# The morphology and properties of silica nanoparticles synthesized by sol-gel reaction in elastomer matrix.

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## ABSTRACT

In our studies the influence of different dispersing agents f.e. alkylammonium bromide, chloride, octadecylamine, magnesium stearate on the synthesis and character of silica particles prepared by a sol-gel reaction was investigated. The silica with different surface morphology was synthesized from tetraethoxysilane (TEOS) in suspension medium - decane (an appropriate model for the elastomer). The character and structure of used dispersants strongly interacted on the shape, the particle size distrbution and morphology of synthetized silicas. In comparision the reaction in the presence of dispersants was conducted "in-situ", directly, in elastomeric medium. For this purpose the mixtures of hydrogentated butadiene-acrylonitrile HNBR and ethylene-propylene rubbers EPM containing different amount of tetraethoxysilane and dispersants were prepared. Before the vulcanization the rubber mixtures were swelled in atmosphere of carbon dioxide or were allowed to stand in atmosphere with high moisture 70% to catalyze the sol-gel reactions. The analysis of SEM images of the vulcanisates showed the presence of silica particles synthesized “in-situ” in elastomer matrix. We observed the influence of TEOS addiction on the crosslink density of elastomers and mechanical properties.

***Keywords***: sol-gel reactions, silica, elastomers, tetraethoxysilane, nanocomposites

## 1 INTRODUCTION

The sol-gel reactions are popular processes to obtain a wide range of materials including silicas[1]. As a precursors of silica in sol-gel reactions aloxysilanes are often used, with tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) being especially popular. Sol-gel reactions are multi-step processes, consisting of the growth of colloidal particles followed by the formation of stable networks. Final properties of obtained silicas depend on many factors, such as pH, temperature, duration of the reactions, the concentrations of reacting substances, the molar ratio $H_2O/Si$, the nature and concentration of the catalysts as well as the process of drying[2,3] Various fillers are often blended with elastomers to achive reinforcing effect. Controlling the dispersion of the filler in the matrix is difficult because of the viscosity of the elastomeric materials.The goal of our studies was to determine if the well-dispersed silica filler could be prepared in an elastomeric matrix by the sol-gel processes using TEOS as precursor. Furthermore, it was also of interest to determine if the dispersing agents could act as catalysts able to influence on the morphology of synthesized silica nanoparticles. As a model of our system the sol-gel reactions were conduct in decane. Neither methanol nor water was added in the decane suspension as it is imposible to mix them with true elastomer.

## 2 EXPERIMENTAL

### 2.1 Materials, preparation of rubber mixes and vulcanizates

Tetraethoxysilane (TEOS) (Aldrich) was used as precursor of silica synthesis. Surface properties of obtained silicas were modified by the use of: a) cationic dispersants - alkylammonium chlorides and bromides b) cationic dispersant with amine group – triethanolamine, octadecyl amine c) nonionic dispersant nonyl phenyl polyethylene glycol ether d) anionic dispersants – magnesium, zinc stearate. The elastomers used in this work were: hydrogenated butadiene-acrylonitrile rubber HNBR, containing 34% of acrylonitrile mers (Therban A 3407, Bayer) ethylene-propylene copolymer EPR (Dutral CO 054, Montedison Ferrara, Italy). The composition of the prepared rubber mixes were as follows: HNBR or EPR 100 phr, TEOS 0-20 phr, crosslinking agent DCP (dicumyl peroxide) 3 phr. The rubber mixes were made by a laboratory two-roll mill at a temperature of approximately 35°C. The condition of vulcanization were determined by WG-2 rheometer. The samples were vulcanized at 160°C for the time necessary for a torque increase of rheometric moment by 90% ($\tau_{0.9}$) for no longer then 30 min.

### 2.2 Synthesis of silica particles in a decane

In our work decane was selected as an appropriate model for the elastomer. In order to synthesize the silica the silanes TEOS (20g) and decane (100g) were placed in a flask equiped with a condenser. The mixture was heated in a oil bath at 160°C for 30 min. Then the suspension was cooled to room temperature and was stored in open flask.

After 14 days synthesized silica was filtered and dried in a vacuum drier at 50°C for 48h. The reactions were conducted in the presence of dispersants 10 wt% respectively.

## 2.3 Characterization

The morphology and the surface structure of the obtained silica fillers synthesized in decane from TEOS using different dispersants was determined from scaning electron microscope images by using LEO 1530 microscope (Zeiss). Samples with graphite coated structure were used in these investigation. In the case of vulcanizates the surfaces formed after liquid-nitrogen fracture was examined. The following magnification were used: 2000, 10 000, 20 000, 50 000. The size of particles were determined using Zetasizer NanoS90 equipment (Malvern)

The zeta potential of the silica water dispersion (0.1g/dm$^3$) was determined by Zetsizer 2000 (Malvern).

# 3 RESULTS AND DISCUSSION

The particle sizes of filler synthetized in decane after 72 hours and 14 days were measured (table 1). The character and structure of dispersants had an effect on the final size of the silica particles. Moreover dispersants interacted also on the shape and morphology of synthetized silicas (fig. 1 -5).

| Modifing substances using during sol-gel reaction | Particles size after 72h, nm | Size of dried silica, $\mu$m |
|---|---|---|
| benzalconium bromide | <10 | 0.1 - 1 |
| triethanolamine | <10 | 0.8 – 1.5 |
| octadecylamine | <10 | 0.8 – 1.5 |
| magnesium stearate | <10 | 0.6 – 2.0 |
| dimethyldidodecylammonium bromide | <10 | 0.4 – 1.0 |
| trimethyldodecylammonium bromide | <10 | 0.8 – 1.5 |
| nonyl phenyl polyethylene glycol ether | <10 | 1.0 – 1.3 |
| trimethyldodecylammonium chloride | 10 - 30 | 1.0 – 2.0 |
| tetradodecylammonium chloride | 10 - 30 | 1.0 – 2.0 |
| ammonia | 25 – 65 | >3 |
| tetraethylammonium chloride | 250 – 1000 | >5 |
| tetraethylammonium bromide | 250 - 1000 | >5 |

Table 1: Particles size of synthetized in decane silicas after 72 hours and size of filtered and dried silica.

Silica obtained from TEOS in decane in the presence of benzalconium bromide, triethanolamine and ammonia (fig. 1-3) were characterized by globular structures. We observed the higher tendency to agglomeration in case of silica synthetized using ammonia.

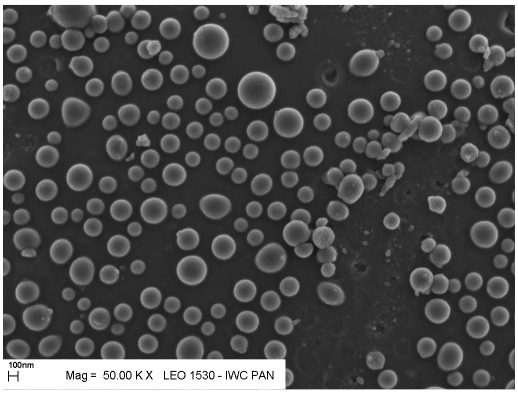


Fig 1: SEM image of silica synthetized in sol-gel reaction in a presence of benzalconium bromide.

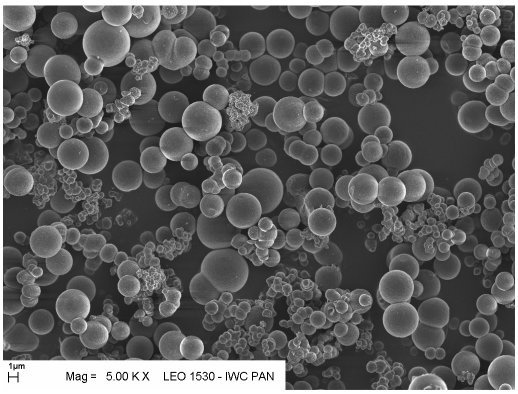


Fig 2: SEM image of silica synthetized in sol-gel reaction in a presence of triethanolamine.

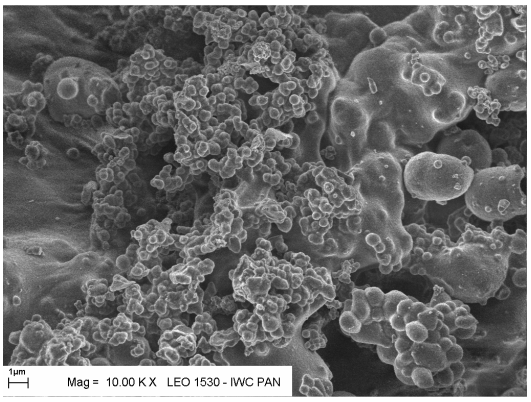


Fig 3: SEM image of silica synthetized in sol-gel reaction in a presence of ammonia.

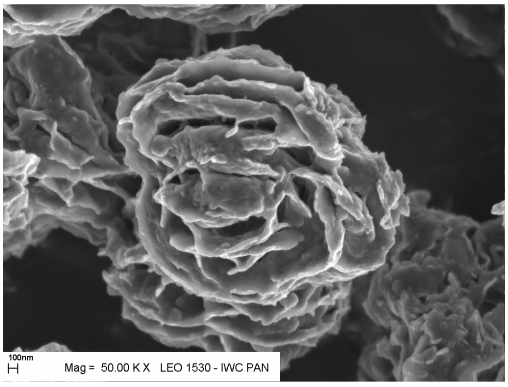


Fig 4: SEM image of silica synthetized in sol-gel reaction in a presence of magnesium stearate.

The more layered morphology of agglomerates with a high degree of surface development characterized silica formed in the presence of magnesium stearate (fig. 4). The substances as tetraethylammonium bromide led to obtain silica with highly aggregated and agglomerated structure (fig. 5).

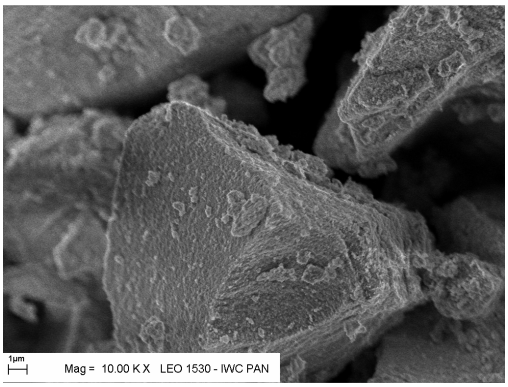


Fig 5: SEM images of silica synthetized in sol-gel reaction in a presence of tetraethylammonium bromide.

The ζ potential of silica water dispersions in a funtion of pH was examined. This parameter for precipitated, commercialy used silicas take negative values in a wide range of pH. In this case the isoelectric point is at about pH=2. The silica synthesized by sol-gel silica using ammonia as a catalyst was characterized by the presence of the isoelectric point at a higher value of pH = 6 (table 2). Introduction of dispersants to the synthesis caused the change in the nature of the surface depending on the type of substance used. Dispersants such as: octadecylamine, dimethyldidodecylammonium bromide, tetradodecyl-ammonium chloride having long hydrocarbon chains caused the isolation of silica surface by dispersant alkyl chains and in this case the range of potential received positive values in the entire pH range. Dispersants influenced on the silica surface energy, as a result the surface became more hydrophobic.

| Modifing substances using during sol-gel reaction | pH of isoelectric point |
|---|---|
| benzalconium bromide | 7 |
| triethanolamine | 7 |
| octadecylamine | --- |
| magnesium stearate | 6 |
| dimethyldidodecylammonium bromide | --- |
| trimethyldodecylammonium bromide | 10 |
| nonyl phenyl polyethylene glycol ether | 7 |
| trimethyldodecylammonium chloride | 8 |
| tetradodecylammonium chloride | --- |
| ammonia | 6 |
| tetraethylammonium chloride | 7 |
| tetraethylammonium bromide | 7 |

Table 2: The pH for the isoelectric point measured for the water dispersions of silicas (0.2 g/dm$^3$)

For the synthesis of silica "in situ" in elastomer the rubber mixes containing various amounts of TEOS were prepared.

| Amount of TEOS, phr | EPR mixtures | HNBR mixtures |
|---|---|---|
| --- | 30 | 43 |
| 5 | 29 | 29 |
| 10 | 28 | 27 |
| 15 | 29 | 21 |
| 20 | 30 | 19 |
| 20 + 1 TEA | 27 | 34 |
| 20 + 1 NF-PEG | 29 | 28 |
| 20 TEOS + 1 St. Mg | 25 | 20 |

Table 3: Vulcanization time $\tau_{0.9}$ (min) for the EPR and HNBR mixtures crosslinked with dicumyl peroxide DCP. TEA – triethanolamine, NF-PEG - nonyl phenyl polyethylene glycol ether, St. Mg – magnesium stearate.

From data compiled in table 3 it appears that in case of HNBR rubber the addition of TEOS resulted in a reduction of vulcanization time $\tau_{0.9}$.

Our investigations showed that the addition of TEOS to EPR and HNBR rubber changed the mechanical properties of rubber vulcanisates (table 4-5). The tensile strenght for the EPR vulcanisates containig TEOS increased as a result of strengthening effect caused by the formation of silica particles in elastomer matrix. As is shown in table 5 application of TEOS in presence of magnesium stearate led to a significant increase the tensile strength of HNBR vulcanisates.

| Amount of TEOS, phr | $SE_{100}$, MPa | TS, MPa | Eb, % |
|---|---|---|---|
| --- | 0.85 | 1.20 | 422 |
| 5 | 0.67 | 3.20 | 788 |
| 10 | 0.61 | 2.88 | 753 |
| 15 | 0.57 | 2.84 | 796 |
| 20 | 0.54 | 2.52 | 832 |
| 20 + 1 TEA | 0.72 | 3.15 | 1162 |
| 20 + 1 NF-PEG | 0.84 | 1.83 | 586 |
| 20 TEOS + 1 St. Mg | 1.07 | 1.98 | 474 |

Table 4: Mechanical properties of EPR vulcanisates. $SE_{100}$ $SE_{100}$ – 100% modulus, TS – tensile strength, Eb – elongation at break.

| Amount of TEOS, phr | $SE_{100}$, MPa | TS, MPa | Eb, % |
|---|---|---|---|
| --- | 0.94 | 7.65 | 617 |
| 5 | 0.67 | 5.60 | 627 |
| 10 | 0.65 | 6.23 | 650 |
| 15 | 0.74 | 7.94 | 640 |
| 20 | 0.73 | 9.59 | 656 |
| 20 + 1 TEA | 0.97 | 7.39 | 505 |
| 20 + 1 NF-PEG | 0.96 | 7.23 | 496 |
| 20 TEOS + 1 St. Mg | 1.17 | 11.53 | 458 |

Table 5: Mechanical properties of HNBR vulcanisates.

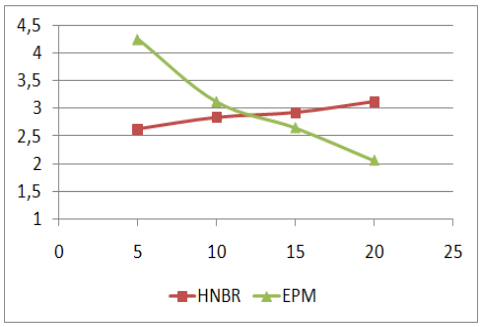


Fig. 6: Crosslink density $\nu*10^5$ (mol/cm$^3$) of EPM and HNBR vulcanisates containing different amount of TEOS.

The addition of TEOS decreased the crosslink densities of EPR vulcanisates (fig. 6). The opposite effect in case of HNBR rubber was obserwed. The crosslink density of vulcanisates increased with increasing amount of TEOS.

The analysis of SEM images of the vulcanisates showed the presence of silica particles synthesized "in-situ" in elastomer matrix using as a precursor TEOS or TEOS in presence of dispersants (fig 7-8).

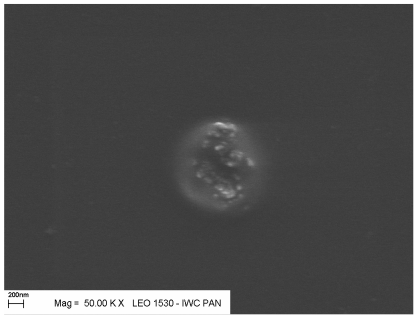


Fig. 7: SEM image of the silica particles synthesized "in-situ" in HNBR vulcanisate using 20 phr TEOS.

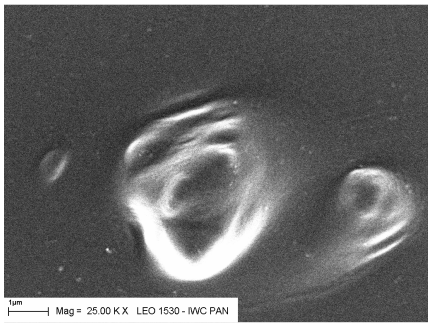


Fig. 8: SEM image of the silica particles synthesized "in-situ" in EPR vulcanisate using TEOS and triethanolamine .

## 4 CONCLUSIONS

Using appropriate dispersants in the synthesis of silica sol-gel method can affect surface energy and ζ potential of the formed silica. Depending on the used dispersant obtained silica had different morphology and surface structure. Most of dispersants used during sol-gel synthesis led to obtain silica with spherical structures and a high tendency to agglomerate. The addition of TEOS and dispersants to rubber mixtures influenced on mechanical properties and crosslink density of the vulcanisates. SEM pictures of vulcanisates showed the presence of silica particles synthesized "in-situ" in elastomer matrix.

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