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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Das, Amit , Jurk, René , Stöckelhuber, Klaus Werner and Heinrich, Gert(2008) 'Silica-Ethylene Propylene Diene Monomer Rubber Networking by *In Situ* Sol-Gel Method', Journal of Macromolecular Science, Part A, 45: 1, 101 – 106

**To link to this Article:** DOI: 10.1080/10601320701683447

**URL:** <http://dx.doi.org/10.1080/10601320701683447>

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# Silica-Ethylene Propylene Diene Monomer Rubber Networking by *In Situ* Sol-Gel Method

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Received January, 2007, Accepted June, 2007

Triethoxysilyl-grafted ethylene propylene diene monomer rubber (EPDM) was prepared with the silane coupling agent, bis-[3-(triethoxysilyl)propyl]-tetrasulfide (TESPT), and thus modified rubber has been treated by an *in situ* sol-gel method with the objective to grow silica particles inside the rubber matrix. TESPT grafted EPDM rubber, filled with the silica particles grown by making use of the described method, was found to exhibit excellent physical properties, despite the fact that the fraction of silica fillers in this material is found to be very low. In particular, thus produced filled rubber has higher reinforcing efficiency that is attributed to the formation of a rubber-silica network. In addition, better silica dispersion is observed in the shear modulus measurements at low dynamic deformation amplitudes, which is in qualitative agreement with the ‘Payne’ effect that quantifies the ability of fillers to promote the formation of rubber-filler networks. No such effect of network formation was observed when an *in situ* sol-gel experiment was performed in the absence of TESPT. TEM observations showed that even if the amount of silica fillers in rubber is as small as 5 phr or less, the uniform mono-dispersed distribution of the silica primary particles is still the main factor responsible for the reinforcement of the rubber matrix.

**Keywords:** silica; silane coupling agent; sol-gel; rubber; nanocomposite

## 1 Introduction

Although carbon black is still considered one of the most important reinforcing agents in the rubber industry, precipitated silica shows the tendency to become a dominant filler material in tire technology. Rapidly growing interest to silica and clay minerals as effective substitutes (1, 2) for carbon black fillers is caused by increasing demands for economic fuel consumption and improved road safety imposed on the tire production technology in the last two decades. For example, hydrated silica is extensively used in silica filled rubber compounds that are produced by the mechanical mixing of silica and rubber. Despite its frequent use, there exists a number of difficulties in the process of filling in the rubber matrix with silica particles. Specifically, here we refer to the strong interaction between silica fillers, incompatibility of silica and rubber, high viscosity caused by filling and the absorption of curatives by fillers (2). The most important disadvantage of silica as a filler is in the very strong

interaction between silica particles, which is caused by the hydrogen bonding of the silanol groups to the silica surface. This interaction prevents fillers from uniformly dispersing throughout the rubber matrix, ultimately giving rise to the formation of large aggregates of silica particles (3). The described problem of silica agglomeration and incompatibility of silica and rubber can be diminished by making use of different types of silane coupling agents (4, 5).

Growing of the *in situ* sol-gel derived silica nano-particles is one of the promising routes for producing a polymer matrix filled with uniformly dispersed silica particles (6–14). There are the two basic methods that serve for reinforcing a rubber matrix by the sol-gel derived silica, specifically before-the-vulcanization reinforcement (15) and after, the vulcanization reinforcement (13, 14) methods.

The former method is more suitable for practical purposes, otherwise the finished rubber article would be deformed by swelling in the tetraethylorthosilicate (TEOS) solutions, which is usually used for the silica generation by an *in situ* method. It was reported (4) that reinforcing efficiency offered by the *in situ* sol-gel reaction of tetraethylorthosilicate (TEOS) in the presence of bis-[3-(triethoxysilyl)propyl]-tetrasulfide (TESPT), a silane coupling agent, is much higher than those obtained either by conventional mechanical mixing or by the *in situ* sol-gel reaction without TESPT.

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This means that TESPT offers an additional positive contribution to a well developed rubber-silica network, even in the reinforcement by *in situ* silica. Ikeda et al. (8) reported that grafting of aminopropyltriethoxysilane (APS) onto the backbone of epoxidized natural rubber could be a promising method to incorporate silica into the rubber matrix. Recently, it is reported that modified polychloroprene-silica composite containing triethoxysilyl group, subjected to *in situ* sol-gel reaction, exhibits excellent physical properties by the virtue of grown silica particles on the backbone of modified chloroprene rubber (16).

This research effort was initiated to study the effect of grafting a silane coupling agent on the generation of an *in situ* silica before its use in the vulcanization reaction. EPDM rubber was selected and efforts were undertaken to graft the silane-coupling agent onto the rubber backbone prior to the vulcanization reaction. Actually, the grafting of silane coupling takes place during the vulcanization reaction, i.e., during the presence of all rubber curatives and silica, when the formulations are made with a silica and silane coupling agent. The aim of our present study is to find the role of the silane functional group, previously attached as a pendant moiety on the EPDM rubber backbone, on the formation of silica by the *in situ* sol-gel process and also to investigate the filler networking of silica developed by the *in situ* process where TEOS is used as a silica precursor. In this technique, it is expected that silica particles will be grown from an ethoxy pendant moiety off a rubber chain. This technique is also expected to prevent the TESPT dissolving out from the rubber matrix into the TEOS solution during swelling, in the case where the silane coupling agent is mixed with the rubber without any grafting.

## 2 Experimental

### 2.1 Materials

Ethylene propylene diene rubber (Buna EP G 6850, ENB content 7%; Ethylene content 55 wt.%; Mooney viscosity, ML (1 + 4) at 125°C = 60) was provided from Lanxess, Leverkusen, Germany. Silane coupling agent, namely bis-[3-(triethoxysilyl)-propyl]-tetrasulfide (Si-69), and precipitated silica were supplied by Degussa AG, Hanau. Tetraethylorthosilicate (Merck, Darmstadt, Germany), n-butyl amine (Merck, Darmstadt, Germany) and accelerator Rhenogran AP 8 (Rhein Chemie, Mannheim, Germany), were used as received.

### 2.2 Preparation of In-Situ Generated Silica in EPDM Rubber

EPDM was mixed with 4 phr TESPT (Si-69) in an internal mixer (Rheocord HAAKE RC300p, System HAAKE R600p Thermo Electron GmbH, Karlsruhe, Germany) at 160°C, having a rotor speed of 50 rpm for a predetermined time. It

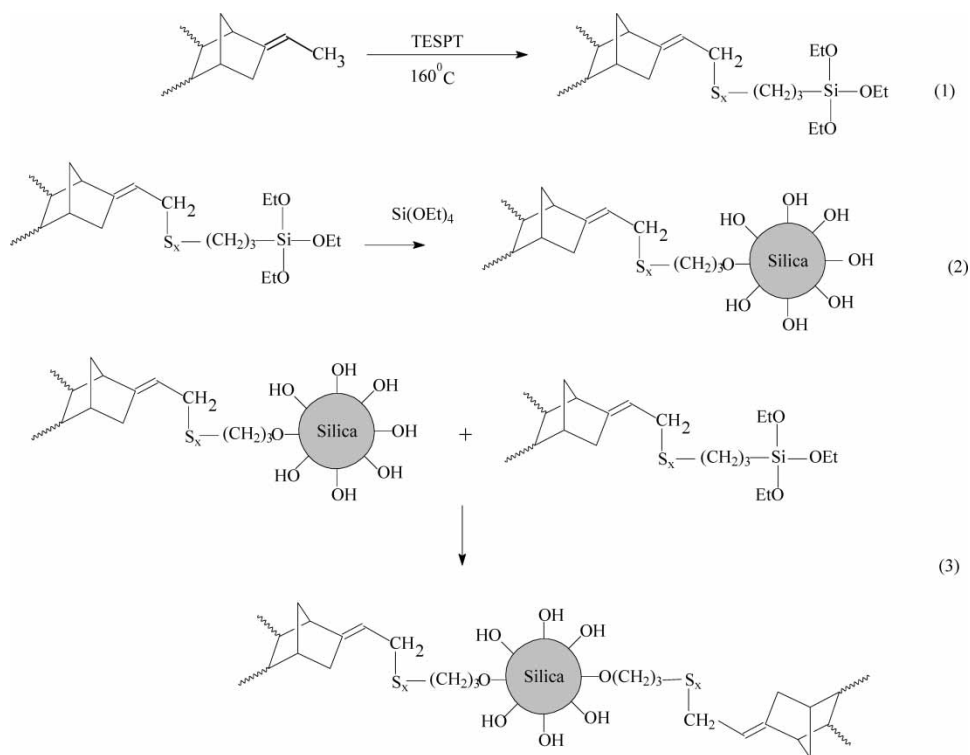
was observed from the rheometric study at 160°C that there is no increment of torque within 15 min time. Therefore, the maximum preheating time in the mixer was chosen up to 11 min. The material thus obtained was transformed into a thin sheet using an open two roll mixing mill, followed by subjecting the film to swelling in the tetraethylorthosilicate solution (TEOS) for 72 h. After removal from the TEOS solution, the rubber was dipped into 10% n-butyl amine aqueous solution for 24 h to get silica particles by the condensation reaction of TEOS. The obtained sheet was dried for several days at room temperature. Finally, the sheet was again dried in a vacuum oven for 8 h at 70°C. The silica filled EPDM rubber was mixed with rubber accelerators and curatives and cured at 160°C, up to the respective optimum curing time ( $t = t_{90}$ ) obtained from the rheometer. The samples are designated in the following way. EPDM-G means only vulcanized gum rubber without any filler. EPDM-TEOST-6-SG and EPDM-TEOST-11-SG is attributed to samples with 6 min and 11 min preheating in the presence of TESPT. SG means that the sol-gel method was followed to generate silica particles. EPDM-TEOST-SG is designated for that compound which has been mixed with TESPT by a two-roll mill and the mix was subjected to sol-gel reaction. EPDM-SG stands for that compound where only rubber was subjected to the sol-gel reaction without any TESPT, and EPDM-VN3 is prepared by mixing EPDM and commercial silica in the open two-roll mill.

### 2.3 Characterization

Rheometric tests were carried out by a moving die rheometer (MDR; SIS-V50, Scarabaeus, Langgöns, Germany) at 160°C with an amplitude of  $\pm 0.5^\circ$  and a frequency of 1.67 Hz. Dynamic strain amplitude measurements were also done with the same MDR. For this measurement, the sample was cured up to corresponding  $t_{90}$  at 160°C, and then the MDR was cooled and conditioned to 60°C for 10 min. Then, the strain sweep analysis was carried out from 0.14 to 140% of strain at 60°C at 0.5 Hz frequency. Tensile tests were carried out with a Zwick 1456 (Model 1456, Z010, Ulm Germany), using a crosshead speed of 200 mm/min (ISO 527). The silica content was measured via thermo gravimetric analysis, using a TA TGA, Q 500 instrument (USA) with a heating rate of 10°C/min. For TEM analysis, ultra-thin sections of the samples were cut by a microtome at about -100°C and the images were obtained using a Libra 120 transmission electron microscope (Zeiss, Oberkochen, Germany), having an acceleration voltage of 200 kV.

## 3 Results and Discussion

It is well known that the sulphur bridge, present in TESPT, can react with an olefinic moiety on the diene rubber to form a pendant ethoxysilane moiety. Simultaneously, this ethoxy part reacts with a silanol group on silica, bringing



**Sch. 1.** Formation of silica particle bonded to rubber.

about formation of rubber silica bonds (5). Therefore, it is expected that if only rubber and silane coupling agents are allowed to react at high temperature (160°C) then rubber can be modified by grafting the silane-coupling agent on the backbone of rubber (17) (Step 1, Sch. 1). This mixing was carried out in an internal mixer up to a predetermined time to ensure no crosslinking in the rubber matrix. The details are provided in the experimental section.

Sample designation, amount of the silica and curing characteristics are found in Table 1. It is evident from this table that in the presence of TESPT, the amount of *in situ* silica is higher than with the absence of TESPT in the rubber matrix. This indicates that the triethoxy group of the silane-coupling agent provides a silica nucleation site and thus more silica particles are formed. However, the amount of silica is less for the TESPT containing compound which

**Table 1.** Preparation and curing characteristics of EPDM rubber compound

Sample code <sup>a</sup>	Method	Amount of silica [g]	Maximum rheometric torque ( $R_{\infty}$ )	$t_{90}$ [min]	$t_2$ [min]	Reinforcing efficiency RE [MPa/g]
EPDM	Gum, without filler	0	14.7	28.23	3.50	—
EPDM-TESPT-6-SG <sup>b</sup>	6 min heating at 160°C with TESPT	6.3	13.2	7.10	0.68	0.06
EPDM-TESPT-11-SG	11 min heating 160°C with TESPT	4.75	11.2	5.39	0.49	0.12
EPDM-TESPT-SG	Room temperature mixing with TESPT in two roll mill	12.65	14.7	3.89	0.55	0.03
EPDM-SG	Only milling in two roll mill	4.46	14.3	5.83	0.87	0.03
EPDM-VN3 <sup>c</sup>	Silica in two roll mill	4.75	13.7	25.66	2.93	0.01

<sup>a</sup>For each mix 2 phr (per hundred gram of rubber) stearic acid, 5 phr ZnO, 4 phr SDT 50, and 0.5 phr sulphur were mixed as curatives before vulcanization process.

<sup>b</sup>SG signifies processed with sol-gel technique.

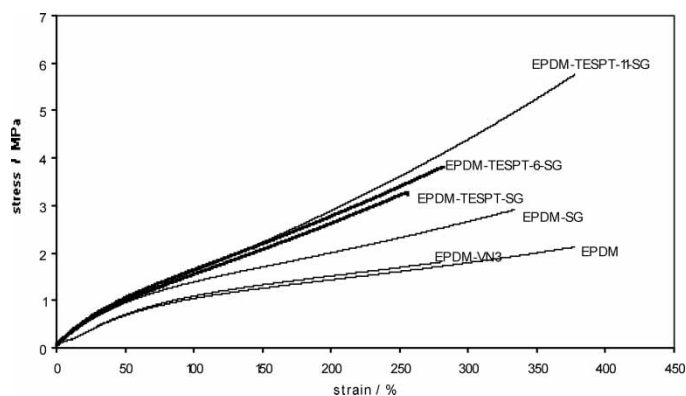
<sup>c</sup>4. 75 phr Ultrasil VN3 was mixed by mechanical mixing to compare with EPDM-TESPT-11-SG.

has been heated in the internal mixer for 11 min as compared with an unmodified (without being heated) compound (compare EPDM-TESPT-11-SG with EPDM-TESPT-SG). This may be due to the fact that non-grafted TESPT comes out from the rubber matrix to the surface of the EPDM rubber and, consequently, TESPT provides more silica nucleation sites which results in more silica on the surface and not in the bulk. Therefore, during mixing, the thus produced silica is incorporated in the rubber matrix. In the presence of TESPT, the amount of *in situ* silica decreases with the increase of mixing time in the internal mixer at 160°C. It may be due to the fact that during thermal treatment the grafting of TESPT fragments (Step 1, Sch. 1) on the backbone of rubber, as well as the condensation between two Si-(OEt)<sub>3</sub> takes place simultaneously to form the Si-O-Si linkage. As a result, the number of silica growing nucleation sites is decreased providing a less amount of sol-gel silica. The same explanation can be given for the compound EPDM-SG, where TESPT was not used and, therefore, much less silica was formed. Clearly, some sort of cross-linking might have been produced by the Si-O-Si linkage during thermal treatment of EPDM with the silane coupling agent, but the number of this type of crosslinking is so negligible that on further processing the rubber compound is not affected. It is also important to note that before crosslinking the rubber matrix, the sol-gel reaction was carried out, but the amount of generated silica particles is less and directly proportional to the amount of TEOS in the swollen EPDM matrix.

Thorough analysis of curing data shows that the maximal rheometric torque is observed for those compounds that have no prehistory of thermal grafting (EPDM-TESPT-SG). The magnitude of torque attains its minimum value for the EPDM compound (EPDM-TESPT-11-SG) heated during 11 min. High values of torque magnitude is also achieved by using the gum compound. The curing time is found remarkably reduced for those rubber compounds that have undergone the sol-gel reaction. In this latter case, n-butylamine was used for condensation reaction of TEOS. When remaining in the rubber matrix, this amine acts as a cure synergistic pair with AP-8 accelerators. As expected, the scorch time appears to be higher for the compounds that have not been preliminarily treated by the sol-gel technique.

The stress-strain diagrams observed for EPDM vulcanizates are plotted in Fig. 1. This Figure shows that the maximum tensile properties are achieved for the vulcanizate that is produced by a preheating procedure (in the course of 11 min heating) in the presence of the silane coupling agent. The corresponding gum vulcanizate shows inferior tensile properties.

It is interesting to note that sol-gel vulcanizates are always stiffer and they have a larger tensile strength, as compared to the conventional filled system EPDM-VN3. This fact can be interpreted as that the silica particles derived in the sol-gel process provide a stronger reinforcement compared to the



**Fig. 1.** Tensile stress-strain plot of silica filled EPDM vulcanizates.

conventional silica filled vulcanizates. The shapes of the curves describing the stress-strain relations for the gum (EPDM) and vulcanizates filled with 4.7 phr silica (EPDM-VN3) are the same for the values of elongation that are less than that corresponding to 50% extension of the initial rubber sample. For larger elongations, the stress observed for the silica filled compound is bigger than that found for its unfilled counterpart measured at the same value of elongation. At the same time, the maximal elongation is found to be higher for the unfilled gum than for vulcanizates filled with 4.7 phr silica. Therefore, we may conclude that 4.7 phr silica, conventionally blended in EPDM rubber, shows no, or only marginal reinforcing activity. In contrast to this observation, a sample filled with with 4.7 phr silica grown *in situ* at TESPT grafted EPDM shows a pronounced reinforcement effect (Fig. 1). In this case, the shape of the stress-strain curve is steeper as compared to that observed for the conventional sample and leads to higher maximum stress. Even such a small amount of silica fillers grown *in situ* by the sol-gel method as 5 phr or less can provide considerable reinforcement of the EPDM rubber.

For better quantitative understanding, we introduce the reinforcement efficiency (RE) (11) that is to be derived from the tensile strengths measurements. RE is defined as the quotient of the 100%-moduli  $M_{100}$  (stress at 100% elongation) of a filled vulcanizate ( $M_{100, \text{filled}}$ ) and its unfilled counterpart ( $M_{100, \text{gum}}$ ), referred to the amount of filler (in wt.%). This reinforcement efficiency is defined by:

$$RE = (M_{100, \text{filled}} - M_{100, \text{gum}}) / \text{wt. \% filler}$$

As is evident from Table 1, the RE value of EPDM-TESPT-11-SG is quite high in comparison with the other vulcanizates. For this compound (EPDM-TESPT-11-SG), the nucleation of the silica particles takes place at the pendant ethoxy group at the polymer backbone, which was induced by the prior reaction with TESPT. Therefore, the direct rubber silica bonding (Step 2, Sch. 1) can occur, resulting in a more uniform dispersion of silica nano-particles in the rubber matrix and causing a strong reinforcement of the vulcanizates.

Obviously, this type of strong reinforcement by using a small amount of silica is caused by the formation of silica bridges between pairs of the rubber chains, as shown in Step 3, Sch. 1.

As is evident from Fig. 1, the elongation at break is also quite high for the EPDM-TESPT-11-SG compound (compare EPDM-TESPT-11-SG with the others). For this type of the rubber vulcanizate, the polysulfidic linkage (18, 19) (Sch. 1) between the rubber and filler is the main factor responsible for larger elongations.

It is worth mentioning that 4.7 phr nanosilica fillers provide the maximum tensile properties of the EPDM rubber system. A higher amount of filler loading leads to agglomeration of the filler particles, which results in a decline of the above described physical properties of the composite. This process of agglomeration through the interaction between fillers particles can be better understood by studying the strain dependence of the dynamic modulus at lower strain values (20, 21). In this method, the shear storage modulus  $G'$  is measured as a function of the strain amplitude. Usually, at higher filler loadings, the modulus remains constant with increasing the deformation in the low strain amplitude range, and in the higher strain region the value of  $G'$  decreases with increasing strain. Being indicative of the formation of the filler networks inside the polymer matrix (19–21), this behavior of the shear modulus is known as the 'Payne Effect' (20). It is evident from Fig. 2 that the gum EPDM shows lowest  $G'$  at low deformations. This effect being most pronounced for the sample EPDM-VN3, i.e., the filler network is more developed for the conventional mixed silica rubber. Among the considered set of filled rubbers, the sample EPDM-TESPT-11-SG exhibits lowest values of  $G'$ , which indicates that the sol-gel grown silica particles are well dispersed, i.e., show less tendency to the agglomeration and thus providing a pronounced reinforcement of the rubber matrix. It is important to mention that the 'Payne effect' is most pronounced when the amount of filler loading achieves sufficiently high values that exceed the percolation threshold. In the considered case of low silica amount, the

fillers are thus unable to form a continuous macroscopic filler network throughout the rubber matrix. Nevertheless, we observe variation in the  $G'$  values in the region of very low strains, despite the fact that the absolute value of  $G'$  is very small. This may be interpreted as, few filler clusters are formed even at low filler concentrations, thus creating local filler networks that are concentrated in the confined spatially separated domains rather than being distributed throughout the whole rubber matrix. Note that the steep drop in  $G'$  at higher strain values ( $\approx / > 50\%$ ) is due to the slippage of the specimen. Therefore, the same drop is also observed with the unfilled gum sample.

The TEM observation supports the above discussion that in the presence of grafted alkoxyisilyl groups; the silica particles are grown as more or less mono-dispersed spheres, similar to that of primary particles (Fig. 3, EPDM-TESPT-11-SG). In the presence of TESPT in the rubber matrix (in the absence of heat treatment), the amount of silica is higher, but the size distribution of the particles more poly-disperse and some of the particles form primary particle agglomerates (Fig. 3: EPDM-TESPT-SG). Furthermore, Fig. 3 shows a very small number of silica particles for EPDM-SG where no TESPT has been used before applying the sol-gel process. This indicates that in EPDM rubber the presence of TESPT plays a crucial role in the formation of silica particle from TEOS.

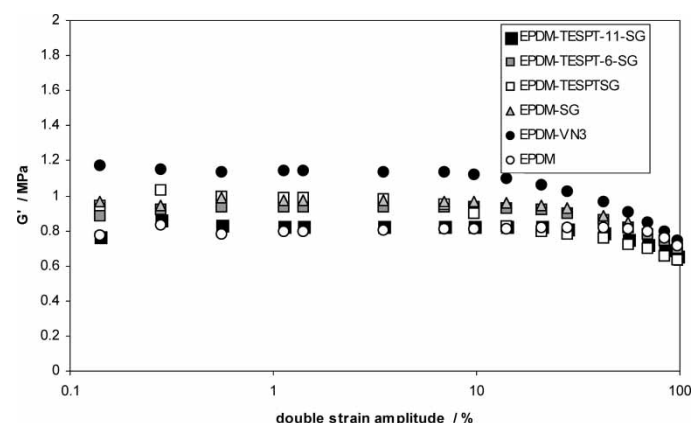


Fig. 2. Strain dependence of  $G'$  at 60°C for EPDM vulcanizates.

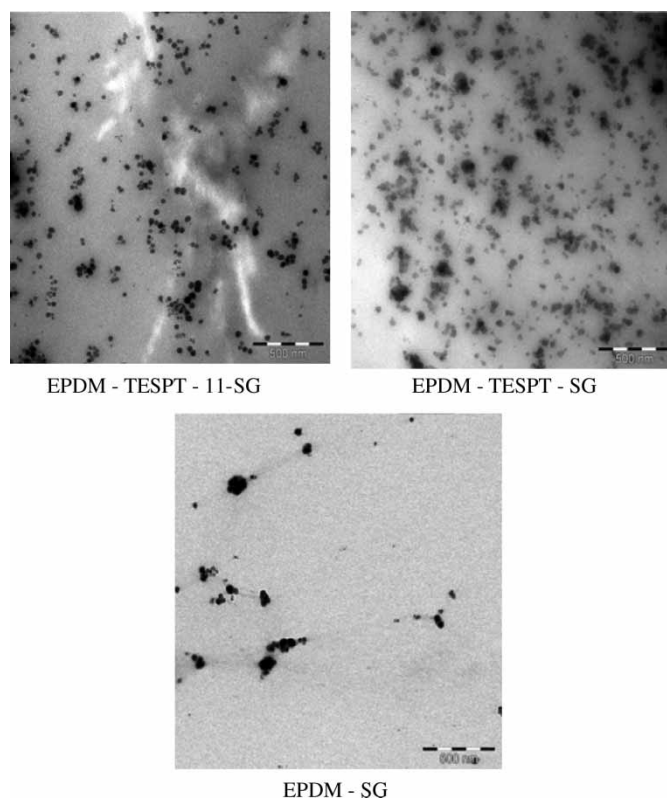


Fig. 3. TEM images of the sol-gel derived silica filled EPDM matrix.

#### 4 Conclusions

We found that grafting of TESPT fragments to the backbone of EPDM rubber provides nucleation sites for precursor of the silica nano-particles, which in turn leads to the formation of a strong silica-rubber network chemically bonded to the rubber matrix. Furthermore, the pendant TESPT moiety on the backbone of EPDM rubber plays a major role in uniformly dispersing the silica particles throughout the rubber matrix. *In situ* sol-gel derived silica fillers have superior reinforcing efficiency, as compared to the externally added silica at the same concentration of these fillers in the rubber matrix. The mono-dispersed silica particles are found to strongly anchored at the rubber backbone by the silane-coupling agent, which enforces pronounced reinforcement effect of these fillers on the rubber matrix, even if the concentration of silica particles in this matrix is very low.

#### 5 Acknowledgments

We thank to DIK (Deutsches Institut für Kautschuktechnologie e. V., Hannover (Germany)) for providing the TEM pictures. Dr. Carla Recker, Continental AG, Hannover (Germany) is acknowledged for her helpful discussion. This work was funded by the German Federal Ministry of Education and Research (BMBF) Grant 03X0002E.

#### 6 References

- Arroyo, M., López-Manchado, M.A. and Herrero, B. (2003) *Polymer*, **44**, 2447.
- Iler, R.K. *The Chemistry of Silica*; John Wiley & Sons: New York, p. 8, 1979.
- Wolf, S. (1996) *Rubber Chem. Technol.*, **69**, 325.
- Kohjiya, S. and Ikeda, Y. (2000) *Rubber Chem. Technol.*, **73**, 534.
- Plueddemann, E.P. *Silane Coupling Agent*; Plenum Press: New York, 1982.
- Wang, S., Xu, P. and Mark, J.E. (1991) *Rubber Chem. Technol.*, **64**, 746.
- Wen, J. and Mark, J.E. (1994) *Rubber Chem. Technol.*, **67**, 806.
- Hashim, A.S., Kohjiya, S. and Ikeda, Y. (1995) *Polym. International*, **38**, 111.
- Ikeda, Y., Tanaka, A. and Kohjiya, S. (1997) *J. Mater. Chem.*, **7**, 1497.
- McCarthy, D.W., Mark, J.E. and Schaeffer, D.W. (1998) *J. Polym. Sci. Part B: Polym. Phys.*, **36**, 1167.
- Hashim, A.S., Azahari, B., Ikeda, Y. and Kohjiya, S. (1998) *Rubber Chem. Technol.*, **71**, 289.
- Murakami, K., Iio, S., Tanahashi, T., Kohjiya, S., Kajiwara, K. and Ikeda, Y. (2001) *Kautsch. Gummi Kunstst.*, **54**, 668.
- Ikeda, Y. and Kohjiya, S. (1997) *Polymer*, **38**, 4417.
- Murakami, K., Osanai, S., Shigekuni, M., Ito, S., Tanahashi, H., Kohjiya, S. and Ikeda, Y. (1999) *Rubber Chem. Technol.*, **72**, 119.
- Ikeda, Y. and Kameda, Y. (2004) *J. Sol-Gel. Sci. Technol.*, **31**, 137.
- Sunada, K., Takenaka, K. and Shiomi, T. (2005) *J. Appl. Polym. Sci.*, **97**, 1545.
- Lugisland, H.-D. (2000) *Kautsch. Gummi Kunstst.*, **53**, 10.
- Hashimoto, K., Harada, T., Ando, I. and Okubu, N. (1970) *J. Soc. Rubber Ind. Japan*, **43**, 652.
- Biswas, T., Naskar, N. and Basu, D.K. (1995) *J. Appl. Polym. Sci.*, **58**, 981.
- Payne, A.R. (1965) *J. Appl. Polym. Sci.*, **9**, 2273.
- Kraus, G., Childers, C.W. and Rollmann, K.W. (1966) *J. Appl. Polym. Sci.*, **10**, 229.