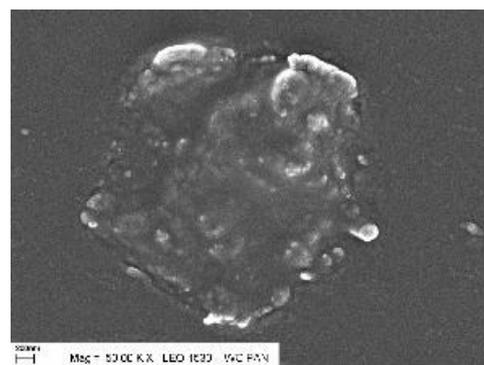


Fig. 15. SEM image of EPM vulcanizate obtained from rubber mixture containing 20 phr of TEOS. Rubber mixture was immersed in chamber of 70% moisture before the vulcanization.

The catalysis of sol-gel reaction by presence of triethanolamine led to formation of smaller, less than 1 μm particles of silica (Fig. 16). Also the incorporation of TEOS together with non-ionic dispersant 4-nonylphenyl-polyethylene glycol allowed to synthesize small, less than 500 nm particles of silica. No empty void between silica aggregates and elastomer matrix was present.



Fig. 16. SEM image of EPM vulcanizate obtained from rubber mixture containing 10 phr of TEOS and 1 phr of triethanolamine. Rubber mixture was immersed in chamber of 70% moisture before the vulcanization.



Fig. 17. SEM image of EPM vulcanizate obtained from rubber mixture containing 10 phr of TEOS and 1 phr of 4-nonylphenyl-polyethylene glycol. Rubber mixture was immersed in chamber of 70% moisture before the vulcanization.

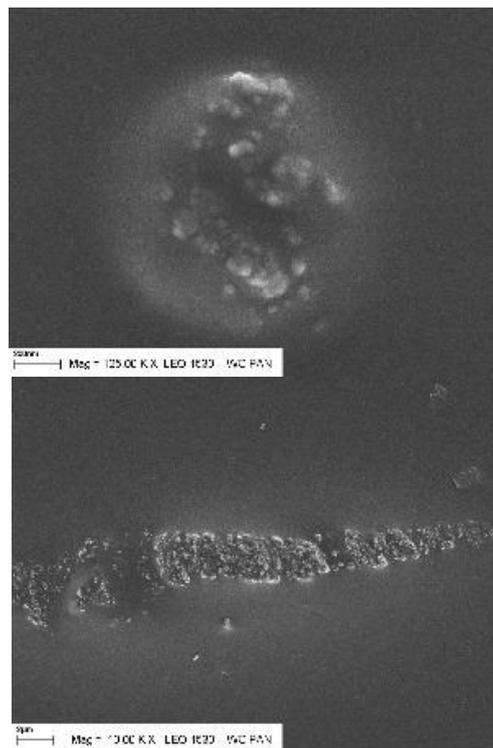


Fig. 18. SEM images of HNBR vulcanizates obtained from rubber mixture containing 20 phr of TEOS. Rubber mixture was treated with ammonia vapor before the vulcanization.



Fig. 19. SEM image of HNBR vulcanizate obtained from rubber mixture containing 20 phr of TEOS. Rubber mixture was immersed in chamber of 70% moisture before the vulcanization.

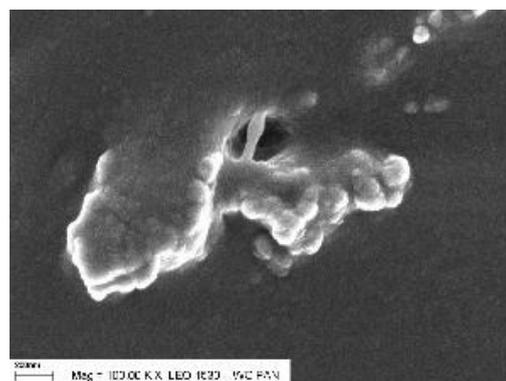


Fig. 20. SEM image of HNBR vulcanizate obtained from rubber mixture containing 10 phr of TEOS and 1 phr of triethanolamine. Rubber mixture was immersed in chamber of 70% moisture before the vulcanization.

Fig. 18 shows the SEM image of HNBR vulcanizate treated before the curing with ammonia vapor. For this way obtained vulcanizates we noted the higher concentration of formed silica particles in rubber comparing to HNBR vulcanizates immersed in chamber with high moisture (Fig. 19). It was found that due to an inhomogeneous incorporation of TEOS during mixing with elastomer the higher concentration of formed silica and lack of solid particles in some areas occurred. The uneven dispersion of silica throughout elastomer matrix was observed.

Fig. 19 shows the SEM image of HNBR vulcanizate immersed in chamber of 70% moisture before the rubber curing. For this way treated rubber mixtures the size of synthesized silica particles in-situ in HNBR matrix was in range 100-500 nm. The application of TEOS together with triethanolamine led to formation of the larger aggregates of silica (0.2 – 1 μm). The silica particles were surrounded with rubber matrix indicating good filler/polymer contact and filler/polymer interphase interactions (Fig. 20).

Opposite to HNBR vulcanizate prepared by mixing of TEOS separately with rubber, which was characterized by high inhomogeneity, the combination of TEOS with 4-nonylphenyl-polyethylene glycol improved the mixing of silane during rubber preparation. Therefore the higher compatibility resulted in more homogenous dispersion of formed silica particles throughout matrix (Fig. 21).

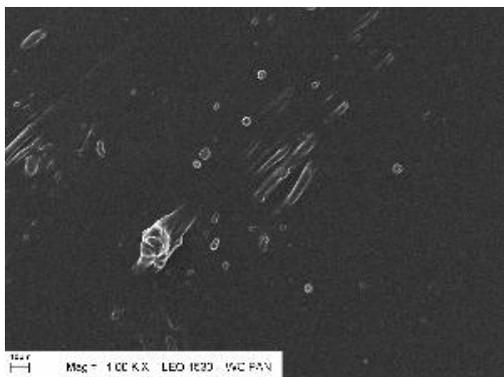


Fig. 21. SEM image of HNBR vulcanizate obtained from rubber mixture containing 10 phr of TEOS and 1 phr of 4-nonylphenyl-polyethylene glycol. Rubber mixture was immersed in chamber of 70% moisture before the vulcanization.

C. Properties of EPM and HNBR Rubber Containing Silica Obtained by Sol-Gel Reactions.

Additionally EPM and HNBR rubber mixtures containing silica precipitated in decane were prepared. For this purpose 10 phr of dried synthesized by sol-gel reaction silicas were incorporated into elastomer using two-roll mill, rubber mixtures were cured using dicumyl peroxide (3 phr). To compare the rubber mixture filled with 10 phr of two conventional silicas, precipitated Zeosil 175MP and fumed nanometric Aerosil 380 were studied. The rheometric properties of rubber mixtures are presented in Table VI. The curing characteristics indicated that the incorporation of silicas synthesized by sol-gel reactions into rubber mixtures in most cases extended the vulcanization time of rubber mixtures comparing to samples filled with conventional, commercially available silicas. For both rubber the mechanical properties of vulcanizates were worse comparing to samples containing nanometric silica Aerosil 380.

TABLE VI. Rheometric and mechanical properties of EPM and HNBR vulcanizates, τ_{90} optimum cure time, TS – tensile strength, E_B – elongation at break. Silica was obtained by sol-gel reactions in presence of: TEA – triethanolamine, NF-PEG - 4-nonylphenyl-polyethylene glycol, MgSt – magnesium stearate, CTAB - trimethylhexadecylammonium bromide, DIDD MBA - dimethyldidodecylammonium bromide.

	HNBR			EPM		
	τ_{90} min.	TS MPa	E_B %	τ_{90} min.	TS MPa	E_B %
Zeosil 175 MP	12	10.8	406	15	2.1	326
Aerosil 380	8	14.9	411	13	2.9	354
SiO ₂ MgSt	10	11.5	458	25	2.0	474
SiO ₂ CTAB	8	10.3	423	18	1.9	397
SiO ₂ ODA	13	9.0	579	21	2.0	624
SiO ₂ TEA	14	7.4	505	22	1.6	348
SiO ₂ DIDD MBA	13	13.8	458	17	2.0	411
SiO ₂ NF-PEG	18	7.2	496	28	1.8	586

The values of tensile strength of HNBR vulcanizates depended on type of substance used during synthesis of silica. For the HNBR vulcanizates filled by silica obtained in presence of magnesium stearate, trimethylhexadecylammonium bromide and dimethyl-didodecylammonium bromide the similar or higher values of tensile strength than for the conventional silica Zeosil 175MP were reported. The addition of sol-gel silica to EPM rubber resulted in comparable strength of vulcanizates like observed for the EPM rubber containing Zeosil 175MP.

IV. CONCLUSION

Using the appropriate dispersants in the silica synthesis by the sol-gel method we can affect the zeta potential of the silica dispersion. The use of dispersants caused a shift in the zeta potential curve as a function of pH towards higher pH values compared to those obtained by traditional methods. Depending on the type of dispersant used to synthesize the silica, the powders obtained had different morphology and surface structure. The type of surfactant used also affected the size and surface structure of the aggregates and agglomerates. Most of the dispersants resulted in formation of the spherical filler structures with a high tendency to agglomerate. Introduction of tetraethoxysilane (TEOS) to elastomer blends caused a decrease in the viscosity of both EPM and HNBR rubber mixtures. The incorporation of TEOS decreased the cross-linking density of EPM and HNBR vulcanizates comparing to pure rubbers. The HNBR vulcanizates obtained from the mixtures in which the sol-gel reaction was catalyzed by the ammonia vapors are characterized by a higher tensile strength than vulcanizates containing the same amount of TEOS treated using other methods. In the case of EPM vulcanizates, depending on the catalysis of the sol-gel reaction, we observe the effect of the silane on mechanical strength of vulcanizates. Additionally for EPM vulcanizates, there is clear effect of increasing the amount of TEOS on the tear strength of vulcanizates. Catalysis of the sol-gel reaction by ammonia or the immersion in atmosphere of 70% moisture caused precipitation of silica in the elastomeric medium, what was confirmed by SEM images of vulcanizates.

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