

In Situ Synthesis of Rubber Nanocomposites

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Abstract The preparation and characterization of rubber based nanocomposites prepared by in situ generation of inorganic oxides by means of the hydrolytic sol–gel process are reviewed in the present chapter. The sol–gel approach has been applied to several rubber matrices to prepare reinforced vulcanized and unvulcanized rubbers. Several synthetic procedures are presented while the most investigated filler is silica obtained by hydrolysis and condensation of tetraethoxysilane. The effects of the different preparation conditions and of the filler content are generally discussed in terms of morphology (investigated by electron microscopy and small angle X-ray scattering) and mechanical properties (modulus, strength and extensibility). The mechanical properties of the in situ filled nanocomposites are generally better than those of the corresponding materials prepared with the conventional mechanical mixing of preformed particulates and elastomers. This enhancement is generally attributed to a lower tendency to filler–filler aggregation due to a lower particle surface interaction resulting from the ‘bottom-up approach’ of the sol–gel process applied to the preparation of organic–inorganic hybrid materials.

1 Introduction

The improvement of the mechanical properties (reinforcement) of elastomeric materials by addition of rigid fillers represent one of the most important aspects in the field of rubber science and technology [1]. The concurrent enhancement of

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stiffness (elastic modulus) and, possibly, of elongation at break due to the presence of rigid particles derives from hydrodynamic effects mainly depending on the filler volume fraction but also affected by the filler shape factor (aspect ratio). The interactions between rubber and filler, which can be increased if good dispersion and distribution of the particulate are achieved, play a fundamental role for the increase of elastic modulus. The surface characteristics of the particles (presence of reactive/functional groups, wettability and surface energy) and the chemical nature of the rubber represent the key parameters for these interactions.

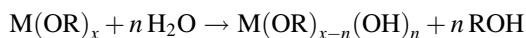
Concerning the field of fillers having dimensions in the nanometric scale, polymer matrix nanocomposites have attracted extraordinary attention in the last decade on the basis of their excellent mechanical and barrier properties compared to the conventional microcomposites, usually at very low filler content. Layered silicates, ceramic nanoparticles (such as silica, titania, zirconia, etc.), carbon nanofibers and nanotubes are typical examples of materials used as nanosize reinforcing additive [2]. The usual method for the preparation of nanocomposites is based on the top-down approach according to which preformed nano-objects are dispersed within the polymeric matrix by physical-mechanical dispersion and distribution (melt or solution mixing). Even if very attractive from an industrial point of view, this method presents some severe limitations related to the difficulties to obtain an effective dispersion due to the strong tendency to particles aggregation phenomena and the significant increase of melt viscosity because of the complex rheology of nanocomposite systems.

In particular, in the specific case of rubber composites, it is well known that carbon black represents the most effective reinforcing additive for elastomeric compounds notwithstanding the strong limitation due to the black coloration imparted to the final part. Alternatively to carbon black, also silica is another filler widely employed in the rubber industry, thanks to some advantages deriving from its use such as high tear strength, good abrasion resistance and reduction in heat build-up [3]. The main drawbacks associated with the use of conventional silica as reinforcing additive instead of carbon black are the higher compound viscosity, the incompatibility of silica and rubber, the more difficult mixing and processing, the longer vulcanization time, the lower cross-linking density and the absorption of curative additives by silica. Most of these disadvantages are due to the very strong interaction occurring among silica particles and caused by the hydrogen bonding of the silanol groups present onto the silica surface. This interaction inhibits an uniform dispersion of the filler within the rubber matrix giving rise to the formation of particles' aggregates. Silica agglomeration and silica-rubber incompatibility are generally reduced by using different types of silanes as coupling agents.

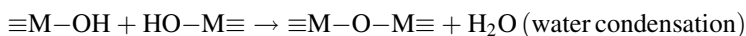
In order to minimize these problems and alternatively to the usually employed processing technique (mechanical mixing) for the preparation of filled vulcanized rubber, the in situ generation of silica (or other inorganic oxides) by using the sol-gel process has been recognized as a novel and interesting technique for the preparation of rubber composites.

The classical aqueous (or non-hydrolytic) sol–gel process [4] consists of a two-step hydrolysis-condensation reaction starting with metal alkoxides $M(OR)_x$, typically tetraethoxysilane (TEOS), according to the following scheme:

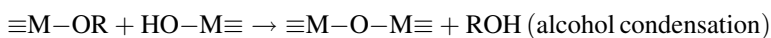
Step 1: Hydrolysis



Step 2: Condensation



and/or



The presence in the reactive system of an organic oligomer or polymer (bearing or not suitable groups reactive towards to the sol–gel process) leads to the formation of organic–inorganic hybrid structures composed of metal oxide (silica or other) and organic phases intimately mixed each other. This synthetic procedure belongs to the so-called ‘bottom-up’ approach for the preparation of hybrid materials and, depending on the experimental conditions, permits the synthesis of composite structures in which the dimensions of the dispersed phase are under 100 nm (nanocomposites). The optical, physical and mechanical properties of these nanocomposites are strongly dependent not only on the individual properties of each component, but also on important aspects of the chemistry involved such as uniformity, phase continuity, domain size and the molecular mixing at the phase boundaries.

The morphologies of the hybrid materials are strictly dependent on the characteristics of the organic polymer such as the molecular weight, the presence and the number of reactive functionalities as well as the solubility of the polymer in the sol–gel system.

The nature of the interface between organic and inorganic phases is generally used to grossly divide these materials into two distinct classes. In Class I, organic and inorganic components are simply embedded and only weak bonds (hydrogen, dipolar and van der Waals bonds) give the cohesion to the whole structure. On the contrary, in Class II materials, the two phases are linked together through strong chemical bonds (covalent or ionic bonds).

Several applications of organic–inorganic hybrid nanocomposites prepared by sol–gel and other procedure have been already extensively reviewed [5–8]. It is also important to underline that the use of the sol–gel procedure for the preparation of rubber matrix nanocomposites could present some peculiarity mainly due to the possibility to vulcanize a preformed organic polymer (‘green’ rubber).

The majority of the reported papers deals with the preparation and characterization of elastomers filled with in situ generated silica obtained from TEOS as precursors while a much more limited literature on other inorganic oxides such as titania, zirconia and alumina is available. Several synthetic procedures are proposed and the characterization is mainly devoted to mechanical and/or thermomechanical properties, such as quasi-static tensile measurements or dynamic mechanical analysis, and to morphology investigation by means of scanning and transmission electron microscopy and/or small-angle X-ray scattering. One of the main targets is the development of nanocomposites with improved properties with respect to similar materials obtained with the conventional mechanical mixing of rubber and preformed nanoparticles.

In the present chapter a general overview on the in situ generation of silica or other reinforcing fillers within elastomeric phases reported in literature is presented and discussed for different elastomeric matrices.

2 General Synthetic Strategies

From a generic point of view, the in situ generation of an inorganic oxide phase (usually having a spherical or quasi-spherical shape) by means of the sol-gel process within an elastomeric polymer can be carried out according to different strategies, as step-by-step schematically described in the following.

Solution procedure (procedure A)

- (i) dissolution of both the metal alkoxide (metal oxide precursor) and unvulcanized rubber in a common solvent;
- (ii) addition of water (directly added or absorbed from the external humid atmosphere), sol-gel catalysts (basic or acidic) and vulcanization ingredients (optional) and activation of the sol-gel process at a given temperature and for a given reaction time;
- (iii) removal of solvent and by-products (usually water and alcohols) by evaporation or precipitation in a non-solvent;
- (iv) vulcanization of the filled 'green' rubber (optional).

Swelling of unvulcanized rubber (procedure B)

- (i) immersion and swelling of films or sheets of unvulcanized rubber in metal alkoxide;
- (ii) immersion of the swollen rubber in a basic or acidic aqueous solution and activation of the sol-gel process at a given temperature and for a given reaction time;
- (iii) mechanical mixing (usually by using a conventional two-roll mill) of the filled 'green' rubber with the vulcanization ingredients and vulcanization (optional).

Swelling of vulcanized rubber (procedure C)

- (i) immersion and swelling of films or sheets of vulcanized rubber in metal alkoxide;
- (ii) immersion of the swollen vulcanized rubber in a basic or acidic aqueous solution and activation of the sol–gel process at a given temperature and for a given reaction time.

It can be anticipated that the procedure A (in solution) ensures a highly homogeneous dispersion of the in situ generated filler within the rubber matrix also for high reinforcing metal oxide contents. The swelling of unvulcanized rubber (procedure B) is highly attractive especially for industrial applications thanks to its solvent-free approach while the swelling of vulcanized rubber (procedure C) is very simple and can be in principle applied to already moulded three-dimensional articles (even if limitations in the maximum amount of filler generated can be present due to the cross-linked structure of the swollen rubber).

3 Rubber Based Nanocomposites

3.1 Polydimethylsiloxane Based Nanocomposites

Polydimethylsiloxane (PDMS) is the most important member of the class of polysiloxanes and presents some interesting properties thanks to the presence of Si–O–Si linkages in the polymeric backbone such as good thermal stability, water repellency, excellent resistance to oxygen, ozone and UV-light, anti-stickiness and low chemical reactivity. As drawbacks, PDMS is characterized by very poor mechanical properties, in particular tensile strength, and it requires the addition of reinforcing additives (usually mineral fillers) in order to achieve the mechanical properties required depending on the final application.

PDMS is traditionally reinforced with silica and the filler–matrix interactions are ensured through hydrogen bonding between silanol groups of silica surface and oxygen atoms of PDMS macromolecules. Surface modification of silica particles permits the optimization of the interactions between mineral filler and polymer. Due to the concurrent presence of Si–O groups in both silica and PDMS, it is not surprising that these represent one of the first systems investigated in the field of in situ generation of silica within polymeric matrix, as indicated by the pioneeristic works of Mark [9, 10].

3.1.1 PDMS-Silica Nanocomposites

According to a slight modification of the above described procedure C (swelling of vulcanized rubber), Rajan et al. [11] reported a method (named *controlled hydrolysis*, CH) for the in situ generation of silica particles in which, after swelling

Table 1 PDMS/SiO₂ composites: sol–gel catalysts, filler content and mechanical properties (adapted from Ref. [11])

Catalyst	Silica (wt%)	Ultimate strength (MPa)	Elongation (relative length) at rupture
None	0.0	0.082	1.77
Dibutyltin diacetate	5.4	0.538	1.68
	8.9	0.818	1.63
	14.2	0.712	1.09
Dibutyltin dilaurate	6.0	0.543	2.01
	8.0	0.831	1.93

of cross-linked PDMS in TEOS, the required water of hydrolysis was simply absorbed from the air and the catalyst was generated from tin salts (dibutyltin diacetate or dilaurate). These PDMS nanocomposites had a silica content up to 14 wt% and were characterized by an unusually high transparency (if compared to similar materials obtained with aqueous ammonia as catalysts) as quantitatively judged by UV–VIS spectroscopy. Electron microscopy showed that silica domains were very small (30–50 nm in diameter) and well dispersed, as expected from the transparency of the composites. Tensile stress–strain measurements indicated that the particles provide very good reinforcement. Data reported in Table 1 indicate that the ultimate tensile strength and Young’s moduli increased with higher silica content and elongation at break remained almost the same of the unfilled PDMS (up to a silica content of about 9 wt%).

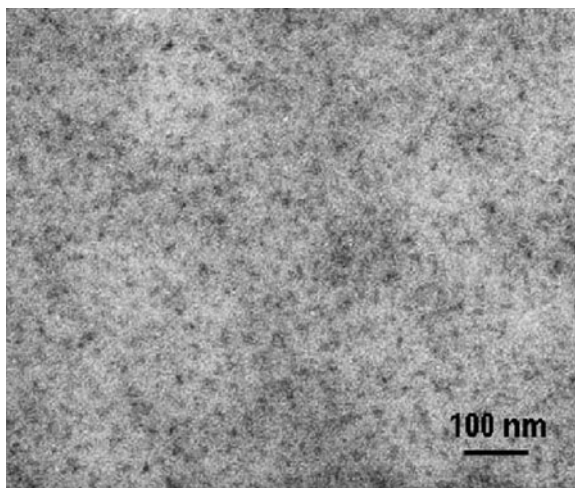
The dependence of silica particle dimensions on PDMS cross-linking density, silica content and catalyst concentration was investigated by small-angle X-ray scattering [12].

Of particular interest were the relationships between particle size and molecular weight of the network chains (M_c , mesh sizes), amount of filler introduced and catalyst concentration.

Silica particle sizes were smallest for the smallest values of M_c , presumably due to constraining effects deriving from the very short network chains. At fixed M_c and filler concentrations, higher catalyst concentrations gave larger particles. Increase in silica concentration generally had little effect on particle size at low and high loadings, but markedly increased sizes at intermediate levels (10–20 wt%), presumably caused by coalescence of isolated small particles into considerably larger aggregates.

Films comprised of PDMS and in situ generated SiO₂ were applied on silicon, aluminum and polystyrene substrates. The surfaces in contact with air and with a substrate were investigated by using several surface technique [13]. The hybrid sample surfaces generated in contact with air were characterized by a silica-free PDMS top layer of about 2 nm; in the surfaces in contact with the substrates SiO₂ was located at or just beneath the outermost atomic layer. In contact with polar liquids such as water, polar hydroxy groups present at the surface of SiO₂ can easily stretch out to the outer-most atomic layer. Quite surprisingly, no significant correlation was found between the roughness of the surfaces and the amount of in situ generated SiO₂ present in the materials.

Fig. 1 TEM image of PDMS/SiO₂ composites (silica content 10 phr) (reproduced with permission from Ref. [14])



Bokobza et al. [14, 15] applied the same synthetic procedure to obtain similar composites by starting from a cross-linked vinyl-terminated PDMS. Authors found that the in situ generated silica structures were uniformly dispersed within the elastomeric matrix (see Fig. 1) but different morphologies were obtained as a function of the used tin-based catalyst and thus of the type of growth processes. The hydrophilic character of the silica surface was responsible of extensive interaction with PDMS chains leading to a significant improvement in the mechanical properties of the composites.

An interesting comparison among PDMS reinforced with different types of fillers has been published by Bokobza [16]. Three different techniques of incorporation of silica were compared: the conventional mechanical mixing process, in situ filling process and introduction of spherical colloidal silicas (Stöber silicas). In addition, results obtained with other types of fillers (layered silicates and fibrous clays) were reported and discussed. Among the different types of reinforcement of PDMS imparted by silica particles, the in situ filling process was by far the most efficient. As reported in Table 2, the modulus, ultimate stress and extensibility increased by increasing the filler loading. Moreover, larger increases were observed over the silica particles percolation threshold.

Table 2 PDMS/SiO₂ composites: mechanical properties (adapted from ref. [16])

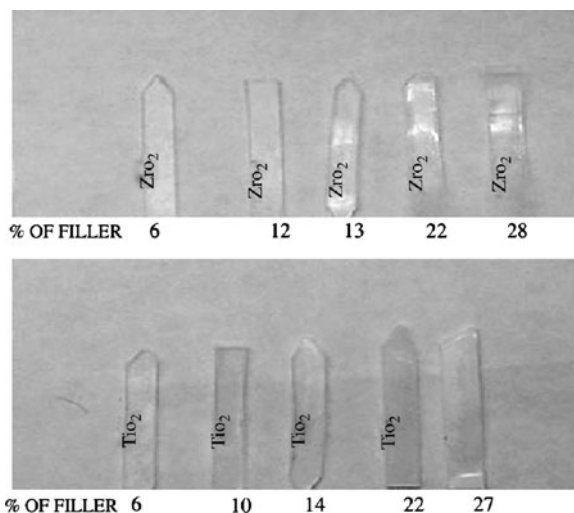
Compound	Stress at 100% strain (MPa)	Stress at 200% strain (MPa)	Tensile strength (MPa)	Elongation at break (%)
Unfilled sample	n.r.	n.r.	0.43	91
10 phr SiO ₂	1.44	4.98	7.64	242
18 phr SiO ₂	2.49	7.86	10.70	240
30 phr SiO ₂	5.19	10.35	21.54	313
40 phr SiO ₂	7.99	16.38	27.34	275

3.1.2 PDMS-Titania and PDMS-Zirconia Nanocomposites

The same CH method was used by Murugesan and Mark [17, 18] for the preparation of PDMS containing in situ generated titania and zirconia starting from different alkoxides and the obtained materials were compared to those prepared according the so-called conventional ‘water excess process’ (WE, based on the direct addition of stoichiometric water to the cross-linked PDMS swollen in the corresponding metal alkoxide). The composites prepared by the CH method were characterized by a greater amount of filler (higher conversion of alkoxides to zirconia or titania) for the same reaction time. The optical transparency of the prepared materials is reported in Fig. 2 and UV–VIS analysis showed that the transmittance values of PDMS/ZrO₂ were significantly higher than those of PDMS/TiO₂ (47 and 28% for composites containing 6 wt% of filler and 16 and 0.01% for composites containing 28 wt% of filler, respectively) according to the fact that titania particles formed small aggregates compared to zirconia, as evidenced by small-angle X-ray scattering analysis and leading to a higher opacity.

Thermogravimetric analysis showed that PDMS/ZrO₂ composites had a lower thermal stability with respect to PDMS/TiO₂ composites, which were inherently more stable due to the formation of different phases at high temperatures. Concerning the mechanical properties, all the PDMS/ZrO₂ and PDMS/TiO₂ composites (independently on the preparation method) had mechanical properties much improved with respect to the unfilled elastomer. The reinforcement of zirconia filled composites was greater compared to titania filled composites even for similar amount of filler presumably due to the smaller dimension of ZrO₂ particles, consistently with the above discussed transparency.

Fig. 2 Transparency comparison of PDMS/ZrO₂ and of PDMS/TiO₂ composites (reproduced with permission from Ref. [18])



3.1.3 PDMS-(mixed oxides) Nanocomposites

Wen and Mark [19] reported the in situ generation of silica–titania mixed oxide within a PDMS network (previously cross-linked with TEOS). TEOS and tetrabutyl titanate (TBT) were the precursors of the correspondent oxides. Since the TEOS hydrolysis is extremely slow compared to titanium alkoxides, hydrolysis of a mixture of them generally results in phase segregation leading to a physical mixture of two oxides instead of a true mixed oxide. This problem has been avoided carrying out a partial hydrolysis of pure TEOS with subsequent addition of the more reactive TBT. The sol–gel process has been activated by placing the swollen PDMS in 2 wt% diethyleneamine aqueous solution at room temperature leading to composites with a silica–titania content ranging from 10 to 22 wt%. TEM analysis carried out on PDMS/SiO₂–TiO₂ composites showed a filler average diameter of 20–25 nm, with a relatively narrow diameter distribution and with very little aggregation of particles. A further interesting observation was the increase of the particle size by decreasing the cross-linking density of the rubber, as already evidenced for PDMS/SiO₂ nanocomposites [12].

The analysis of equilibrium swelling data on the basis of the Kraus' theory [20] suggested that the composites were of the *adhering type* in which the rubber matrix is restricted by the filler through attachments onto the filler surface.

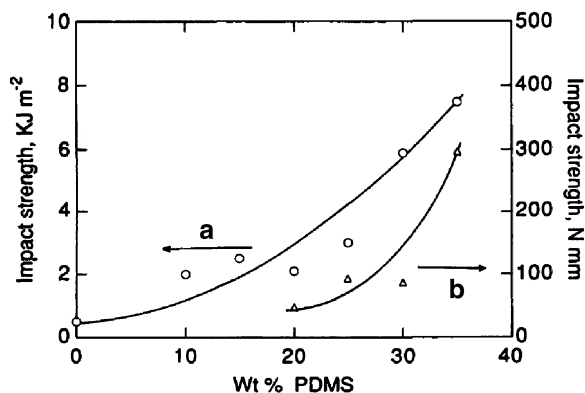
Concerning mechanical properties, stress–strain isotherms represented as plots of modulus against reciprocal elongation according to the Mooney–Rivlin equation [21, 22] indicated that, compared to the silica-filled PDMS networks, the mixed-oxide based composites had better extendibility and had upturns which occurred at higher elongations (but were smaller because of the lower reinforcing effect provided by TiO₂).

The presence of in situ generated silica–titania mixed oxides also increased the onset temperature for thermal degradation of PDMS, on the contrary of that showed by physical mixing of preformed silica and/or titania nanoparticles.

The same authors reported a further study [23] on the preparation and characterization of PDMS/SiO₂ and PDMS/TiO₂–SiO₂ composites having inorganic contents ranging from 30 to 100 wt% and in which the sol–gel reaction (conversion of TEOS in SiO₂ and of TBT in TiO₂ and corresponding mixed oxides) occurred simultaneously with the cross-linking of PDMS due to the co-condensation of hydroxyl-terminated PDMS and TEOS. Experimental data indicated that this last process was dominant and that the majority of the PDMS was incorporated in the silica network. The addition of PDMS was found to shorten the gelation times and to increase the rates of increase in modulus of the network structure. The impact strength and the fracture surfaces of the materials were studied with the finding that the presence of PDMS significantly increases their impact strength and ductility, as shown in Fig. 3.

The growth processes and resulting structures of the reinforcing fillers were investigated by small-angle X-ray scattering by Breiner and Mark [24]. The systems were found to yield dense particles with fractally rough surfaces and the results were used to interpret mechanical properties of these composites.

Fig. 3 Dependence of impact strengths on PDMS content for PDMS/SiO₂ composites. The impact strength were obtained from **a** the Charpy pendulum impact test and **b** the falling-weight impact test (reproduced with permission from Ref. [23])



The reinforcement with mixed oxides seems to synergistically combine the best properties of titania and silica: the titania provides additional reinforcement at low strains and allows for higher elongations to be obtained, whereas the silica contributes to the reinforcement over the entire range of allowable strain and gives rise to the very desirable upturn in modulus at high elongations.

Wen and Mark [25] also reported the precipitation of silica–zirconia and silica–alumina mixed oxides (at a concentration ranging from 10 to 22 wt%) into PDMS networks using a sol–gel approach according the above described method. The resulting filled networks were found to have very good mechanical properties. In comparison with networks filled only with silica, these materials had good extensibilities as well as high strengths. Filler particle diameters were generally several hundred angstroms, but also in this case were found to decrease with increase in cross-linking density of the networks. The distributions of particle size were relatively narrow, and there was very little particles aggregation. The presence of in situ generated silica–titania and silica–zirconia mixed oxides also improved the thermal stability of the PDMS.

3.2 Natural Rubber Based Nanocomposites

Bokobza and co-workers [26, 27] reported the preparation and the characterization of natural rubber (NR) composites containing in situ generated silica particles by hydrolysis and condensation of TEOS before the vulcanization of the rubber matrix in solution (according to the procedure A) and after the vulcanization of the rubber (according to the procedure C) with or without the addition of a silane coupling agent (bis(3-triethoxysilylpropyl) tetrasulfide, TESPT). The silica content of the prepared composites varied from 8 to 21 phr.

Tensile stress–strain experiments showed that, at a given strain, the stress increased by increasing the silica content showing a significant reinforcing effect due to the presence of in situ generated silica.

It is generally accepted that the increase of the stiffness (modulus) deriving from the generation or incorporation of active filler within a polymeric matrix is related to two factors: (i) a hydrodynamic effect arising from the presence of rigid particles and (ii) an increase in the cross-linking density due to polymer–filler interactions. The first term can be quantitatively described by the following Guth and Gold equation [28, 29]:

$$G = G_0(1 + 2.5 \cdot \phi + 14.1 \cdot \phi^2)$$

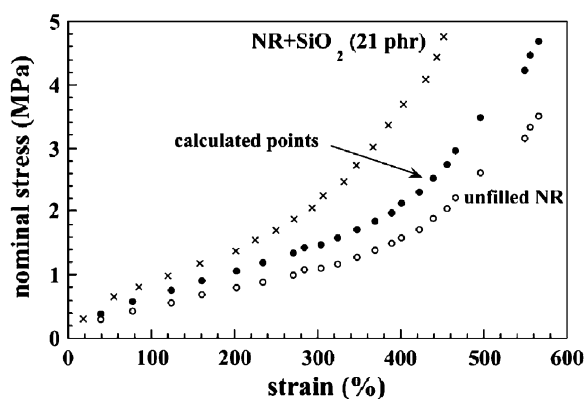
where G and G_0 represent the moduli of the composite and the unfilled polymeric matrix, respectively, and ϕ represents the volume fraction of the filler.

As shown in Fig. 4, the stress–strain curve calculated by using the Guth and Gold equation was lower with respect to the experimental curve indicating that, besides a hydrodynamic reinforcement, the presence of filler–rubber interactions must be considered. Similar conclusions were also reported analysing the stress–strain data according to the Mooney–Rivlin plots and on the basis of equilibrium swelling tests.

Authors also demonstrated that silica particles generated before rubber vulcanization (according to the procedure A) inhibit the cross-linking reaction of the rubber compound by sulphur. The presence of a filler networking structure, due to the aggregation of silica particles via the silanol groups present on the surface, was suggested by the Mooney–Rivlin plot analysis. On the other hand, the tendency to form a particle–particle network was avoided when silica was generated in the already vulcanized rubber (according to the procedure C) and small and well dispersed particles were observed.

Pissis and co-workers [30, 31] investigated the molecular dynamic of the above discussed materials. Broadband dielectric relaxation spectroscopy investigations reported in these papers demonstrated that, in addition to the α relaxation related to the glass transition of the rubber matrix, a slower α relaxation was observed and assigned to polymer chains close to the polymer/silica interphase whose mobility

Fig. 4 Experimental and calculated (Guth and Gold equation) stress–strain curves for NR/SiO₂ composites (reproduced with permission from Ref. [26])



is restricted due to interaction with the silica surface. Authors reported an estimation of the thickness of this interphase of about 2.1–2.4 nm.

Poompradub and co-workers [32, 33] prepared in situ silica reinforced NR by means of the procedure in solution (procedure A) with *n*-hexylamine as basic catalysts without any subsequent vulcanization and investigated the preparation conditions and the rheological and mechanical properties of the prepared rubber composites (having a silica content ranging from 10 to 70 phr).

Different solvents were used for the synthesis (CCl_4 , CHCl_3 and tetrahydrofuran, THF) and it was found that the lower amount of silica in rubber matrix was generated when CCl_4 and CHCl_3 were used compared with THF. The best behaviour of THF was attributed to its higher water solubility and polarity.

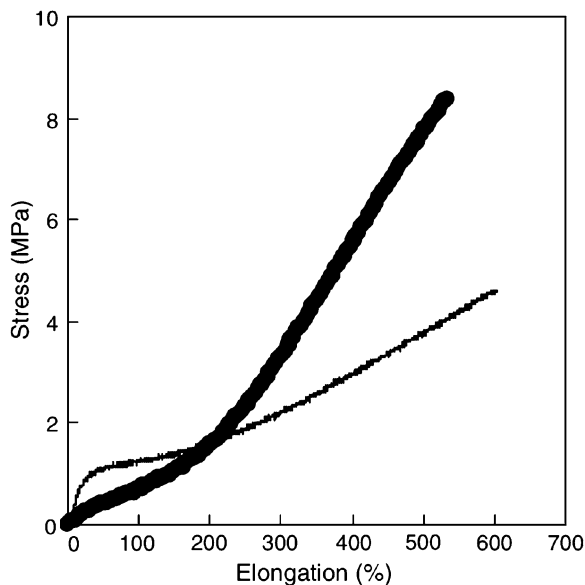
As expected, they observed an increase in Mooney viscosity by increasing the in situ generated silica content. Interestingly, at the same filler content the viscosity of composites containing in situ generated silica was lower compared to that of rubber reinforced with preformed silica dispersed by mechanical mixing. This behaviour has been attributed to the presence of a lower amount of silanol groups onto the surface of in situ generated silica with respect to commercial preformed silica, as further supported by dynamic mechanical analysis which suggested that the silica–silica interactions of the in situ generated silica were weaker, resulting in a better dispersion in the rubber matrix.

Also the moduli and compression set values of NR filled with in situ generated silica were improved with respect to the commercial silica ones. The reinforcement has been modelled by using the Guth and Gold equation with a shape factor $f = 2.53$ (according to the morphology evidenced by TEM analysis). Authors concluded that the volume fraction of filler, the particle–particle interaction and the anisotropy of silica particles represent the three main factors affecting the reinforcing effect due to the in situ generation of silica within the NR matrix.

Ikeda and Poompradub [34–37] reported the preparation and the characterization of NR composites containing in situ generated silica particles from TEOS in the presence of amines as catalyst before the vulcanization of the rubber (thus according to the procedure B). As a general procedure, sheets of NR having a thickness of about 1 mm were prepared by two-roll milling and immersed in TEOS at room temperature or slightly higher and for different times. The swollen NR sheets were further immersed in aqueous solution of amine-based catalyst at 40°C for 75 h in order to carry out the conversion of TEOS to silica. NR sheets containing the in situ generated silica were mixed with sulphur-based vulcanizing agents in a two-roll mill at room temperature. Then, the rubber compound was moulded by hot-pressing to produce vulcanized sheets of about 1 mm of thickness.

As expected, the amount of in situ generated silica was found strongly dependent on the amount of TEOS in the swollen NR and on the type of catalyst. Authors found that the polarity and the basicity of amine catalyst were crucial for controlling the conversion of TEOS to silica. In this respect, primary alkylamines with suitable hydrocarbon segments (*n*-hexylamine, *n*-heptylamine and *n*-octylamine) produced the highest amount of in situ generated silica (up to about 80 phr). Due to its higher solubility in water, *n*-hexylamine was found to be the

Fig. 5 Stress-elongation curves for NR/SiO₂ composites (*filled circle* in situ generated SiO₂; *filled square* SiO₂ mechanically mixed) (reproduced with permission from Ref. [34])



most effective catalyst. Almost independently on the type of catalyst, all the silica particles were generated in the level of nanometric size (average particle size ranging from 25 to 45 nm) and with spherical shape.

The tensile properties of the materials have been investigated and compared to those of rubber unfilled and filled with preformed nanosized silica by using the conventional mechanical mixing method. Stress-strain curves reported in Fig. 5 indicate that for the same filler content (71 phr) and for comparable network chain densities, the in situ silica reinforced rubber showed the lower stress at the elongation up to about 200% and higher stress at the elongation beyond about 200%.

The high modulus at low elongation for conventional silica filled rubber has been assumed to be due to the formation of larger aggregates of particles suggesting a better dispersion in the case of in situ silica reinforced rubber. On the other hand, the high modulus at high elongation for in situ silica filled rubber has been attributed to a stronger interaction between NR matrix and in situ generated silica particles.

The reinforcement effect due to in situ generated silica was compared to that of carbon black (both low structure and high structure carbon black stocks) [38]. Physical and mechanical properties of NR reinforced with in situ generated silica were in between those of carbon black filled composites and conventional silica filled composites (both prepared by mechanical mixing).

Ikeda and co-workers [39, 40] also reported a detailed investigation on the effect of a coupling agent (γ -mercaptopropyltrimethoxysilane, γ -MPS) on NR filled with in situ generated silica. The addition of γ -MPS was found to improve the reinforcement effect. The diameter of in situ generated silica particles was in

the range 20–45 nm and their dispersion within the rubber matrix became homogeneous by adding the silane coupling agent thanks to a reduction of silica–silica interactions. The concurrent use of in situ generated silica and γ -MPS also prevented the delay of sulphur curing and increased the wettability of NR onto the particles' surface, which resulted in the increase of reinforcement of the vulcanized composite.

Ikeda et al. [41, 42] recently reported an interesting investigation on the applicability of 3D-TEM, a technique that combines transmission electron microscopy with computerized tomography, to visualize and analyze the three-dimensional state of NR containing in situ generated silica.

Tangpasunthal and co-workers [43, 44] described the in situ generation of silica within NR latex. Mixtures of TEOS and other alkyltriethoxysilanes (TESPT, vinyltriethoxysilane, ethyltriethoxysilane and *i*-butyltriethoxysilane) were directly added to a commercial grade NR latex, containing ammonia and thus permitting the direct formation of silica through the sol–gel reaction thanks to the presence of a basic pH. Compounds with sulfur-based vulcanizing agents were subsequently prepared by two-roll milling and vulcanized by hot pressing.

The conversion of alkoxysilanes to silica within the rubber was almost complete for TEOS but decreased when the alkyl group of the alkyltriethoxysilane increased in size. Silica particles with sizes between 100 and 500 nm and evenly dispersed without extensive aggregation were obtained. The presence of TESPT, a coupling agent widely used in rubber industry, resulted in an increase of the mechanical properties and the rate of sulphur cure. Hardness, tensile and tear properties of vulcanized NR reinforced with in situ generated silica were higher than those of similar composites prepared by conventional mechanical mixing. Among the different alkyltriethoxysilane investigated, vinyltriethoxysilane seemed to be the most promising taking into account the high enhancement in tensile modulus and resistance to tear of the vulcanized rubber.

3.3 Epoxidized Natural Rubber Based Nanocomposites

Epoxidized natural rubber (ENR)/silica nanocomposites were prepared by Bhowmick and co-workers [45, 46] according to the solution procedure A. TEOS (as precursor for the in situ generation of silica) and ENR were dissolved in THF and the sol–gel process was activated at room temperature under hydrochloric acid catalysis. Alternatively to NR, ENR with adequately high epoxy content was chosen as rubber matrix taking into account that epoxy groups, randomly distributed along the chain backbones, give higher glass transition temperature and, most importantly, increased polarity and thus stronger interaction with the in situ generated silica. In fact, it is well known that under acidic conditions, the epoxy groups are likely to open up as a diol moiety which can undergo intermolecular hydrogen bonding with the silanol groups. After

solvent elimination, some samples were vulcanized with benzoyl peroxide or dicumyl peroxide. The composite films appeared transparent up to 50 wt% of TEOS loading. Dispersion of the discrete silica particles having dimensions ranging from 15 to 100 nm (by increasing the TEOS content) was observed. Infrared spectroscopic studies indicated the occurrence of chemical interaction within the rubber–silica interfaces which was further supported by the insolubility of the respective samples in THF under the ambient conditions. Dynamic mechanical analysis further corroborated the interactive nature of the in situ generated silica with the ENR matrix.

All the ENR/SiO₂ composites showed a significant improvement in mechanical properties with increased TEOS loading within the rubber. A maximum increment in tensile strength (200%) and tensile modulus (170%) with respect to the unfilled ENR was observed for the uncured composites with the highest TEOS content (50 wt%). Further reinforcement was noticed when the rubber in the nanocomposites was cured with either benzoyl peroxide or dicumyl peroxide. The dicumyl peroxide cured hybrid composites displayed 112% improvement in tensile strength over the control cross-linked rubber sample, probably due to synergisms of nanosilica reinforcement and cross-linking of the rubber phase in the hybrids.

The effect of polymer-silica interaction on THF swelling and dynamic mechanical properties have been investigated and compared to those of acrylic rubber/silica and poly(vinyl alcohol)/silica composites [47]. A further comparative study on structure–property relationship of hybrids prepared under different pH levels has been published by the same authors [48]. The silica particles were formed in the nanometer scale (average diameter <100 nm) at low pH (equal or lower than 2) beyond which aggregation occurred, although the conversion of TEOS to silica was not strictly influenced by the various pH conditions. These nanocomposites were optically clear and showed superior mechanical reinforcement over the microcomposites containing aggregated silica structures with lower optical clarity. Furthermore, the nanocomposites exhibited higher storage modulus both at the glassy and the rubbery regions as compared to those of microcomposites. As evidenced by dynamic mechanical analysis, the $\tan\delta$ peak heights were also minimum and the glass transition temperature shifted to higher temperature for those nanocomposites.

An interesting and alternative synthetic procedure has been proposed by Hashim et al. [49, 50] according to which ENR sheets were first cross-linked with 3-aminopropyltriethoxysilane (APS) by hot pressing. After vulcanization, ENR sheets were swollen in TEOS and subsequently subjected to a sol–gel reaction in butylamine aqueous solution. Silica content was up to about 30 wt% according to conversions of TEOS to silica higher than 60%. The obtained sol–gel vulcanized rubber were more rigid and stronger than a typical sulphur-cured vulcanized ENR containing comparable amount of silica. Comparative stress–strain and dynamic mechanical property analysis suggested that chemicals bonds were formed between the silica particles and the rubber network thanks to the dual reactivity of APS with respect rubber vulcanization and sol–gel reaction.

3.4 Isoprene Rubber Based Nanocomposites

Messori and Bignotti [51] recently published a work on the in situ generation of silica from TEOS within synthetic *cis*-1,4-polyisoprene (isoprene rubber, IR), the synthetic counterpart of NR. According to the solution procedure A, the sol–gel process was activated in solution of toluene, in the presence of all components and by absorbing the water required for the hydrolysis of TEOS from the external humid atmosphere. After solvent elimination, vulcanization of the rubber was attained for some sample by thermal activation of dicumyl peroxide as vulcanizing agent. The conversion of TEOS to silica was quantitative for samples with a low initial TEOS concentration while for initial concentrations higher than 20 wt% the yield in silica was in the range 60–80% almost independently on the formulation and the curing conditions (presence or absence of coupling agent, vulcanization or not of IR phase).

The in situ generated silica particles were homogeneously dispersed in the vulcanized rubber with a spherical shape and an average dimension which increased from a few nanometers to the submicron scale (300–400 nm) by increasing the concentration of inorganic phase. Swelling experiments evidenced that good polymer–filler adhesion was observed in the presence of coupling agents, while no definite conclusions could be drawn for vulcanized materials produced in the absence of the coupling agent. The dynamic mechanical behaviour of the various elastomers became increasingly nonlinear for silica contents higher than 20 wt%. In addition, only in this range of compositions the filler exerted on the low amplitude storage modulus a remarkable reinforcement, which was related to the silica content through a power law with exponent $\alpha = 4$, in agreement with the prediction of a model proposed by Huber and Vilgis [52] as reported in Fig. 6.

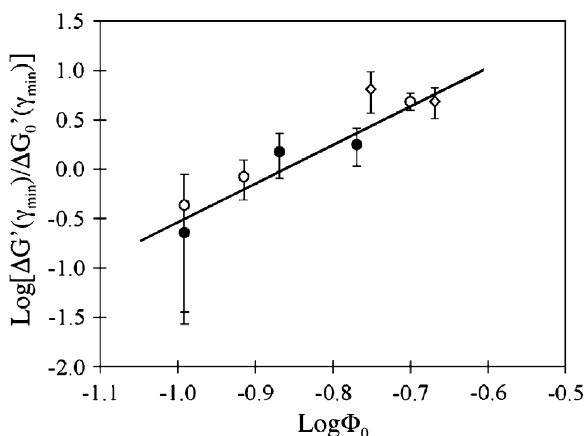


Fig. 6 Huber and Vilgis model: excess storage modulus at the lowest strain amplitude investigated (γ_{\min}) versus silica volume fraction (Φ_0) for IR/SiO₂ nanocomposites (*open diamond* unvulcanized rubber; *filled circle* vulcanized rubber; *open circle* vulcanized rubber with coupling agent). The *straight line* represents the best-fitting power law with exponent $\alpha = 4$ (see text) (reproduced with permission from Ref. [51])

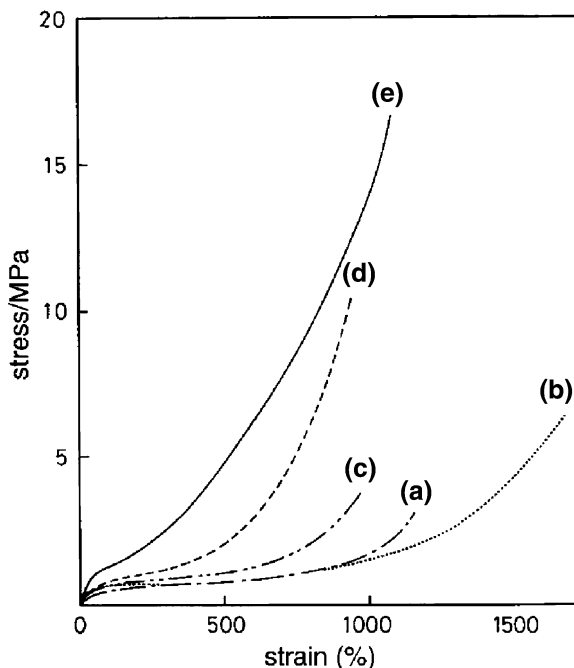
A synthetic procedure based on direct addition of water to the reactive medium and of octyltriethoxysilane as coupling/surfactant agent at different reaction times was recently proposed by Messori et al. [53]. For long enough reaction time, the sol–gel process led to a quantitative conversion of TEOS precursor to silica with the obtainment of a homogeneous distribution of spherically shaped particles. The delayed addition of octyltriethoxysilane was effective for controlling the average size and the aggregation phenomena of the in situ generated silica. Dynamic mechanical analysis carried out on filled IR showed a significant reinforcement (in terms of storage modulus increment) with respect to the pristine elastomer. On the other hand, both swelling and extraction tests suggested that the sol–gel process perturbed the vulcanization process of IR leading to a slight decrease of the cross-linking degree of the rubber matrix.

3.5 *Styrene-Butadiene Rubber Based Nanocomposites*

Ikeda et al. [54, 55] described the preparation of styrene-butadiene rubber (SBR) reinforced with in situ generated silica from TEOS under different catalytic conditions. Composites were prepared by swelling of vulcanized SBR in TEOS or in TEOS-THF mixture in the presence of basic (*n*-butylamine) or acid (hydrochloric acid) catalysts for the sol–gel reaction. Hydrochloric acid was found to be inadequate for the sol–gel reaction in the system comprised of vulcanized SBR swollen in TEOS because the aqueous solution of hydrochloric acid was not well dissolved in TEOS and, as a consequence, silica was formed only in the surface layer of the vulcanized rubber [55]. In order to avoid this problem, pre-swelling of vulcanized SBR was carried out in THF before the sol–gel reaction and, under these conditions, in both the acidic and basic aqueous solutions mixed with THF, the in situ formation of silica occurred homogeneously in the SBR matrix. The size of in situ generated silica was observed to be influenced by the cross-linking density, i.e. the larger the cross-linking density, the smaller the size of in situ formed silica particles, according to what already reported for other systems [12, 19, 25]. Comparing with the silica-filled vulcanized SBR prepared by conventional mechanical mixing, the homogeneity of dispersion of the silica particles was found to be important for the reinforcement of vulcanized rubber. Stress–strain curves for different materials are reported in Fig. 7, from which a marked improvement of mechanical properties (modulus and tensile strength) is evident for composites prepared under basic condition with respect to SBR unfilled and filled with conventional silica. In addition, the size of silica particles obviously affects the reinforcement of the rubber. The larger the in situ silica particles, the better the mechanical properties found in this study.

Interestingly, and contrary to what generally expected, the $\tan\delta$ peaks (T_g) detected by dynamic mechanical analysis were found to decrease by about 2–4°C with respect to unfilled rubber. Authors proposed that this to be due to the swelling in TEOS, which may contribute to the disentanglement of the SBR chains in the

Fig. 7 Stress–strain curves of vulcanized **a** SBR; **b** SBR/SiO₂ (mechanically mixed, SiO₂ 22 wt%); **c** SBR/SiO₂ (pre-swelling in THF, acid catalysis, SiO₂ 13 wt%); **d** SBR/SiO₂ (pre-swelling in THF, basic catalysis, SiO₂ 24 wt%) and **e** SBR/SiO₂ (basic catalysis, SiO₂ 23 wt%) (reproduced with permission from Ref. [54])



vulcanizate followed by lowering of T_g . The plasticization of the rubber by residual oligomers from the sol–gel reaction might contribute to this lowering of T_g .

Ikeda et al. [56] also reported an investigation on the effect of TESPT as coupling agent in the preparation of SBR filled with in situ generated silica. The presence of TESPT resulted in a much higher reinforcing efficiency with respect to conventional mechanical mixing and the in situ method without TESPT. The higher reinforcing efficiency was attributed to the formation of a silica–rubber network, which also changed the dynamic mechanical behaviour of the vulcanized rubber. Transmission electron microscopy analysis showed in situ silica incorporation of very fine particles in comparison to the sol–gel process without TESPT.

Similarly to the above described approach used by Hashim for ENR [49, 50], de Luca and co-workers [57, 58] prepared a Class II hybrids comprising of epoxidized SBR, TEOS (as silica precursor) and APTS (as coupling agent) in order to enhance the interaction between organic and inorganic phases. The epoxy groups of the rubber reacted with the amino groups of APTS forming an intermediate amino-silane/rubber compound which in turn was reactive towards the sol–gel reaction of TEOS to silica. The pre-reaction between epoxidized SBR and APTS was carried out in THF and TEOS and water were subsequently added (the alkaline pH for the sol–gel synthesis was provided by the APTMS itself). Large amounts of silica were incorporated using combinations of the inorganic precursors TEOS and APTS. Non-solubility of the materials in THF indicated the formation of a network, the microstructure of which varied according to the concentrations of the inorganic precursors employed. The mechanical properties

increased considerably by increasing the amount of silica incorporated and SEM analysis revealed the presence of phase separation for high TEOS content.

In situ silica generation from TEOS has been also applied in the case of blends of SBR and reclaim rubber (RR) by De and co-workers [59]. They presented an interesting comparison of mechanical properties of nanocomposites comprised of SBR/RR blends containing silica both in situ generated and mechanically mixed. They also investigated the effect of the presence of TESPT as coupling agent. Authors concluded that the mechanical properties of conventional nanocomposites were better than those of in situ generated ones in the absence of TESPT but a reverse trend was observed in the presence of the coupling agent.

3.6 Acrylonitrile-Butadiene Rubber Based Nanocomposites

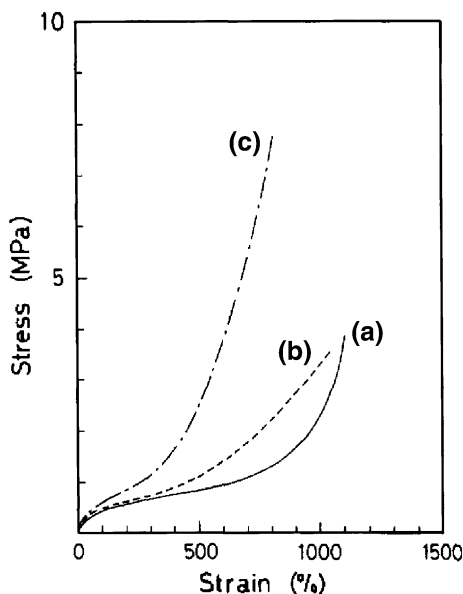
In situ silica reinforcement was applied to acrylonitrile-butadiene rubber (NBR) vulcanizates which were swelled in TEOS and subsequently soaked in an aqueous solution of ethylenediamine [60]. The amount of in situ generated silica within the NBR vulcanizates (conversion of TEOS to silica of 63%) was limited due to the high polarity of NBR and the resulting low degree of swelling of NBR in TEOS. The presence of γ -MPS in the rubber vulcanizate increased the conversion of TEOS to silica during the sol-gel reaction (conversion of TEOS to silica higher than 90%), compared to the system without γ -MPS. The obtained silica particles were very fine and very homogeneously dispersed.

The same authors also proposed the in situ generation of silica from TEOS within NBR vulcanizates pre-mixed with conventional silica both in the presence or not of γ -MPS [61]. They observed that the reinforcement efficiency tended to increase with the increase of mechanically pre-mixed silica. Both transmission electron and scanning electron microscopies showed that the simultaneous use of pre-mixed silica and γ -MPS promoted the formation of large silica particles and clusters with a relatively good dispersion by the sol-gel reaction of TEOS in the rubber vulcanizate as further evidenced by the results of hysteresis measurements. This behaviour has been attributed to the surface modification of conventional silica by the sol-gel reaction of TEOS and the presence of γ -MPS which worked as a dispersion agent for silica particles.

3.7 Butadiene Rubber Based Nanocomposites

In situ silica filling of butadiene rubber (BR) was carried out by the sol-gel process using TEOS [62]. BR was sulphur-cured and the resultant cross-linked BR was firstly swollen in TEOS and subsequently immersed in an aqueous solution of *n*-butylamine at 30°C for 24 h and at 50°C for 72 h to activate the sol-gel reaction of TEOS. The in situ generated silica was homogeneously dispersed in the rubbery

Fig. 8 Stress–strain curves of vulcanized **a** BR; **b** BR/SiO₂ (mechanically mixed, SiO₂ 22 wt%); **c** BR/SiO₂ (in situ generated, SiO₂ 16 wt%) (reproduced with permission from Ref. [62])



matrix with spherical shape and size in the range 15–35 nm. As already reported for other systems, the size of in situ generated silica was influenced by the cross-linking density, i.e. the larger the cross-linking density, the smaller the size of in situ silica formed in the vulcanized rubber. Concurrently, the interaction between filler and BR matrix seemed to become larger. Compared to the conventional silica-filled BR vulcanizate, which was prepared by mechanical mixing of the silica particles, the vulcanized rubber with the in situ generated silica showed better mechanical properties (in terms of both modulus and strength, as shown in Fig. 8).

Mark and Zhou reported the preparation and characterization of *trans*-1,4-polybutadiene (tPBD) reinforced with in situ generated silica after swelling of the cross-linked tPBD with TEOS in the presence of a tin-based catalyst and by absorbing the required water from the external humid atmosphere [63]. The silica dimensions varied from below 100 nm at low silica content (<2 wt%) to 2–5 μm at higher content (up to 20 wt%). Concerning the mechanical properties, small amounts of silica (up to 2 wt%) increased the extensibility and stress at rupture with a subsequent increment of toughness.

3.8 Acrylic Rubber Based Nanocomposites

Following an approach very similar to those of ENR, Bhowmick and Bandyopadhyay [46, 64] reported the preparation and the characterization of acrylic rubber (ACR) reinforced with in situ generated silica by means the acid-catalyzed

hydrolysis-condensation of TEOS in solution of THF (procedure A). The proportion of TEOS was from 0 to 50 wt% (macrophase separation occurred beyond this last maximum content of TEOS). For comparison, composites were also prepared with preformed silica up to 30 wt% of its loading. After solvent elimination, some sample was vulcanized with benzoyl peroxide or with a mixed curing system comprised of hexamethylenediamine and ammonium benzoate. All the hybrid composites prepared by sol-gel technique were transparent while, on the contrary, the composites of ACR with mechanically mixed preformed silica were opaque at all compositions. Infrared spectroscopic analysis revealed the absence of significant shifts in peak position for carbonyl absorption in all the hybrid composites, suggesting that a homogeneous dispersion of silica particles within the organic matrix occurred without any significant interaction between the two phases. This conclusion was further supported by the complete dissolution of the uncured hybrid in THF at room temperature. Morphological analysis revealed the presence of discrete spherical silica particles with an average diameter that increase from 20 to 90 nm by increasing the TEOS content (from 10 to 50 wt%).

The storage modulus detected by dynamic mechanical analysis above glass transition temperature increased by increasing the TEOS content according to the reinforcing effect of nanosilica network structure present in the rubber matrix. The $\tan\delta$ peak height was gradually reduced, the peak broadened and the T_g values of the composites shifted towards higher temperatures by increasing the inorganic filler content in the composites.

Concerning mechanical properties of the hybrid composites, the tensile strength increased by increasing the silica content. For the same silica content, the tensile strength of composites filled with in situ generated silica was significantly higher than that of conventional composites. The nanolevel mixing of in situ generated silica particles and the formation of strong Si-O-Si network within the ACR matrix were responsible for greater reinforcement in the rubber matrix. In the case of conventional silica filled rubber, the bigger sized silica particles did not provide higher surface area for interactions such as that of in situ generated silica and hence they were not as effective as the former.

On curing the rubber phase, with either benzoyl peroxide or hexamethylenediamine/ammonium benzoate, the tensile strength was further increased, although benzoyl peroxide cured samples showed lesser improvements than the corresponding mixed cross-linking system.

In order to verify the effect of the polarity of the rubber matrix on the properties of this class of composites, Bhowmick and co-workers [65, 66] synthesized acrylic copolymers and terpolymers by bulk polymerization of ethyl acrylate (EA), butyl acrylate (BA) and acrylic acid (AA) and used them as rubber matrix for the preparation of silica filled composites by using the usual procedure based on the acid-catalyzed hydrolysis-condensation of TEOS in THF solution. Authors reported a morphological investigation showing the presence of silica particles with an average diameter lower than 100 nm. The average diameter of silica particles was lower in the case of high extent of polarity and hydrophilicity of the rubber matrix, suggesting that these molecular parameters control the in situ

generated silica particles size. In all the cases, no significant chemical interaction occurred at the silica–rubber interface, as depicted from spectroscopic analysis (FT-IR and NMR). In general, the mechanical properties increased by increasing the polarity of the matrix due to better rubber-silica interaction and uniform nanosilica dispersion. Also in this case, cross-linking further improved the mechanical properties.

3.9 Ethylene–Propylene–Diene Monomer Rubber Based Nanocomposites

Ethylene–propylene–diene monomer (EPDM) rubber was modified with TESPT in an internal mixer in order to graft triethoxysilyl groups onto the polymeric backbone [67]. Triethoxysilyl-grafted EPDM sheets were swollen with TEOS and subsequently immersed in *n*-butyl amine aqueous solution to in situ generate silica particles. The silica filled EPDM rubber was finally mixed with vulcanizing agents and cured by hot pressing. Authors concluded that TESPT fragments present in the macromolecular chain of EPDM acted as nucleation sites for the growing of silica which in turn led to the formation of a strong silica-EPDM network chemically bonded to the rubber matrix. The pendant triethoxysilyl groups on the EPDM backbone played a fundamental role in uniformly dispersing silica particles within the rubber. For similar silica loadings, EPDM modified with in situ generated silica showed superior reinforcing efficiency with respect to materials prepared by ex situ process (mechanical mixing of precipitated silica within the rubber).

3.10 Other Rubber Based Nanocomposites

Matějka and co-workers [68, 69] reported some studies on rubbery epoxy resins reinforced with in situ generated silica from TEOS and with a silica content ranging from 6 to 22 wt%. The epoxy resin and the hardener were diglycidyl ether of bisphenol A (DGEBA) and polyoxypropylene-diamine (Jeffamine[®] D2000), respectively. Long flexible polyether chain lead to a rubbery cured material and moreover it solubilizes siloxane structures formed in the sol–gel process resulting in a transparent hybrid. Authors reported several preparation methods:

- (i) one-stage process, in which all reactants were mixed in *iso*-propyl alcohol solution and reacted simultaneously;
- (ii) two-stage ‘simultaneous’ process, in which TEOS was pre-hydrolyzed under acidic conditions in *iso*-propyl alcohol solution and subsequently added to DGEBA and Jeffamine[®] D2000 to activate the simultaneous formation of both organic and inorganic networks;

- (iii) two-stage 'sequential' process with preformed epoxide network, in which the cured epoxy resin was firstly prepared by stoichiometric reaction between DGEBA and Jeffamine[®] D2000 and subsequently swelled in the sol-gel solution (TEOS, water and acid in *iso*-propyl alcohol) to activate the in situ generation of silica.

Compact and large silica aggregates (100–300 nm in diameter) were observed in the case of hybrids obtained with one-stage process, whereas open polymeric structures of smaller aggregates (50–100 nm in diameter) composed of fractal particles were formed during the two-stage procedure with the pre-hydrolyzed TEOS. Moreover, this two-stage process resulted in a much faster gelation of the silica. In these 'simultaneous' processes, the silica network was formed faster than the epoxide one and its structure was not influenced by the presence of the epoxide and amine. However, in the case of the two-stage 'sequential' process, the pre-formed organic network suppressed growth of the silica aggregates by inter-particle condensation and the relatively smallest silica domains (10–20 nm) were formed.

Authors concluded that the synthetic procedure controls the reaction mechanism, final structure and morphology. In particular, contrary to what shown by basic and neutral catalysis, acid catalysis promotes rapid hydrolysis of siloxane groups which results in the high content of silanol groups and an extensive grafting to the epoxide network. Grafting between organic and inorganic phases resulted in the formation of an interphase epoxide layer with reduced mobility and increased glass transition temperature.

Concerning the mechanical properties, an increase in modulus by two orders of magnitude was achieved at a low silica content (10 vol%). Interestingly, dynamic mechanical analysis revealed the presence of a co-continuous morphology of the epoxy matrix and of the silica phase (and the silica-glassy epoxide phase) continuously extending through the macroscopic sample.

Sunada and co-workers [70] reported the synthesis of alkoxysilane-modified polychloroprene latex by the emulsion copolymerization of 2-(3-triethoxysilylpropyl)-1,3-butadiene and chloroprene. This latex was mixed with unmodified polychloroprene (CR) latex and TEOS to obtain composites by sol-gel reaction in the latex under basic catalysis. After vacuum drying, the composites were compounded with curing agents by two-roll milling and subjected to vulcanization by hot pressing. Electron microscopy showed that the silica particles in unvulcanized composites had various diameters ranging from 0.1 to 0.6 μm , and their size became larger with the decrease of the silica content. Compared to similar composites prepared by conventional mechanical mixing with preformed silica, vulcanized CR/SiO₂ composites obtained with in situ generation of filler showed that the tensile modulus and tear strength improved with an increase of the amount of modified CR.

The metallocene-based poly(ethylene-octene) (POE) elastomer, which was developed using a metallocene catalyst by Dow and Exxon, has received much attention because of its peculiar properties such as uniform distribution of comonomer content and narrow molecular weight distribution.

Wu et al. [71, 72] reported a systematic investigation on composites comprised of POE or POE grafted with maleic anhydride or acrylic acid (POE-g-MAH or POE-g-AA, respectively) as elastomeric matrix and in situ generated silica or silica–titania mixed oxides. The composites were prepared by addition of solutions of (i) TEOS, water and hydrochloric acid or (ii) silicic acid, tetraisopropyl orthotitanate (TTIP), water and hydrochloric acid to POE or POE-g-MAH or POE-g-AA melted in an internal mixer at a temperature of 160–170°C.

FT-IR, ^{29}Si -NMR and XRD analysis showed that Si–O–C, Ti–O–C, Ti–O–Ti, Si–O–Si and Si–O–Ti linkages were formed in silica and silica–titania reinforced elastomers supporting the expected formation of covalent bonds between organic and inorganic phases and of SiO_2 – TiO_2 mixed oxides. It was found that there are maximum values of tensile strength and glass transition temperature at about 10 wt% of inorganic filler (see Table 3). Authors explained this behaviour assuming that an excess of SiO_2 or SiO_2 – TiO_2 particles might cause separation between the organic and inorganic phases with a reduction of their compatibility.

From the reported data it is interesting to observe that superior properties were obtained in the case of hybrids based on POE grafted with maleic anhydride or acrylic acid (POE-g-MAH or POE-g-AA) with respect to pure POE. The higher polarity and the presence of reactive groups (anhydride or carboxylic) in the grafted elastomer allowed the formation of stronger chemical bonds between organic and inorganic phases.

The literature concerning the in situ generation of inorganic oxides through the sol–gel process within thermoplastic elastomers (TPE) is relatively limited.

Lai et al. [73, 74] reported the preparation of thermoplastic polyurethane (TPU) reinforced with in situ generated silica starting from TEOS as precursor or from polysilicic acid extracted from an aqueous sodium metasilicate solution with THF. A solution procedure (procedure A) with acidic catalysis (hydrochloric acid or acetic acid) was adopted in both approaches to prepare the hybrid materials.

Spectroscopic and dynamic mechanical analysis showed the presence of interfacial interactions between the organic and inorganic phases. Storage modulus increased at all concentrations of silica due to its reinforcement effect while the tensile strength exhibited a maximum value for filler content of 10–15 wt%. In contrast, the cutting strength decreased, probably due to a reduction of the energy dissipation from silica as physical cross-links. The acetic acid catalyzed system

Table 3 Glass transition temperature and tensile strength (TS) values POE-based composites

Filler content (wt%)	POE/ SiO_2		POE-g-MAH/ SiO_2		POE/ SiO_2 – TiO_2		POE-g-AA/ SiO_2 – TiO_2	
	T_g (°C)	TS (MPa)	T_g (°C)	TS (MPa)	T_g (°C)	TS (MPa)	T_g (°C)	TS (MPa)
0	–60	27	–58	15	–60	27	–59	17
3	–58	28	–56	38	–58	28	–54	37
10	–55	31	–52	52	–56	32	–48	56
20	–58	26	–56	27	–58	28	–57	30

showed better optical properties than the hydrochloric acid catalyzed system. The modified process with extraction showed improved mechanical properties and better optical properties than the conventional sol–gel process without extraction.

4 Concluding Remarks

The sol–gel process has been established as a versatile, effective and innovative method for the in situ preparation of rubber nanocomposites. The great majority of the published studies concerns the generation of silica from TEOS within the most common elastomers even if some example of in situ generation of other oxides such titania, zirconia, alumina or mixed oxides is present in the literature. Different synthetic strategies can be applied to obtain materials with tailored properties, in particular the in situ generation of inorganic fillers can be obtained in solution or directly in the rubber, either swollen in metal alkoxides or in the melt state. Depending on the preparation conditions, the vulcanization of the rubber matrix can be carried out before, simultaneously or after the sol–gel process and the resulting morphologies and ultimate properties are generally affected by the specific synthetic procedure. As a general observation, finer morphologies (lower filler dimensions) are realized by increasing the cross-linking density of the vulcanized rubber presumably due to constraining effects deriving from the organic network. It seems also very promising that the mechanical properties (modulus, strength and extensibility) of the in situ filled nanocomposites are generally better than those of the corresponding materials prepared with the conventional mechanical mixing of preformed particulates and elastomers. This enhancement is generally attributed to a lower tendency to filler–filler aggregation due to a lower particle surface interaction resulting from the ‘bottom-up approach’ of the sol–gel process applied to the preparation of organic–inorganic hybrid materials.

Future developments on in situ synthesis of rubber nanocomposites should involve further systematic studies on the possibility to use silica precursors alternative to TEOS as well as the incorporation of metal oxides different than silica, exploring the different reinforcing effect of titania, zirconia or other. Also the use of non-hydrolytic sol–gel process, which is characterized by the absence of water as reactant for the generation of inorganic oxides, should be an interesting field of research and development.

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