

# RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## Controlled Growth of *In Situ* Silica into NR /CR Blend by Solution Sol-Gel Method and the Studies of Composite Properties

Naresh D. Bansod,<sup>1</sup> Bharat P. Kapgate,<sup>1</sup> Chayan Das,<sup>1\*</sup> Debdipta Basu,<sup>2</sup> Subhas Chandra Debnath,<sup>3</sup> Kumarjyoti Roy<sup>3</sup> and Sven Wiessner,<sup>2,4</sup>

<sup>1</sup>Department of Chemistry, Visvesvaraya National Institute of Technology, Nagpur, India

<sup>2</sup>Department of Elastomers, Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany

<sup>3</sup>Department of Chemistry, University of Kalyani, West Bengal, India

<sup>4</sup>Technische Universität Dresden, Institut für Werkstoffwissenschaft, Dresden, Germany

### Abstract

Silica is grown, *in situ* into natural rubber (NR) /chloroprene rubber (CR) blend (at 40/60 ratio), by solution sol-gel method, where silica content in rubber blend is increased in a controlled manner exceeding the limit found for the same blend ratio, in soaking sol-gel method. Reaction conditions have been optimized to get adequate conversion of tetraethoxysilane (TEOS, a silica precursor) to silica. Rheological, thermal, mechanical and viscoelastic properties of all the composites are compared with those of the unfilled rubber blend at similar condition. Thermal and mechanical properties of the composites are found to improve consistently as silica content in the composite increases owing to increased rubber filler interaction as revealed in dynamical mechanical analysis (DMA). Further improvement in the properties is observed for a particular composite where a silane coupling agent (( $\gamma$ -aminopropyl) trimethoxysilane,  $\gamma$ -APS) is used in the reactive sol-gel system during *in situ* generation of silica. This is attributed to the uniform distribution of silica in the rubber matrix and strong rubber filler interaction, caused by bifunctionality of silane, as revealed by morphology and DMA studies respectively. Reinforcement effect of silica is evaluated by comparing the experimental results with theoretical values obtained from Guth-Gold model and modified Guth model. Present study supplements the *in situ* silica generation in NR/CR

blend of 40/60 ratio, following solution sol-gel method, to the earlier study involving soaking sol-gel method where maximum reinforcement was found for this composition.

**Keyword:** Rubber blend; *In situ* silica; Mechanical properties; Morphology; Silane treatment

## 1 Introduction

Rubber blends comprising of natural rubber (NR) and chloroprene rubber (CR) in suitable proportion find many useful applications due to the combined features of the components in the blend that cannot be exhibited by the individual component.<sup>1-3</sup> NR is well known for its good mechanical properties, elasticity and dynamic property while CR shows excellent resistance to solvent, chemical, fire, heat and ozone attack.<sup>2-4</sup> Blending of NR with suitable proportion of synthetic rubber such as CR, styrene butadiene rubber (SBR), nitrile rubber (NBR) etc. has been proven to overcome the limitation of NR.<sup>2-4</sup> For example, the addition of CR into NR helps to overcome the main shortcoming of NR like poor oil and ageing resistance. Nevertheless, incorporation of filler into rubber matrix is extremely essential to achieve adequate mechanical properties to make it fit for practical application.<sup>2-6</sup> Silica is an important non black type of reinforcing filler which is generally added into rubber matrix by external mixing. However, good dispersion of silica in rubber matrix to achieve proper reinforcement effect remains a major issue for the external silica loading in rubber matrix.<sup>7-10</sup> In this context, incorporation of silica, *in situ* into rubber matrix, has appeared to be a very efficient technique in recent times. There are many reports available in literature on *in situ* silica incorporation in rubber including natural rubber, synthetic rubber or rubber latex.<sup>11-15</sup> But studies on rubber blends, filled with *in situ* silica, are rather limited in literature.<sup>4</sup> Recently, we reported the dual role of *in situ* silica for NR/CR blend composite where *in situ* silica enhanced the compatibility of otherwise immiscible NR/CR blend in addition to

imparting reinforcement effect.<sup>16</sup> It may be mentioned here that the blend compatibility is a major concern for such heterogeneous blends comprised of polar and nonpolar rubber as far as mechanical properties of the composite is concerned.<sup>17-19</sup> However, in that work, amount of silica generated, *in situ* into rubber blend, is limited since we adopted soaking sol-gel method. It may be mentioned here that, for a particular blend ratio, amount of silica generated by soaking sol-gel method remains fixed at any particular reaction condition. Interestingly, the best composite properties were shown by NR/CR blend at ratio 40/60 although silica content was maximal for the NR/CR blend at 80/20 ratio. More uniform dispersion of silica particle in rubber matrix along with good degree of enhancement in blend compatibility brought by *in situ* silica for that particular blend ratio produced the best results for that particular composite. In present work, we have further extended our studies on this particular blend ratio (NR/CR at 40/60) adopting solution sol-gel method, where amount of silica generation in the rubber matrix is controlled to overcome the limitation of silica generation associated with soaking sol-gel method. Detailed studies of NR/CR composites, filled with varying amount of *in situ* silica (up to 30 phr) are done and the results are compared with unfilled one. Furthermore, silane treatment of silica in the reactive sol-gel system was done for a selected composite using ( $\gamma$ -aminopropyl)trimethoxysilane ( $\gamma$ -APS), as a silane coupling agent. It is known that the use of appropriate silane in the reactive sol-gel system during generation of *in situ* silica could effectively improve the silica dispersion and enhance rubber-filler interaction (Fig. 1).<sup>20-22</sup> Studies on moisture curing of CR by  $\gamma$ -APS had established the existence of a strong interaction between CR and  $\gamma$ -APS.<sup>23,24</sup> In fact, the silica dispersion and rubber-filler interaction is found to improve drastically, in this study, by using this silane with respect to the unsilanized silica filled composite at same silica content. The results of silane treated silica filled composites are compared with those with unsilanized silica filled composite.

**Fig. 1** (a) Interaction between the silanol group of silica and chlorine atom of CR (b) Linkage between  $\gamma$ -APS modified silica and CR.

## 2 Experimental

### 2.1 Materials

Chloroprene rubber (LANXESS Bayprene 116, XD grade) and natural rubber (RSS 4) were obtained from Heritage Rubber (Nagpur, India). Tetraethylorthosilane 98% (TEOS) and n-butylamine were purchased from Across Organic (New Jersey, USA).  $\gamma$ -aminopropyl trimethoxysilane (97%) ( $\gamma$ -APS) was purchased from Sigma–Aldrich. Toulene, zinc oxide (ZnO) and stearic acid were purchased from fisher scientific. Ethanol was purchased from Merck. Ethylene thiourea (ETU) was purchased from National chemicals (Vadodara, India). Magnesium oxide (MgO), sulphur, *N*-cyclohexylbenzothiazole-2-sulphenamide (CBS) were received from Sara Polymer Pvt. (Nagpur, India).

### 2.2 *In situ* silica generation

Silica particles were generated *in situ* into NR/CR blends of 40/60 ratio by solution sol-gel process, both in the presence and absence of silane coupling agent ( $\gamma$ -APS). 12 gm of NR and 18 gm of CR were dissolved together in toluene and set to stirring for homogenous mixing (for sample **2-6**). After that varying amount of TEOS, water, ethanol (TEOS: Water: Ethanol mole ratio = 1:2:4) and n-butylamine (0.096 mol with respect to TEOS) as catalyst were added to the solution with continuous stirring for 15 min. For example, for composite **2**, 18.1 ml of TEOS, 2.9 ml of water, 1.8 ml of n-butylamine and 14.9 ml of ethanol were added in rubber solution. For sample **6**, 0.58 ml of  $\gamma$ -APS was added in rubber solution in addition

to the other reagents. Then the solution was refluxed for 1 h at 130 °C. The solution was kept for gelling at room temperature for 4 days followed by vacuum drying at 50 °C.

### 2.3 Formulation and compounding of rubber

*In situ* silica filled NR/CR blends were masticated on a two roll mill for 5 minute before compounding with other crosslinking ingredient. Then all crosslinking ingredients (ZnO, MgO, stearic acid, CBS, ETU and sulphur) were added stepwise and mixed for 10 minutes to obtain homogenous rubber mixture. This process was followed for all the *in situ* silica filled composites (2-6). Similarly unfilled sample (1) was prepared by solution blending, NR and CR in 40/60 ratio dissolved together in toluene and set to stirring for homogenous mixing. Then the dried rubber sheet was compounded with other crosslinking ingredient on a two roll mill without any filler. Formulation of all the composites is given in Table 1. The resultant compounds were then vulcanized, using compression moulding machine, at 160 °C as per their respective cure time ( $t_{90}$ ) given in Table 3.

**Table 1** Formulation of rubber compounds (NR/CR)<sup>a</sup> in phr (parts by weight per hundred parts of rubber)<sup>b</sup>.

## 3 Characterizations

### 3.1 Curing Studies

The minimum torque ( $M_L$ ), maximum torque ( $M_H$ ), delta torque, cure rate index (CRI), cure time ( $t_{90}$ ) and scorch time ( $ts_2$ ) for all the compounds were determined by using a Monsanto Rheometer R-100 at an amplitude of 3°. The measurements were carried out at 160 °C for 60 min.

### 3.2 Scanning Electron Microscopy (SEM)

The surface morphology of NR/CR blends were investigated by using scanning electron microscope (Zeiss Ultra Plus; Carl Zeiss Microscopy GmbH, Jena, Germany). The samples were cut with an ultramicrotome and sputter coated with 3 nm platinum to prevent charging on the surface.

### 3.3 Thermogravimetric Analysis (TGA)

Thermal stability and silica content of the rubber vulcanisates were determined by thermogravimetric analysis and derivative thermogravimetry (DTG) by using a thermal analyzer TG-DTA 7200 (Hitachi, Japan). About 5-10 mg of sample was kept on a platinum pan and heated in the temperature range 40 to 500 °C under nitrogen atmosphere and heating was continued upto 700 °C under air at a heating rate of 10 °C/min.

### 3.4 Mechanical Characteristics

Stress-strain studies were carried out using a Zwick tensile tester (model 1456, Z010, Ulm Germany) using dumb-bell shaped test specimen at uniform speed of 200 mm min<sup>-1</sup>. The hardness of the vulcanized sample was measured by a Shore A durometer (BSE testing machine India). All tests were performed at ambient temperature.

### 3.5 Swelling study

The cross-linking density of all the vulcanized samples was determined by the equilibrium swelling method using toluene as solvent. The cured samples of known weight were allowed to swell for 7 days in fresh toluene at room temperature. After each 24 hour solvent were changed with fresh toluene. After 7 days, samples were taken out and adhered liquid was rapidly removed by blotting with tissue paper and weighed immediately. It was vacuum dried at 80 °C till a constant weight was obtained. Crosslinking density  $\nu$ , defined by the number of elastically active chains per unit volume was determined by Flory-Rehner equation (1)<sup>25</sup>

$$v = \frac{-[\ln(1 - Vr) + Vr + xVr^2]}{Vs(Vr^{\frac{1}{3}} - Vr/2)} \quad (1)$$

where,  $V_s$  is the molar volume of the toluene (106.2),  $V_r$  is the volume fraction of rubber in swollen gel and  $\chi$  is the Flory-Huggins rubber-solvent interaction parameter.

### 3.6 Dynamic mechanical properties (DMA)

Dynamic mechanical properties were measured over temperature range -100 °C to 140 °C using an Eplexor 2000 N dynamic mechanical analyzer (Gabo Qualimeter, Ahlden, Germany) by using a constant frequency of 10 Hz. All the measurements were done in tension mode. For the measurement of complex modulus,  $E^*$ , a static load of 1% per-strain was applied and then the samples were oscillated to a dynamic load of 0.5 % strain. All the measurements were done with a heating rate of 2 °C min<sup>-1</sup> under liquid nitrogen flow.

### 3.7 Differential scanning calorimeter measurements (DSC)

Measurements were performed using a differential scanning calorimeter, DSC 204 F 1 (NETZSCH, Germany). The samples of 7-10 mg were placed in a standard aluminum pan with pierced lid. The pan was placed into the apparatus at room temperature and heated immediately upto 200 °C at a rate of 30 °C/min and kept five minute at this temperature to remove the volatiles impurities. They were quenched to -70 °C and DSC scan was performed from -70 °C to +70 °C at a heating rate 5 °C/ min under nitrogen atmosphere.



## 4 Results and Discussion

### 4.1 Controlled loading of *in situ* silica into NR/CR rubber blend

In present study, we have adopted solution sol-gel method to incorporate silica *in situ* in NR/CR blend at 40/60 ratio. Here, NR and CR were first dissolved in toluene in proper proportion and mixed thoroughly by mechanical stirring followed by addition of measured quantity of TEOS, the silica precursor. In sol-gel process, tetraethoxysilane undergoes hydrolysis and polycondensation reactions, in catalytic condition, to form silica particles (Fig. 2). There are several factors such as nature of solvent, type and amount of catalyst, type of silica precursor, reaction time and other physical condition that may have significant effect on the sol-gel reaction and consequently can generate silica with different content, shape/size and surface characteristics.<sup>26</sup> In this work, TEOS was used as a silica precursor and *n*-butylamine was used as a catalyst as they are widely used in similar studies.<sup>12</sup> Other than these, we have optimized several reaction parameters like choice of solvent, concentration of catalyst and reaction time to get appreciable amount of silica generation in rubber matrix (described in details in experimental section). The results are summarized in Table 2. It is evident here that silica generation was more when THF was used as a solvent compared to other two solvents. This is due to the polar nature of THF that accounts for higher water solubility and hence provides better miscibility of water and TEOS in the rubber matrix. This in turn increases the rate of hydrolysis and condensation reaction which leads to more silica generation.<sup>5</sup> However, addition of ethanol in calculated amount, which could act as a homogenizing agent,<sup>27</sup> was found to improve the miscibility between toluene and water in the rubber matrix enhancing the hydrolysis of TEOS. Thus, combination of toluene and ethanol yielded more silica than THF alone, when used as solvent, under similar conditions which appeared to be a better alternative approach from economical point of view. It may be noted that the excessive use of ethanol could lead to rubber phase separation from the mixture.

Concentration of catalyst, n-butylamine, was varied from 0.032 to 0.18 mole ratio with respect to TEOS, keeping all other parameter constant and it was found that silica generation was increased with increase in catalyst concentration upto 0.096 mole ratio. Moreover, the reaction time was varied to see it's effect on the silica generation and it was found that there was no significant improvement in silica generation beyond 60 min. Thus in the optimised condition, amount of silica in the NR/CR blend was varied up to 30 phr by varying the amount of TEOS added. From Table 2, it is found that there is 70 % conversion of TEOS into silica for composite (2) (10 phr silica). However, percentage conversion dropped to certain degree for higher silica content and 56 % conversion was achieved for composite 5 and 6 (30 phr silica) (Table 1).

**Fig. 2** Hydrolysis and condensation reaction of tetraethoxysilane (TEOS).

It would be worthwhile to mention here that in soaking sol-gel method, silica content for NR/CR (40/60) rubber blend was found to be 20 phr that was fixed for a particular blend ratio, at a given reaction condition, as the mechanism of silica loading was different in that case. In soaking sol-gel method, sheets of rubber blend are immersed in liquid TEOS (tetraethoxysilane) for sufficient time for swelling of TEOS inside the rubber matrix and the swelled sheets are immersed in catalyst solution at standard condition for sol-gel reaction to occur. Silica generation is governed by the imbibed TEOS inside the rubber blend matrix which is influenced by blend composition.<sup>16</sup> NR, being non polar in nature, has greater TEOS uptake capability than CR leading to more silica generation in the former phase. Thus silica generation in the rubber blend increases with increase in NR proportion in the NR/CR blend in soaking sol-gel method but amount of silica remains fixed for a particular blend proportion. Whereas, in solution sol-gel method, silica content can be varied by controlling

the amount of silica precursor in the reaction mixture as done in the present study. Furthermore, a composite (6 at silica content 30 phr) was prepared using  $\gamma$ -APS (2 phr), in the reactive sol gel system, to see the effect of silane integration on the composite properties at higher silica loading. The specific silane was chosen for its ability to interact with Chlorine atom of CR via the amino functional end and thus it was expected to facilitate the silica dispersion and rubber-filler interaction (Fig. 1 (b)).

**Table 2** Optimization of sol-gel reaction conditions for *in situ* silica loading

#### 4.2 Curing Characteristics

Curing characteristics of all the compounds are illustrated in Fig. 3 and Table 3. It is observed that the minimum torque values of the silica filled compounds are higher than that of unfilled compound and the value gradually increases with increase in silica content. This indicates the increased viscosity i.e. stiffness resulted with the incorporation of silica into rubber blend. Higher maximum torque values with increased silica content are well supported by the crosslinking density values of the compound calculated by Flory-Rehner equation (Equation 1). This is attributed to the strong interaction between the silanol group of silica and chlorine atom of CR which provides additional crosslink's to the rubber matrix (Fig. 1 (a)).<sup>16</sup> For the silane treated silica filled compound (6), minimum torque is found to be higher compared to the compound filled with similar silica content but without silane (5). This could be due to the partial crosslinking, which might take place before actual vulcanization starts, through strong rubber-filler interaction facilitated by bifunctionality of silane.<sup>20-22</sup> This is also well supported by the crosslinking density values.

The scorch time and cure time of the *in situ* silica filled compounds are found lower for silica filled compounds compared to that of unfilled compound that gradually decrease with

increase in silica content. This is little unexpected, as it is known that surface silanols of silica could adsorb the cure accelerators and inhibit the crosslinking reaction.<sup>2,7</sup> However, the strong interaction between the silanol groups of silica and chlorine atom of CR in the blend might suppress the curatives adsorption by silanols.<sup>16</sup> This effect becomes more significant for silane treated silica filled compound (**6**). Cure rate index (CRI) values for the *in situ* silica filled compounds are found higher compared to that of unfilled sample which indicates the faster curing process in former case. Further increase in CRI, brought by silane treatment, indicates enhancement in cure rate. This may be attributed to the strong rubber-silica and rubber-silane-silica interaction (Fig. 1)<sup>16,20</sup>

**Table 3** Curing characteristics of unfilled and *in situ* silica filled compounds

**Fig. 3** Curing characteristics of the unfilled and *in situ* silica filled compounds (**1-6**).

### 4.3 Morphology

Morphology of the composites at different silica loading viz. at 10 phr, 20 phr and 30 phr was investigated by scanning electron microscopy (SEM) and the micrographs are shown in Fig. 4. It is evident that, the silica particles are homogeneously dispersed throughout the rubber matrix with few aggregates at 10 phr silica content in composite **2** (Fig. 4 (a)). With increase in silica loading (20 and 30 phr), the aggregation tendency of silica particles increases and it is much dominant for the sample (**5**) filled with 30 phr (Fig. 4 (c)). Notably, much better silica dispersion along with significant reduction in particle size at same silica loading (30 phr) is found in silane treated silica filled composite **6** (Fig. 4 (d)). For composite (**5**), the particle size distribution is in the range of 100-150 nm for smaller particles while size of larger silica aggregates lies in the range of 300-450 nm (Fig. 4 (c)). On the other hand, in composite (**6**), size of the silica particles is significantly reduced in the range 50-70 nm.

Uniform and homogeneous distribution of silane treated silica particles into rubber matrix for composite **6** is attributed to the bifunctionality of silane that might enhance the rate of sol-gel reaction.<sup>22,28</sup> The hydrolysable trimethoxy groups of silane, present at one end, react with surface hydroxyl (silanol) groups of silica and prevent the aggregation (filler-filler interaction) of silica.<sup>20,21</sup> The organofunctional amino groups, on the other end of silane, interact with the chlorine atom of CR and provide additional crosslink's resulting in strong rubber-filler interaction as shown in Fig. 1(b).<sup>23,24</sup>

**Fig. 4** Scanning electron microscopy (SEM) images of *in situ* silica filled NR/CR composites: (a) composite **2** (10 phr silica), (b) composite **3** (20 phr silica), (c) composite **5** (30 phr silica), (d) composite **6** (30 phr silica treated with  $\gamma$ -APS).

#### 4.4 Thermogravimetric Study

Thermogravimetric analysis was performed to evaluate the thermal stability and silica content of the composites (Fig. 5). *In situ* silica content of the rubber composites (**2-6**) was determined from the residual weight percentage of a particular composite, relative to unfilled one as obtained from thermogravimetric results (Table1). In all the composites (**1-6**), initial weight loss beginning around 100 °C, is due to the combustion of organic additives added for vulcanization and elimination of polycondensation residues that starts with increase in temperature. The onset temperature (300-335 °C) that arises from the degradation of rubber phase, increases slightly as silica content increases. The differential thermogravimetric (DTG) curves of unfilled and filled samples show three peaks. The first peak in the temperature range 335 °C to 350 °C corresponds to the maximum weight loss of the NR phase in the blend and the second peak in the temperature range 430 °C to 440 °C corresponds to the maximum weight loss of CR phase in the blend. It is known that the

double bonds in CR are less reactive towards thermal oxidative degradation as compared to the double bond in NR.<sup>16, 29</sup> The third peak in the temperature range 550 °C to 580 °C, obtained at heating under air flow, is due to the decomposition of carbonaceous residue.<sup>20</sup> It is evident that the addition of silane has little effect on the  $T_{\max}$  of both NR and CR phases as well as on the thermal stability of the composite **6**.

**Fig. 5** Thermogravimetric curves of the unfilled and *in situ* silica filled composites (**1-6**).

#### 4.5 Stress-Strain studies

The influence of *in situ* silica loading on the mechanical properties of the composites was investigated by stress-strain measurement. The test results are given in Table 4 and stress-strain curves are depicted in Fig. 6. It is evident that the moduli at 100 % and 300 % strains become higher by incorporation of silica and gradually increases with increase in silica content in the blend. However, tensile strength becomes less at higher silica content. This is attributed to the large aggregates of silica in the rubber matrix at higher silica content, as found in SEM images, which may impart stiffness to the composite and leads to the drop in tensile strength of the corresponding rubber composites. We wish to mention here that the level of improvement in modulus and tensile strength relative to unfilled sample obtained from solution sol-gel method, in the present study, does not differ much with the results obtained for similar composites with NR/CR blend at 40/60 ratio at 20 phr silica loading, prepared by soaking sol-gel method in our earlier studies.<sup>16</sup> But in present work, silica content in NR/CR blend is increased in a controlled manner and further improvement in mechanical properties is gained which was not feasible in case of soaking sol-gel method for this blend ratio. In present case, moduli at 100% and 300% strain increase approximately four times at 30 phr silica loading compared to those of unfilled sample. Moreover, the values become still

higher by silane treatment of silica for composite **6**, at same silica content (30 phr). This is in accordance with the results found for this particular composite in morphology study where uniform dispersion of silica throughout the rubber matrix was observed. This is due to the presence of the organosilane, ( $\gamma$ -APS) that prevents the silica aggregation (filler-filler interaction) and provides additional crosslinks through its organofunctional amino group.

Hardness values of the elastomeric composite are closely related to the modulus at low strain.<sup>20</sup> As expected, hardness values (Shore A) of the filled composites are found to increase with increase *in situ* silica loading (Fig. 6 (b), Table 4). Nevertheless, the maximum hardness value is shown by composite (**6**). This may be attributed to the highest silica content and enhanced cross-linking density brought up by the silane treatment for this composite in the series.

**Table 4** Mechanical properties of the unfilled and *in situ* silica filled composites (**1-6**).

**Fig. 6** Mechanical properties of the unfilled and *in situ* silica filled composites (**1-6**): **(a)** Stress-strain curves and **(b)** Shore A hardness values and  $\sigma_{100\%}$  moduli

To understand the reinforcement effect of *in situ* silica on the rubber blend, dependence of modulus enhancement ( $E_C / E_0$ ) on the volume fraction of filler has been evaluated experimentally and the results are compared with the theoretical values determined from Guth-Gold model and modified form of Guth model considering shape factor ( $f = 2.53$ ) (given below).<sup>15, 30,31</sup>

$$\text{Guth-Gold Equation (1938): } E_C / E_0 = 1 + 2.5 \phi + 14.1 \phi^2 \quad (2)$$

$$\text{Modified Guth Equation (1945): } E_C / E_0 = 1 + 0.67f\phi + 1.62f^2\phi^2 \quad (3)$$

Where  $E_C$  and  $E_0$  are the young modulus of the filled and unfilled rubber samples respectively,  $\phi$  is the volume fraction of the filler in rubber composite

The experimental as well as predicted values (obtained by both the above models) of  $E_C/E_0$  are plotted against volume fraction of filler and best fitting curves are shown in Fig. 7. It is interesting to note that the experimental values are found to be much higher than those of the predicted values calculated by using Eq. 2 and 3 for the composites (2-5).<sup>15, 30,31</sup> The curve that best fits with experimental data corresponds to volume fraction  $\phi \sim 2.25$ . The reinforcement of rubber matrix caused by filler is a very complex process and depends on several parameters like volume fraction, aspect ratio (shape factor) of filler and their interaction with the rubber matrix. In present case, it is observed that the calculated values obtained by using both volume fraction and shape factor of silica particles are low compared to the experimental results. This modulus enhancement ( $E_C/E_0$ ) is attributed to the strong rubber-filler interaction which is supported by DMA analysis.

**Fig. 7** Plots of modulus enhancement ( $E_C/E_0$ ) versus volume fraction ( $\phi$ ).

#### 4.6 Dynamic Mechanical Analysis

The temperature dependence of storage modulus ( $E'$ ) and loss tangent ( $\tan\delta$ ) of all the composites are shown in Fig. 8 and 9 respectively. It is observed that the storage modulus values are higher for all the silica filled composites (2-6), beyond the glass transition temperature ( $T_g$ ), compared to the unfilled sample. Moreover, in the rubbery region, the storage moduli increase as the silica loading increases. Therefore, it is realized that the silica particles substantially reinforces the compounds. Interaction between the chlorine atom of CR and surface hydroxyl group of silica leads to formation of strong rubber-filler network and



restricts the movement of rubber chains.<sup>32-34</sup> The maximum increase in storage modulus is observed for composite **6** which was prepared by the integration of silane during silica generation for this composite.

Furthermore, the reduction in peak height for both NR and CR phases, in the  $\tan \delta$  versus temperature plot, indicates the reinforcement effect of filler in rubber matrix.<sup>15,35</sup> It is observed here that  $\tan \delta$  peaks, corresponding to the NR phase of the blend in filled composites, show marginal shift towards higher temperature side with slight reduction in peak height. This indicates the development of rubber-filler interaction for the *in situ* silica filled composites that in turn reinforces the rubber matrix and lead to improved mechanical properties as observed in stress-strain studies. On the other hand,  $\tan \delta$  peaks corresponding to CR phase show significant reduction in peak height with increasing *in situ* silica content in the blend.<sup>35-37</sup> Maximum reduction in  $\tan \delta$  peak is observed for composite **6**, filled with silane treated *in situ* silica, for both the NR and CR phases relative to the unfilled sample (26 % reduction in NR phase and 55% reduction in CR phase). This clearly shows that very strong rubber-filler interaction is developed for this particular composite. This observation is consistent with the other results found for this composite.

It may be recalled here that significant enhancement in compatibility of NR and CR phases in the NR/CR blend, induced by *in situ* silica, was observed in the composites obtained from soaking sol-gel method which was ascertained by the shift of  $\tan \delta$  peaks of NR and CR phases towards each other.<sup>16</sup> In present case, however,  $\tan \delta$  peaks of NR phase slightly move towards higher temperature while those of CR phase almost remain constant. It is obvious that silica reinforcement mechanism in these two approaches is different. In soaking sol-gel method, silica is mostly grown in NR phase and migrates towards CR phase during mixing with other ingredients resulting its accumulation at the interface which enhances the compatibility of the blends.<sup>16</sup> On the other hand, in solution sol-gel method, growth of silica

is more likely to take place in CR phase owing to strong CR-silica interaction. This is supported by the strong reinforcement effect of *in situ* silica in CR phase as reflected from the significant reduction in  $\tan \delta$  peak height for this phase (Fig. 9).

**Fig. 8** Storage modulus versus temperature plot of the unfilled and *in situ* silica filled composites (1-6).

**Fig. 9** Loss tangent ( $\tan \delta$ ) versus temperature plot of the unfilled and *in situ* silica filled composites (1-6).

**Table 5** Glass transition temperatures,  $T_g$  (°C) and  $\tan \delta$  peak of the unfilled and *in situ* silica filled composites (1-6)

#### 4.7 Differential Scanning Calorimeter (DSC)

The DSC curves indicate two separate glass transition temperatures ( $T_g$ ) corresponding to NR phase and CR phase for all the composites (1-6) (Fig. 10.) The  $T_g$  of the NR and CR phases for unfilled sample are found at -61.4 °C and -45.5 °C respectively. It may be noted that, the  $T_g$  values obtained from DSC study are different from those found in DMA analysis. This variation may happen due to the different principles involved in these two techniques. DSC measurement is associated with the change in heat capacity as rubber chains evolve from the frozen to unfrozen state, whereas DMA analysis measures the change in mechanical response by the rubber chains.<sup>38</sup> From the DSC thermograms, it is observed that the  $T_g$  of the NR phase is slightly influenced by the silica loading whereas  $T_g$  of the CR phase remains almost unaffected. This small variation for NR phase might be associated with the imposed restriction of rubber chains resulted by the interaction between filler and rubber.<sup>39-41</sup>

**Fig. 10** DSC thermograms of the unfilled and *in situ* silica filled composites (1-6)

## 5 Conclusions

Controlled growth of sol-gel derived *in situ* silica in NR/CR blend (40/60 ratio) is achieved by solution sol-gel process. In soaking sol-gel method, silica content for this blend ratio is limited to 20 phr. Here, silica content in the NR/CR blend is increased by increasing the concentration of silica precursor in optimised reaction condition to gain further improvement in the mechanical properties of the composites. Therefore, composite with silica content up to 30 phr is prepared where mechanical properties improve consistently with increase in silica content. Moreover, silane treatment of silica in the reactive sol-gel system causes much more improvement in the properties of the highest silica filled composite compared to the composite containing same amount of untreated silica. This is attributed to the uniform distribution of silica in rubber matrix as evidenced by SEM image and strong rubber filler interaction as revealed by DMA study for this composite. Improvement in compatibility of the rubber blend relative to unfilled blend is found to be, however, less than that found in soaking sol-gel method. Different mechanism, regarding incorporation and distribution of silica in the rubber blend, occurring in solution and soaking sol-gel method could be the primary reason behind this fact. Thus, maximum reinforcement effect of *in situ* silica is found for NR/CR blend of composition 40/60 with 20 phr silica in soaking sol-gel method while more silica is generated for this blend composition by solution sol-gel method to further enhance the reinforcement effect.

**Acknowledgements:** Mr. N. D. Bansod thanks VNIT, Nagpur for fellowship assistance. The authors are thankful to Prof. Gert Heinrich and Dr. Amit Das, Leibniz-Institut für Polymerforschung, Dresden e.V., Dresden, Germany for extending help and cooperation.

## References

1. D. R. Paul, *Polymer blends*, Elsevier, 1978.
2. P. Sae-oui, C. Sirisinha, T. Wantana, and K. Hatthapanit, *J. Appl. Polym. Sci.*, 2007, **104**, 3478-3483.
3. A. Das, A. K. Ghosh and D. K. Basu, *KGK, Kautsch. Gummi Kunstst.*, 2005, **58**, 230-238.
4. B. P. Kapgate, C. Das, A. Das, D. Basu, U. Reuter and G. Heinrich, *J. Sol-Gel Sci. Technol.*, 2012, **63**, 501-509.
5. B. B. Boonstra, *Polymer* 1979, **20**, 691-704.
6. M. Arroyo, M. A. Lo'pez-Manchado and B. Herrero, *Polym.*, 2003, **44**, 2447-2453.
7. N. Rattanasom, T. Saowapark and C. Deeprasertkul, *Polym. Test.*, 2007, **26**, 369-377.
8. H. Yan, K. Sun and Y. Zhang, *Polym. Test.*, 2005, **24**, 32-38.
9. C. Das and B. P. Kapgate, *Res. J. Recent Sci.*, 2012, **1**, 351-360.
10. B. P. Kapgate, C. Das, D. Basu, A. Das, U. Reuter and G. Heinrich, *J. Elast. Plast.*, 2015 **47**, 248-261.
11. A. Bandyopadhyay, M. De Sarkar and A. K. Bhowmick, *J. Polym. Sci., Part B: Polym. Phys.* 2005, **43**, 2399-2412.
12. M. Messori, *In Situ Synthesis of Rubber Nanocomposites*, in *Recent Advance in Elastomeric Nanocomposites*, Springer, Berlin Heidelberg, 2011, pp. 57- 85.
13. S. Kohjiya and Y. Ikeda, *J. Sol-Gel. Sci. Technol.*, 2003, **26**, 495-498.
14. Y. Ikeda, S. Poompradub, Y. Morita and S. Kohjiya, *J. Sol-Gel Sci. Technol.*, 2008, **45**, 299-306.
15. B. Chaichua, P. Prasassarakich and S. Poompradub, *J. Sol-Gel Sci. Technol.*, 2009, **52**, 219-227.
16. B. P. Kapgate and C. Das, *RSC Advances.*, 2014, **4**, 58816-58825.

17. A. L. Saad and S. El-Sabbagh, *J. Appl. Polym. Sci.*, 2001, **79**, 60-71.
18. P. Kumari, C. K. Radhakrishnan, S. George and G. Unnikrishnan, *J. Polym. Res.*, 2008, **15**, 97-106.
19. C. Nah, S. C. Han, B. W. Jo, W. D. Kim and Y. W. Chang, *J. Appl. Polym. Sci.*, 2002, **86**, 125-134.
20. B. P. Kapgade, C. Das, D. Basu, A. Das, G. Heinrich and U. Reuter, *J. Appl. Polym. Sci.*, 2014, **131**(15), DOI: 10.1002/app.40531.
21. R. Scotti, L. Wahba, M. Crippa, M. D'Arienzo, R. Donetti, N. Santo and F. Morazzoni, *Soft Matter.*, 2012, **8**, 2131-2143.
22. L. Wahba, M. D'Arienzo, R. Donetti, T. Hanel, R. Scotti, L. Tadiello and F. Morazzoni, *RSC Adv.* 2013, **3**, 5832.
23. Y. Ikeda, A. S. Hashim, and S. Kohjiya, *Bulletin of the institute for Chemical Research.* Kyoto University, **72** (5-6), 406-417.
24. S. Yamashita, Y. Nakawaki, and A. Kidera, *Die Makromolekulare Chemie.*, 1987, **188**, 2553-2557.
25. L. H. Sperling, *Introduction to Physical Polymer Science*, Wiley, 2005.
26. C. J. Brinker and G. W. Scherer. *Sol-gel science: the physics and chemistry of sol-gel processing*. Academic press, 2013.
27. P. B. Wagh, A. Venkateswara Rao, and D. Haranath. *Mater. Chem. Phy.* 1998, **53**, 41-47.
28. I. A, Rehman, M. Jafarzadeh and C. S. Sipaut, *Ceram. Int.*, 2009, **35**, 1883-1888.
29. J. Yang and C. Han, *J. Phys. Chem.*, 2013, **117**, 20236-20243.
30. P. Sae-Oui, C. Sirisinha and K. Hatthapanit, *Express Polym. Lett.*, 2007, **1**, 8-12.
31. S. Rooj, A. Das, K. W. Stöckelhuber, D. Y. Wang, V. Galiatsatos and G. Heinrich, *Soft Matter.*, 2013, **9**, 3798-3808.

32. P. Sae-oui, C. Sirisinha, U. Thepsuwan and K. Hatthapanit, *Eur. Polym. J.*, 2006, **42**, 479-486.
33. A. Das, K. W. Stöckelhuber and G. Heinrich, *Macromol. Chem. Phys.*, 2009, **210**, 189-199.
34. K. H. Chung, *J. Appl. Polymer. Sci.*, 2008, **108**, 3952-3959.
35. C. G. Robertson, C. J. Lin, R. B. Bogoslovov, M. Rackaitis, P. Sadhukhan, J. D. Quinn, and C. M. Roland, *Rubber Chem. Technol.*, 2011, **84**, 507-519.
36. C. G. Robertson and C. M. Roland, *Rubber Chem. Technol.* 2008, **81**, 506-522.
37. A. Das, F. R. Costa, U. Wagenknecht and G. Heinrich, *Eur. Polym. J.* 2008, **44**, 3456-3465
38. J. Kim, G. Montero, Y. Habibi, J. P. Hinstroza, J. Genzer, D. S. Argyropoulos and O. J. Rojas, *Polym. Eng. Sci.*, 2009, **49**, 2054-2061.
39. M. A. Kader, W. D. Kim, S. Kaang and C. Nah, *Polym., Int.*, 2005, **54**, 120-129.
40. Y. S. Lee, W. K. Lee, S. G. Cho, I. Kim and C. S. Ha, *J. Anal. Pyrolysis.*, 2007, **78**, 85-94.
41. Peng, Z., Kong, L. X., Li, S. D., Chen, Y., & Huang, M. F. *Compos.s Sci. Technol.* 2007, **67**, 3130-3139.

**Table 1** Formulation of rubber compounds (NR/CR)<sup>a</sup> in phr (parts by weight per hundred parts of rubber)<sup>b</sup>.

| <b>Samples</b>                           | <b>1</b> | <b>2</b> | <b>3</b> | <b>4</b> | <b>5</b> | <b>6</b> |
|--|----------|----------|----------|----------|----------|----------|
| <i>In situ</i> silica                    | -        | 10       | 20       | 25       | 30       | 30       |
| $\gamma$ -APS                            | -        | -        | -        | -        | -        | 2        |
| TEOS (gm) <sup>c</sup>                   | -        | 16.9     | 37.8     | 47.3     | 63.3     | 63.3     |
| % Conversion of TEOS to SiO <sub>2</sub> | -        | 70       | 66       | 66       | 56       | 56       |

<sup>a</sup>NR and CR are at 40 and 60 phr respectively for all the above compounds, <sup>b</sup>Crosslinking ingredients for all the above compounds (in phr) : zinc oxide - 5; magnesium oxide - 4; stearic acid - 1; CBS- 1; sulfur-2 and ethylene thiourea - 0.5. <sup>c</sup> Amount of TEOS added in gm for 30gm of blend (12gm of NR + 18gm of CR).

**Table 2** Optimization of sol-gel reaction conditions for *in situ* silica loading

| Sr. No.                                       | Solvent              | n-butylamine as catalyst<br>(mole ratio to TEOS) | Reaction time<br>(minute) | % conversion |
|---|----------------------|--|---------------------------|--------------|
| Effect of solvent                             |                      |  |                           |              |
| 1   | THF                  | 0.096  | 60                        | 60           |
| 2   | Toulene              | 0.096  | 60                        | 46           |
| 3   | Xylene               | 0.096  | 60                        | 35           |
| 4   | Toluene <sup>a</sup> | 0.096  | 60                        | 70           |
| Effect of reaction time <sup>a</sup>          |                      |  |                           |              |
| 1   | Toulene              | 0.096  | 30                        | 60           |
| 2   | Toulene              | 0.096  | 60                        | 70           |
| 3   | Toulene              | 0.096  | 90                        | 71           |
| 4   | Toulene              | 0.096  | 120                       | 72           |
| Effect of catalyst concentration <sup>a</sup> |                      |  |                           |              |
| 1   | Toulene              | 0.032  | 60                        | 60           |
| 2   | Toulene              | 0.064  | 60                        | 67           |
| 3   | Toulene              | 0.096  | 60                        | 70           |
| 4   | Toulene              | 0.128  | 60                        | 70           |
| 5   | Toulene              | 0.180  | 60                        | 71           |

<sup>a</sup>Ethanol was added in the mixture (TEOS:Ethanol = 1:4 mole ratio)



**Table 3** Curing characteristics of unfilled and *in situ* silica filled compounds

| Sample code  | 1    | 2     | 3     | 4     | 5     | 6     |
|--|------|-------|-------|-------|-------|-------|
| Minimum torque (dNm)                               | 4    | 4.5   | 5.2   | 6     | 6.5   | 8.0   |
| Maximum torque (dNm)                               | 38   | 60    | 65    | 75    | 79    | 81.75 |
| $\Delta$ torque (dNm)                              | 34   | 55.5  | 59.8  | 69    | 72.5  | 73.75 |
| Cure time $t_{90}$ (min)                           | 9.5  | 8.0   | 6.9   | 6.7   | 6.5   | 5.5   |
| Scorch time (min)                                  | 1.75 | 1.5   | 0.72  | 0.75  | 0.5   | 0.5   |
| Cure rate index ( $\text{min}^{-1}$ ) <sup>a</sup> | 12.9 | 15.38 | 16.18 | 16.80 | 16.66 | 20    |
| Crosslinking density ( $\nu \times 10^4$ )         | 1.4  | 2.02  | 3.19  | 4.11  | 5.4   | 6.6   |

<sup>a</sup> Cure rate index (CRI) =  $100/(\text{cure time} - \text{scorch time})$ .

**Table 4** Mechanical properties of the unfilled and *in situ* silica filled composites (1-6).

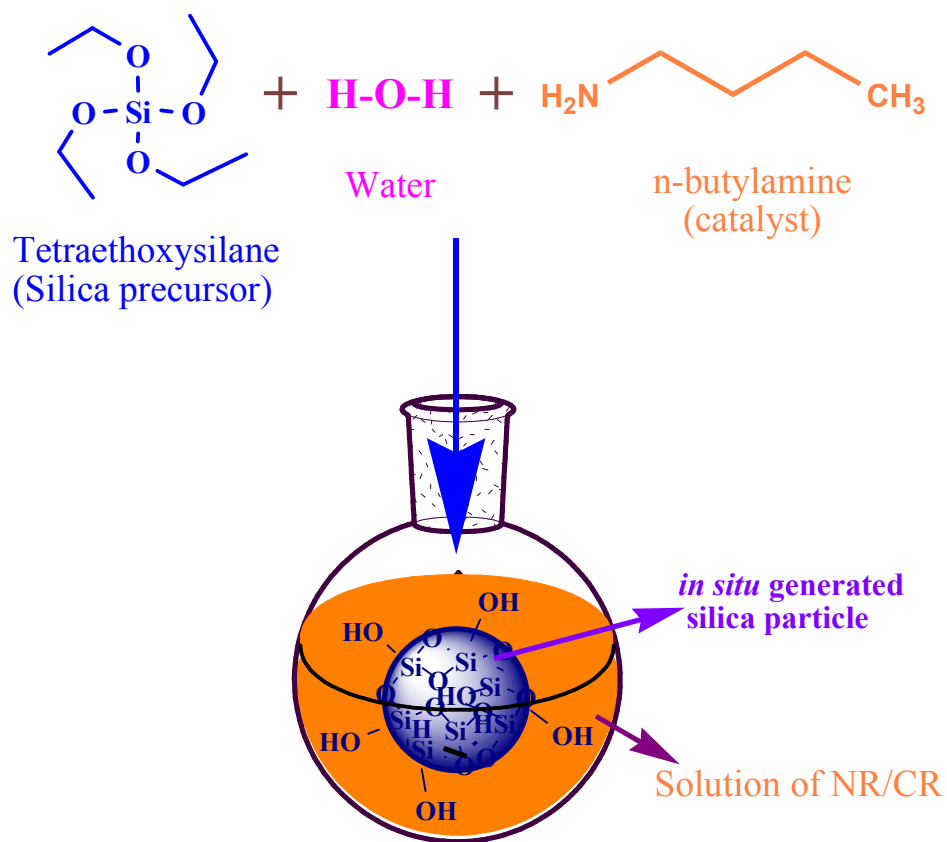
| <b>Sample code</b>      | <b>1</b> | <b>2</b> | <b>3</b> | <b>4</b> | <b>5</b> | <b>6</b> |
|-------------------------|----------|----------|----------|----------|----------|----------|
| $\sigma_{100\%}$ (MPa)  | 0.78     | 1.52     | 1.86     | 2.15     | 3.01     | 3.30     |
| $\sigma_{300\%}$ (MPa)  | 1.62     | 4.35     | 5.04     | 5.45     | 5.83     | 8.08     |
| Tensile Strength (MPa)  | 10.10    | 11.55    | 15.37    | 6.43     | 5.86     | 10.47    |
| Elongation at break (%) | 636      | 469      | 529      | 342      | 306      | 383      |
| Hardness (Shore A)      | 52       | 58       | 64       | 68       | 70       | 75       |

**Table 5** Glass transition temperatures,  $T_g$  (°C) and  $\tan \delta$  peak of the unfilled and *in situ* silica filled composites (1-6)

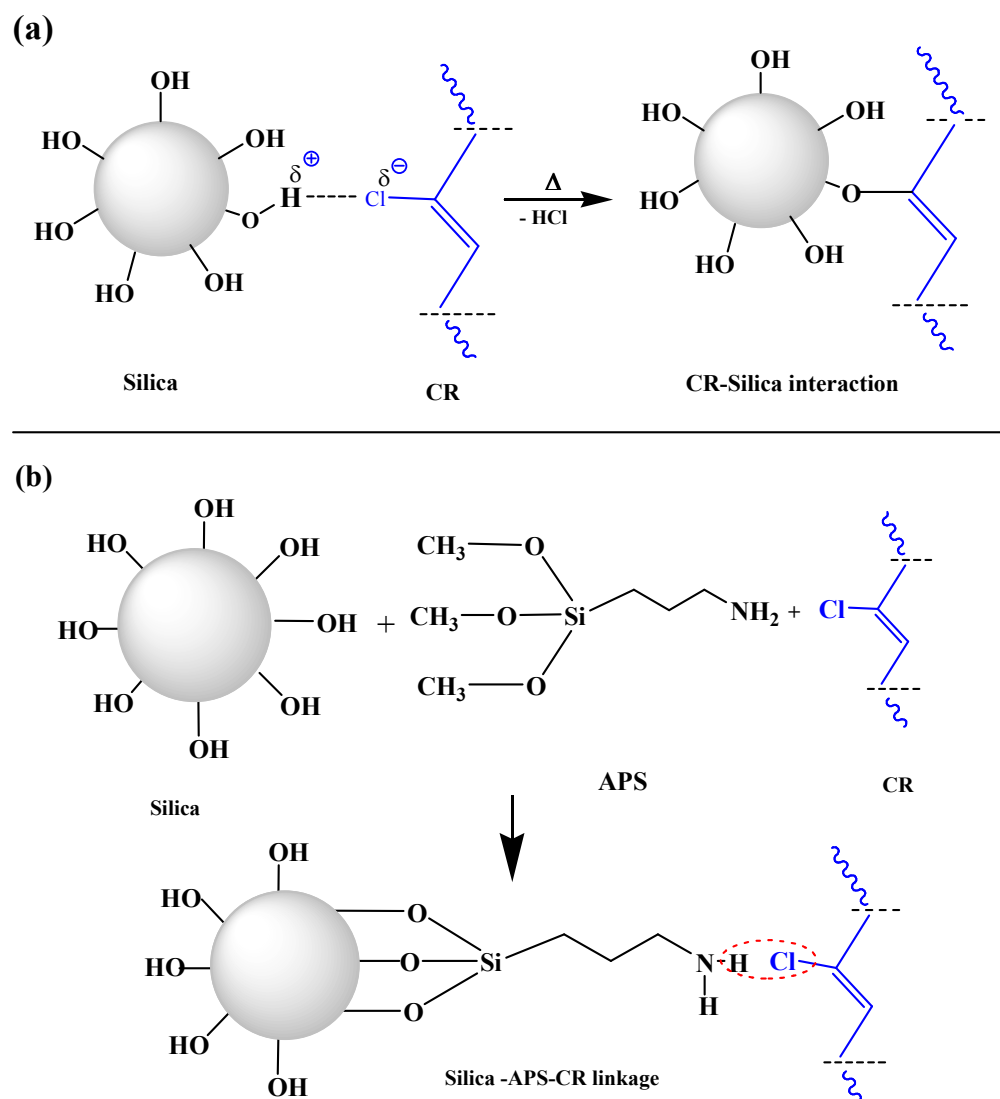
| Sample code | $T_{g(NR)}$ | $T_{g(CR)}$ | $\Delta T_g$ | $\tan \delta_{max}$ |          |
|-------------|-------------|-------------|--------------|---------------------|----------|
|             |             |             |              | NR phase            | CR phase |
| 1           | - 49.9      | -28.1       | 21.8         | 0.35                | 1.83     |
| 2           | - 44.9      | -27.9       | 17.0         | 0.36                | 1.59     |
| 3           | -46.7       | -26.5       | 20.2         | 0.36                | 1.40     |
| 4           | -46.9       | -26.7       | 20.2         | 0.35                | 1.37     |
| 5           | -47.0       | -26.8       | 20.2         | 0.32                | 1.07     |
| 6           | -46.7       | -26.9       | 19.7         | 0.26                | 0.82     |

$T_{g(NR)}$ : glass transition temperature of NR phase;  $T_{g(CR)}$ : glass transition temperature of CR phase;  $\Delta T_g$ : Separation of  $T_g$ .

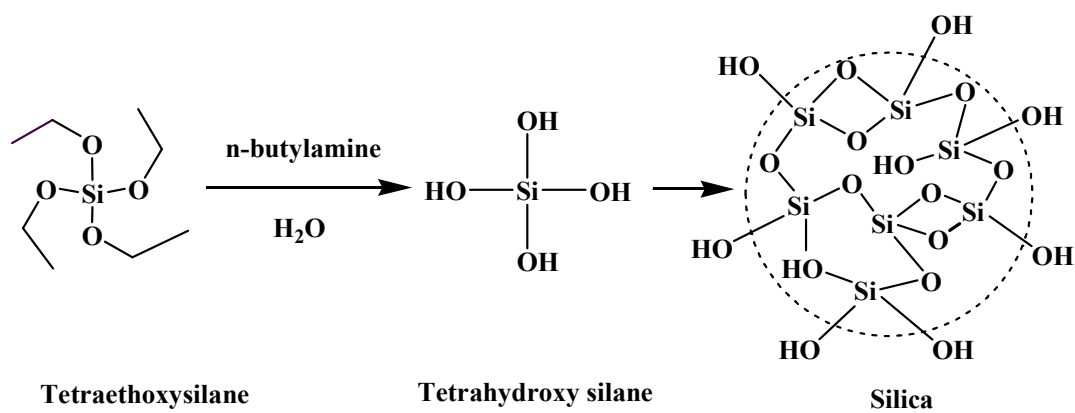
## Graphical Abstract:



Controlled loading of *in situ* silica in NR/CR blend by solution sol-gel method for enhancing the reinforcement



**Fig. 1** (a) Interaction between the silanol group of silica and chlorine atom of CR (b) Linkage between  $\gamma$ -APS modified silica and CR.



**Fig. 2** Hydrolysis and condensation reaction of tetraethoxysilane (TEOS).

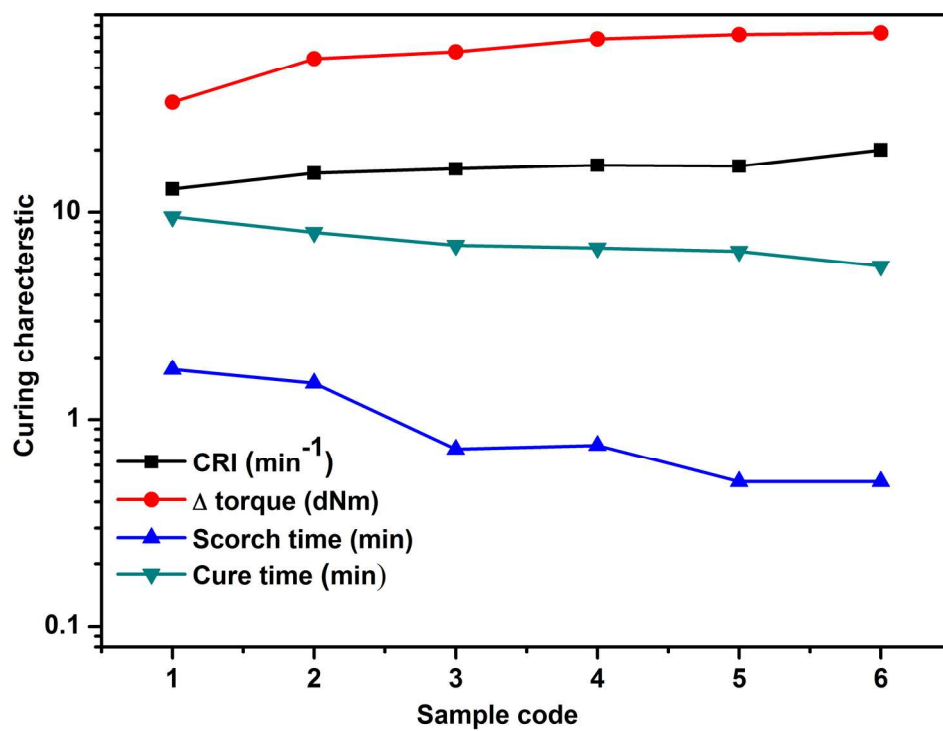
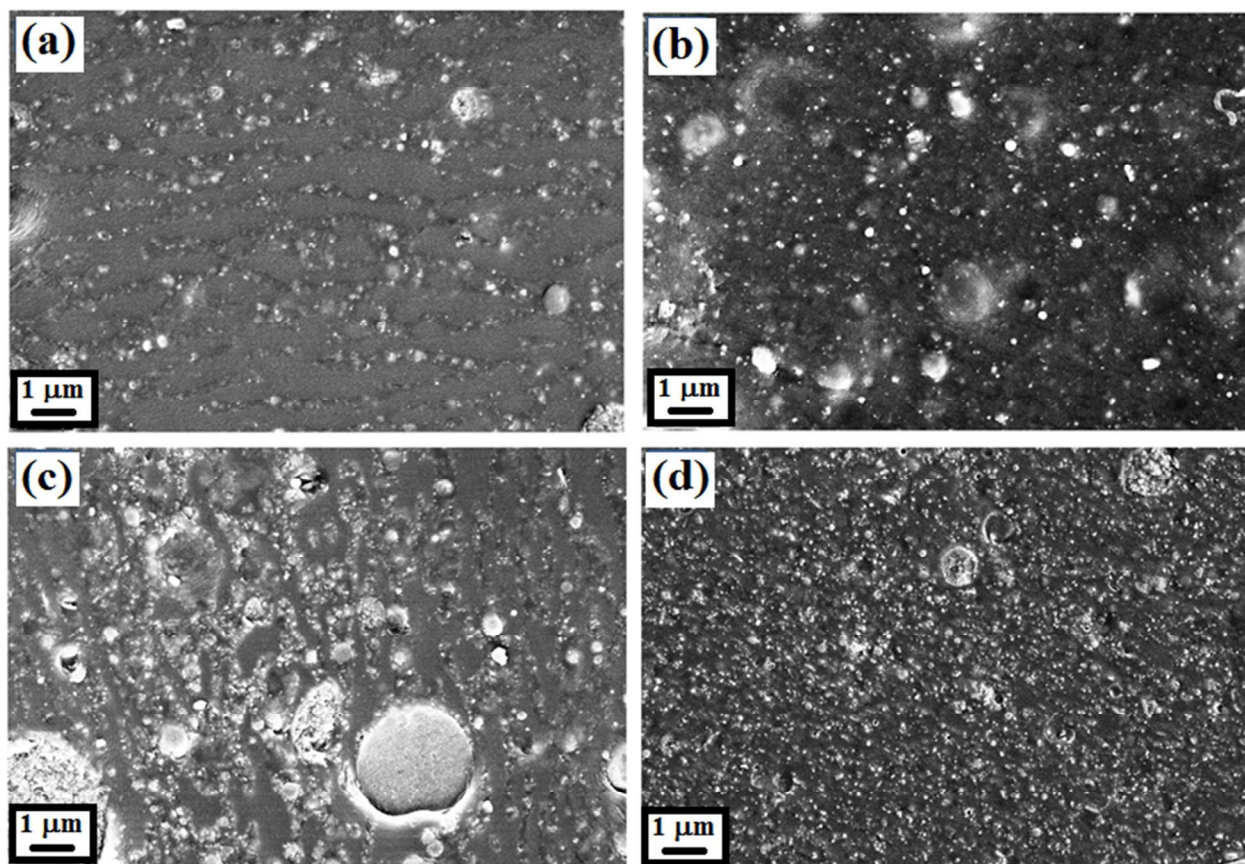


Fig. 3 Curing characteristics of the unfilled and in situ silica filled compounds (1-6).  
181x141mm (300 x 300 DPI)



**Fig. 4** Scanning electron microscopy (SEM) images of *in situ* silica filled NR/CR composites: (a) composite 2 (10 phr silica), (b) composite 3 (20 phr silica), (c) composite 5 (30 phr silica), (d) composite 6 (30 phr silica treated with  $\gamma$ -APS).



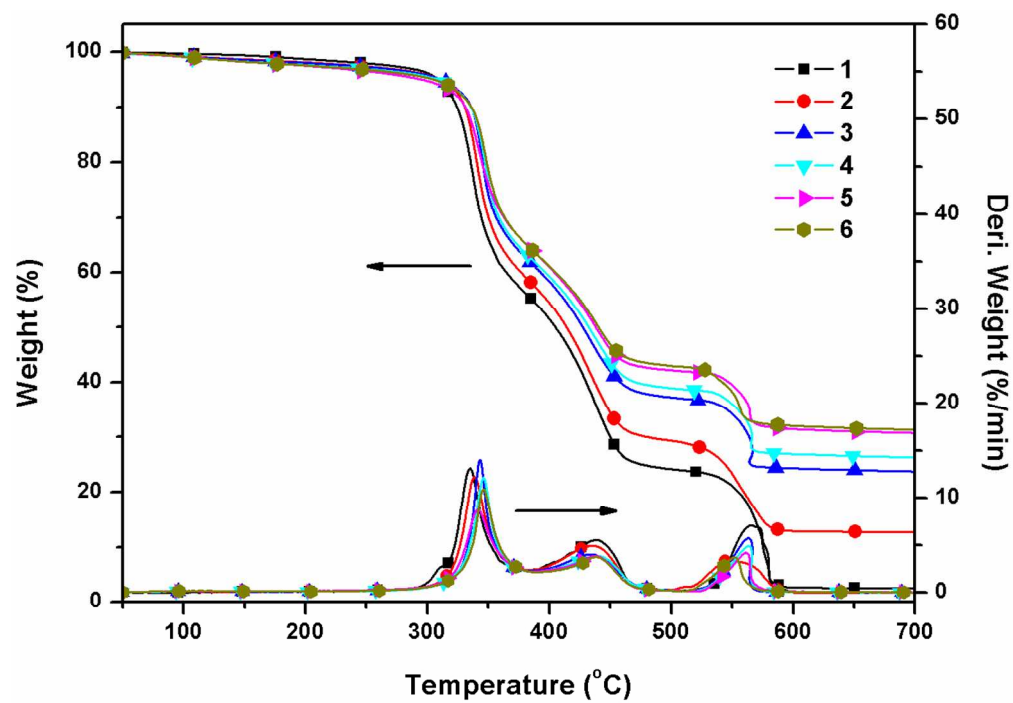


Fig. 5 Thermogravimetric curves of the unfilled and in situ silica filled composites (1-6).  
232x160mm (150 x 150 DPI)

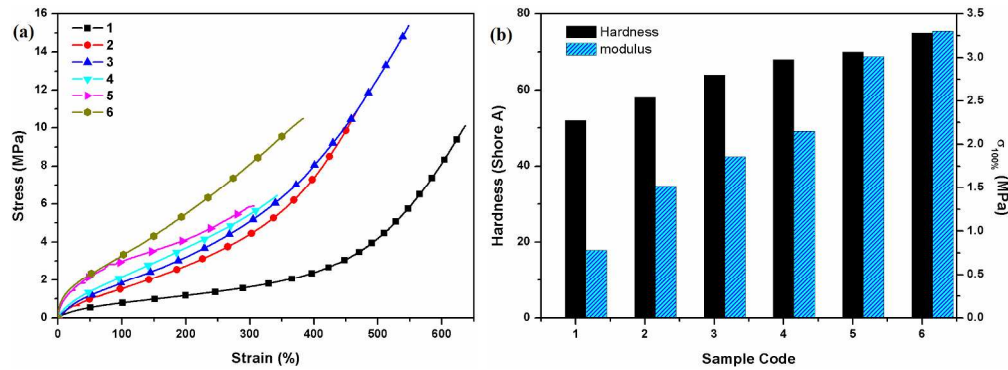


Fig. 6 Mechanical properties of the unfilled and in situ silica filled composites (1-6): (a) Stress-strain curves and (b) Shore A hardness values and  $\sigma_{100\%}$  moduli  
442x160mm (150 x 150 DPI)

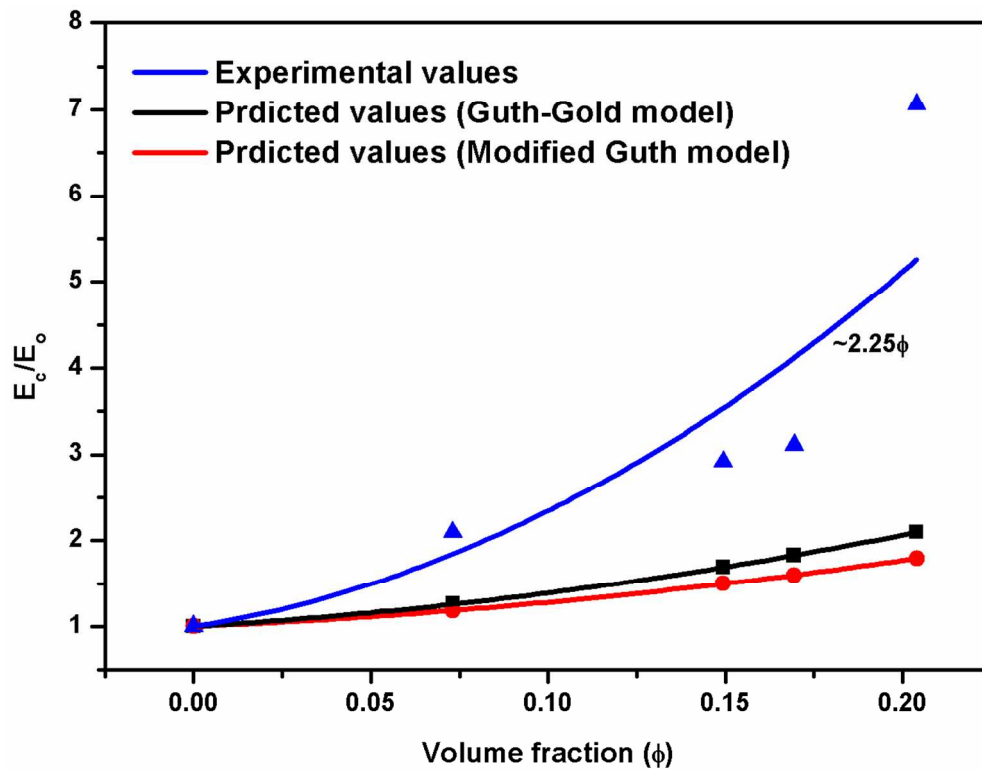


Fig. 7 Plots of modulus enhancement ( $E_c/E_0$ ) versus volume fraction.  
229x175mm (150 x 150 DPI)

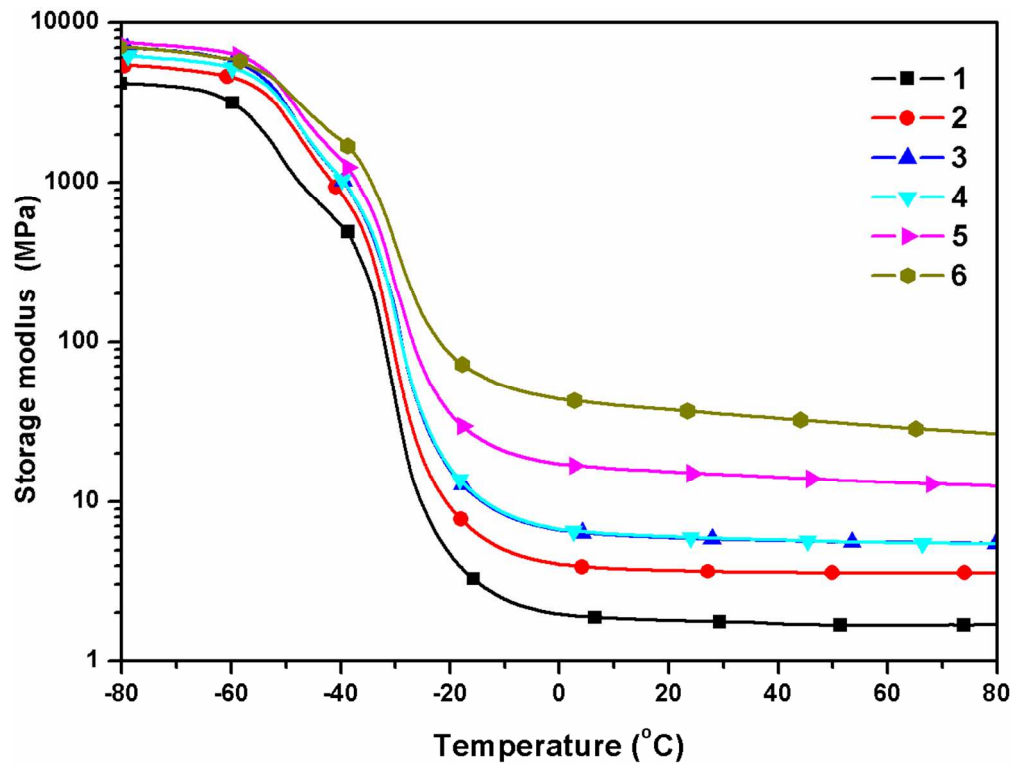


Fig. 8 Storage modulus versus temperature plot of the unfilled and in situ silica filled composites (1-6).  
210x159mm (150 x 150 DPI)

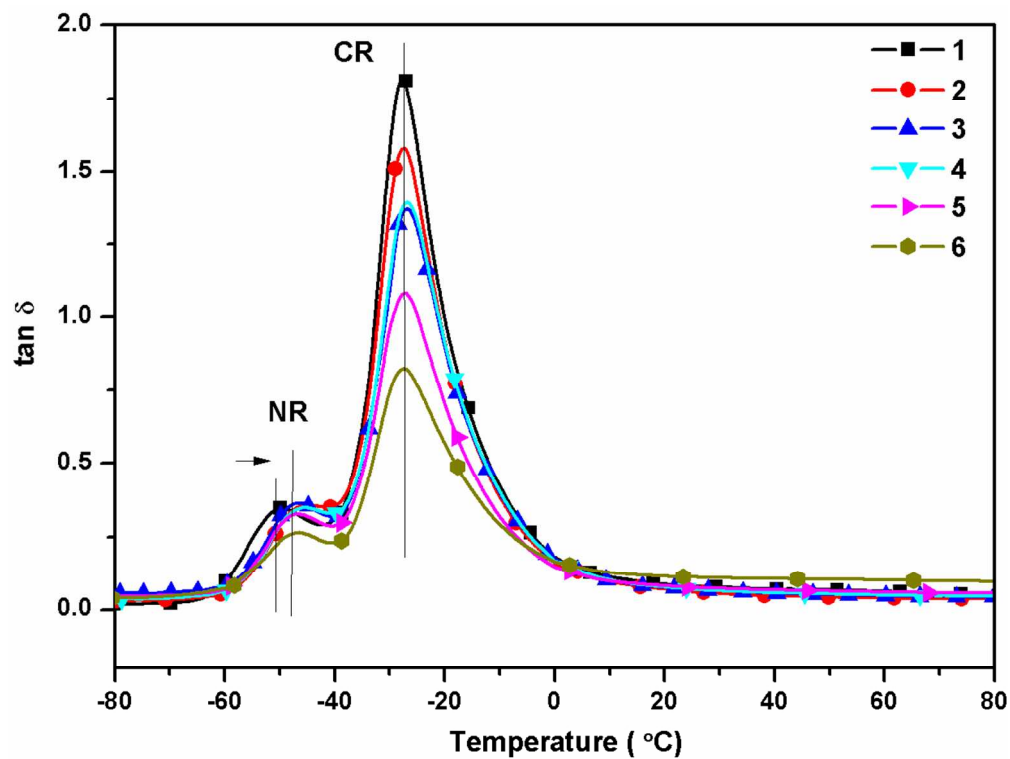


Fig. 9 Loss tangent ( $\tan \delta$ ) versus temperature plot of the unfilled and in situ silica filled composites (1-6).  
208x157mm (150 x 150 DPI)

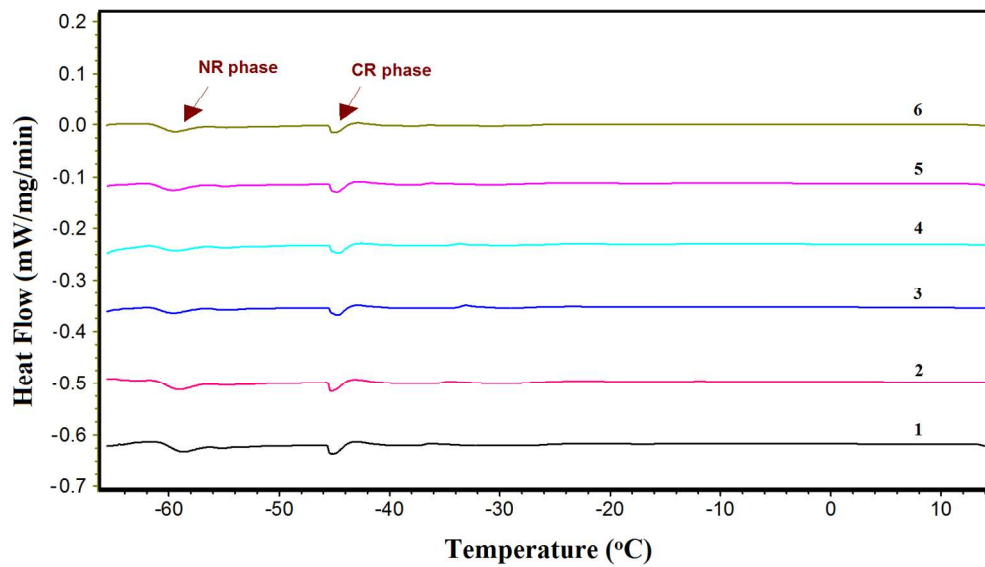


Fig. 10 DSC thermograms of the unfilled and in situ silica filled composites (1-6)  
465x264mm (96 x 96 DPI)