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Reinforcing efficiency and compatibilizing effect of sol-gel derived in-situ silica for natural rubber/chloroprene rubber blends

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Abstract

Nano silica is grown, in-situ, in natural rubber (NR)/chloroprene rubber (CR) blends, by soaking sol-gel method. Much better silica dispersion in the rubber blends is achieved following this technique in comparison to the rubber blends with externally filled silica at same filler loading and same blend composition. This leads to significant improvement in modulus, tensile strength and dynamic mechanical properties of all the in-situ silica filled composites relative to externally filled composites. Additionally, analysis of glass transition temperature (T_g) values reveals that compatibility of NR and CR in the blend is enhanced when silica is incorporated in-situ which in turn contributes in improving the physical properties of the composites. This enhancement in the compatibility of rubber blends is attributed to the preferential accumulation of in-situ silica at the interphase of the two constituent rubbers. Best mechanical properties are shown by the in-situ filled composite with NR/CR at 40/60 blend ratio. This result is in agreement with the rheological properties, thermal properties and viscoelastic behaviors of this particular composite. Ultimate properties of the composites are found to be governed by the blend composition, blend compatibility and state of filler dispersion, as well, in addition to filler content.

Keywords: elastomer blends; nano silica; compatibility; reinforcement

1 Introduction

Rubber blends comprising of different rubbers find many important applications owing to their superior properties which may not be otherwise achieved by individual component.[1, 2] Likewise, blends of NR and CR have been extensively studied by different groups from different viewpoints.[3-12] NR possesses good mechanical and dynamic properties. However, it has several limitations like poor oil and ozone resistance and degradation tendency under thermal ageing.[13] Blending of CR with NR in suitable proportion has been proven to be very useful to overcome such shortcomings of NR.[3-12] In most of the reported works, silica is incorporated in the rubber blends by external mixing for reinforcement purpose.[4,5] Role of silica on the reinforcement and curing characteristics of the individual components viz. NR and CR is different owing to the polarity difference of NR and CR. Highly polar nature of silica, due to presence of large number of hydrophilic silanol groups on its surface, gives rise to strong filler-filler interaction resulting in filler agglomeration in NR matrix.[4, 5] But, presence of CR which is polar in nature, in the blend helps in better filler dispersion and brings in improvement in the mechanical properties resulted from strong CR-silica interaction through hydrogen bonds as well as chemical interaction between allylic chlorine atom and silanol group (Fig. 1).[14, 15] However, for such heterogeneous blends, consisting of polar and nonpolar rubber, blend compatibility is a major concern from the viewpoint of mechanical properties of the composite. To counter this problem, certain polymeric species or multifunctional organic compounds have been used as compatibilizing agents.[16] For example, polyvinyl chloride (PVC) and styrene butadiene rubber (SBR) have been used in NR/CR blend systems to improve the compatibility.[8] Reports on compatibilizing effect of fillers like clay are well documented in literature.[17, 18] Generally filler is premixed with less polar rubber like NR or EPDM to obtain master batch and then it is mixed with polar rubber like HNBR, CR etc.[17-18] During mixing, migration of filler from less polar to more polar rubber takes place with its accumulation at the interphase which enhances compatibility of the blends.[17,18] However, external mixing of silica with NR or EPDM is difficult and requires multistage mixing. In this context, soaking sol-gel method appears to be very effective for in-situ silica generation in less polar rubber matrices, as they have greater swelling tendency in organic TEOS (tetraethoxysilane) the silica precursor.

In the present work, silica generated in-situ in NR/CR blends has been proven to enhance the compatibility between NR and CR in the blend in addition to its superior reinforcement effect with respect to externally added silica. It may be mentioned that although reinforcement effect of in-situ silica is well established [19-21] but it's capability in enhancing the compatibility of two immiscible rubber phase in a blend is not reported till date. Here, we have used soaking sol-gel method for silica generation into rubber blends using non polar TEOS. In this method, sheets of rubber blend are immersed in TEOS for sufficient time, at initial stage, for swelling of TEOS inside the rubber matrix. So, it is expected that NR, being non polar in nature, would have greater solvent uptake capability than CR leading to more silica generation in the former phase. While, it is established fact that externally added silica gives stronger interaction with CR and hence increases crosslinking density in the CR phase of NR/CR blends.[4, 5, 14, 15] Thus, it appeared that studies of compatibilizing capability of in-situ silica, in addition to its reinforcing efficiency, generated by this technique into NR/CR blends would be an interesting piece of study. With this objective, NR and CR are blended in varying proportion to prepare three groups of composite viz. *unfilled, in-situ silica filled* and *externally silica filled* with similar composition. Detailed comparative studies of these composites have been done with reference to their morphology, curing behavior, thermal property, mechanical property and viscoelastic behavior. Moreover, a carbon black filled NR/CR blend composite at 40/60 ratio has been prepared and its properties are compared with respective silica filled composites.

2 Experimental

2.1 Materials

Natural rubber (RSS4), chloroprene rubber (LANXESS Baypren), precipitated silica (Ultrasil VN3) and carbon black (N330, high abrasion furnace black) were obtained from Heritage Rubber (Nagpur, India). TEOS (Tetraethoxysilane 98%) and n-butylamine were purchased from Acros Organics (New Jersey, USA). Toluene was purchased from Fischer Scientific (India). Other curatives viz. sulphur, ZnO (zinc oxide), MgO (magnesium oxide), stearic acid and CBS (N-cyclohexylbenzothiazole-2-sulfenamide) were collected from Sara Polymer Pvt. Ltd (Nagpur, India). ETU (Ethylene thiourea) was purchased from National chemicals (India).

2.2 Preparation of in-situ silica filled composites

Silica particles were generated and grown into unvulcanized NR/CR blends at different ratio by soaking method of sol-gel process. First, NR and CR were blended together for 10 minutes at various blend ratio (Table 1) on a two roll mill to obtain sheets of ca. 2 mm thickness. Then these sheets were allowed to swell in TEOS for 24 hours at ambient temperature. Next, the swollen sheets were removed from TEOS and were immersed in 10 % aqueous solution of n-butylamine (catalyst) for 48 hours at same temperature. Then the sheets were removed and dried at 50^0C for 48 hours and further dried at 80ºC in a vacuum oven to constant weight. In-situ silica filled NR/CR blends were then masticated on a two roll mill for 5 minutes followed by compounding with other crosslinking ingredients for further 10 minutes (curing formulation is given in Table 1). Next, these unvulcanized sheets were press cured by compression molding at 160°C with respect to their corresponding cure times (t_{90})

(Table 2) to obtain vulcanized rubber sheets of 2 mm thickness. This process was used for the preparation of in-situ silica filled composites **5-8**.

2.3 Preparation of unfilled and externally filled rubber blend composites

For the other composites, blending of natural rubber and chloroprene rubber at various blend ratios was carried out on a two roll mill. Composites **9-12** were prepared by externally mixing NR/CR blend with precipitated silica for 15 minutes on a two roll mill followed by mixing of crosslinking ingredients for further 10 minutes. The curing formulation and filler content of composites **9-12** are given in Table 1. Composite **13** was prepared in a same manner but using carbon black as filler instead of silica. Similarly, composites **1-4** were prepared in a same manner as **9-12** but without adding any filler, on a two roll mill. All the above unvulcanized sheets were press cured by compression molding at 160^0C with respect to their corresponding cure times (t_{90}) (Table 2) to obtain vulcanized rubber sheets of 2 mm thickness.

Table 1 Formulation of rubber composites in phr (parts by weight per hundred parts of rubber by weight)

2.4 Characterization techniques

Cure studies of the unvulcanized rubber compounds were performed by using oscillatory disc rheometer (Micro vision enterprises India) with amplitude of ± 3° and a frequency of 1.66 Hz for all the samples at 160°C for 60 minute. Vulcanization of the rubber compounds were carried out according to respective cure time of the compounds. Scanning electron microscopy (SEM) images of silica filled composites were obtained using field emission scanning electron microscope (SEM; Zeiss Ultra Plus; Carl Zeiss Microscopy GmbH, Jena, Germany) equipped with an energy-dispersive X-ray spectrometer (EDX; Quad XFlash 5060, Bruker Corporation, Billerica, MA, USA) at an acceleration voltage of 3 kV. The samples were cut with a ultramicrotome and sputter coated with 3nm Platinum. Thermal properties and in-situ silica content of the rubber vulcanizates were determined by thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) by using a thermal analyzer TG-DTA 7200 (Hitachi Japan). Samples were placed in a platinum pan and were heated in the temperature range 30°-700°C under nitrogen atmosphere at the heating rate of 10°C/min. Silica content of the in-situ filled rubber composites (**5-8**) was determined by comparing the residual weight percentage of a particular composite with it's unfilled analogue of same blend ratio. Tensile tests of dumbbell shaped samples were carried out on a material testing machine (Zwick1456, Z010, Ulm Germany) with crosshead speed 200 mm/min (ISO 527). Hardness of the composites was determined on Shore A scale by shore A durometer (bse testing machines India). Dynamic mechanical analysis was performed with an Eplexor 2000 N dynamic measurement system (Gabo Qualimeter, Ahlden, Germany) by using a constant frequency of 10 Hz in a temperature range -100°C to +140°C. All the measurements were done in tension mode. For the measurement of the complex modulus, E*, a static load of 1% pre-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 under liquid nitrogen flow. Swelling measurements were carried out by soaking the cured sheet in toluene for 7 days at room temperature. After each 24 hour, solvent was changed with fresh toluene. Sheets were removed after seven days and were blotted with blotting paper and weight of the sheets was determined on analytical balance. Crosslinking density (ν), defined by the number of elastically active chains per unit volume, was calculated by Flory-Rehner equation (1).[22]

$$\nu = -[\ln(1-V_r) + V_r + \chi V_r^2] / V_s (V_r^{1/3} - V_r/2) \text{ ....(1)}$$

where, Vs is the molar volume of the toluene (106.2), Vr is the volume fraction of rubber in swollen gel and χ is the Flory-Huggins polymer-solvent interaction parameter.[22, 24]

3 Results and discussion

3.1 Curing behavior

Curing characteristics of all the compounds are illustrated in Table 2. Among the unfilled compounds (**1-4**), consistent delay in cure time and scorch time is observed with increasing CR proportion in the blend. This can be attributed to the scorch prevention characteristics of CR.[25] On the other hand, for the in-situ silica filled compounds (**5-8**), not only the blend proportion but the silica content also influences the cure properties as well. Compounds with higher silica and higher NR contents (**5** and **6**) show some cure retardation effect which might be due to the adsorption of the cure accelerators by the surface silanols of silica. This is as much as expected for a compound composed of non-polar rubber and silica.[4,5,26,27] In contrast, for the compounds with higher CR content (**7** and **8**), this effect is relatively mild owing to strong interaction between CR and silica (Figure 1).[26,27] Maximum torque, which is closely related to the crosslinking density, is found to be improved for all the in-situ silica filled compounds **(5-8)**. This indicates higher crosslinking density in this series arising from the strong CR-silica interaction (Equation (1), Table 2). It is reported in literature that silica itself, as a filler, can crosslink the CR matrix without any curatives (Fig. 1).[15] Nevertheless, the highest value of torque is observed for composite **7** that gives an indication of better compatibility for this particular blend ratio (NR/CR: 40/60) which is supported by significant reinforcement and better rubber-filler interaction for this composite in subsequent studies. For externally silica filled composites (**9-12**), higher compound viscosity (minimum torque) relative to in-situ silica filled composites (**5-8**) is observed. This might be due to the silica agglomeration in the rubber matrix, in former case, resulted from relatively stronger filler-filler interaction as revealed in morphological study (discussed later). Also, lower values of maximum torque and longer cure time for externally filled composites, as compared to those of in-situ silica filled composites, indicate much pronounced cure retardation effect in former case. This might be due to the adsorption of the cure accelerators in greater extent via surface silanols of silica for this group of composites. Notably, this effect is less in composites **11** and **12** with high CR content in the blends. This is due to the preference of silica to move towards CR phase during external mixing owing to strong CR-silica interaction.[26,27]

Table 2 Curing characteristics of NR/CR blend compounds

Fig. 1 Interaction between CR and silanol group on silica surface

3.2 Thermogravimetric study

Silica content of the in-situ filled rubber composites (**5-8**) has been determined from the residual weight percentage obtained from thermogravimetric results (Table 1). It is observed that silica content in the rubber blend composites decreases consistently as the CR content in the blends increases. This trend in silica generation can be explained by the different affinity of NR and CR in absorbing TEOS inside the matrix. In soaking sol-gel method, rubber sheets are immersed in TEOS at initial stage for sufficient time. CR, being polar, has lower degree of swelling in TEOS than that of NR. Since silica generation is governed by the amount of imbibed TEOS inside the rubber matrix, lower degree of swelling leads to less silica generation in the blends with higher CR proportion.[28, 29] Thus, amount of silica generation into rubber matrix is governed by the blend ratio and phase selective swelling.

The onset temperature and T_{max} (temperature at maximum weight loss) for individual NR and CR phases for all the composites are given in Table 3. Thermogravimetric analysis shows fall in onset temperature (300°C-340°C) for the unfilled blends (**1-4**) as NR percentage in the blends decreases. Two peaks are observed in the DTG curves which correspond to the T_{max} for the individual component i.e. NR phase (310°C-355°C) and CR phase (430°C-441°C). It is interesting to note here that, T_{max} values for both the components change with variation in the blend ratio. This clearly shows the influence of blend ratio on the thermal properties of the rubber blend composites (Fig. 2). The improvement in thermal stability brought by silica incorporation in the filled composites, relative to the analogous unfilled composites, is evident from the analysis of thermal data. Incorporation of silica in the rubber matrix certainly results in confinement of rubber chains due to development of polymer-filler interaction. This retards the thermal degradation of the composites and eventually leads to the delayed onset temperature and T_{max}.[30] Nevertheless, the highest level of improvement in thermal property relative to respective unfilled composite is exhibited by composite **7** whose mechanical property and rubber-filler interaction are found to be best in subsequent studies.

Table 3 Thermogravimetric data of NR/CR blend composites

Fig. 2 Thermogravimetric curves of in-situ silica filled composites (**5-8**)

3.3 Morphology

The phase morphology of an elastomer blend is very much dependant on various factors like blend ratio, surface characteristics, viscosity of the components, blending method etc.[28]

Studies of scanning electron microscopy (SEM) reveals presence of nearly spherical in-situ silica particles (aggregates) with average size of 60 nm for all the in-situ filled composites **5-8** (Fig. 3). Growth of silica inside a rubber matrix in soaking sol-gel method proceeds via inverse micelle formation.[31,32] The micelle formed in this system may be viewed as water in oil (water in rubber) type. The primary alkyl amine, used as catalyst, behaves as a surfactant which surrounds the centered water molecules. The polar amine ends are faced towards center while the long alkyl chains are directed outwards to form the reverse micelle as depicted in Fig. 4. The alkyl chain, being a non polar moiety, allows the easy diffusion of non polar TEOS molecules in between the alkyl chains and facilitates their movement towards the interface of micelle. The hydroxyl groups of water hydrolyses the TEOS molecules with the exchange of ethoxy groups and increases the polarity of partially hydrolysed TEOS molecules and eventually more TEOS molecules migrate towards center of micelle. The condensation of hydrolyzed TEOS molecules takes place to form solid silica particles.[31, 32]

It is expected that silica would be generated mostly into NR phase of the blends due to greater solvent (TEOS) uptake capability of NR over CR during soaking stage. However, uniform homogeneous dispersion of silica throughout the rubber blend matrix for composites **5 – 7** is observed where distinct phases of two different rubbers can hardly be observed (Fig. 3). It is well established fact that at mixing stage, solubility parameter of the compounds influences the distribution of filler into rubber blends.[33,34] Hildebrands solubility parameter are reported as 8-8.5 for NR; 9-9.5 for CR and 14-18 for silica.[33,34] Thus it is evident that silica is more compatible with CR than NR leading to migration of silica from less polar NR phase to more polar CR phase which can be a favorable factor in enhancing the compatibility of these two phases in a blend. Such migration of silica from less polar NR phase to more polar CR phase takes place during compounding and vulcanization and this is well documented in literature.[17,18,35,36] Migration of nanoclay and its accumulation at the interphase in the elastomer blends (CR/EPDM) has been shown to be a favourable factor in bringing the enhancement in compatibility of two different rubber phases in a blend.[17] However, for composite **8**, containing lowest NR content a heterogeneous distribution of silica is evident from the SEM image. A continuous CR phase is observed here in which in-situ silica reinforced NR is present as dispersed phase. A better view is presented in supplementary figure, Fig. S1.

Fig. 3 Scanning electron microscopy (SEM) images of NR/CR-in-situ silica filled composites: 80/20- In Si-30 (**5**); 60/40- In Si-30 (**6**); 40/60- In Si-20 (**7**) and 20/80- In Si-15 (**8**)

Fig. 4 Schematic representation of inverse micelle formation for silica growth into rubber matrix

SEM image of externally filled silica composite at 40/60 blend ratio (**11**) is shown in Fig. 5(a) as a representative example. It shows heterogeneous silica distribution into rubber blend matrix with large number of silica aggregates. This clearly exposes worse filler dispersion of silica in the rubber matrix, when added externally at similar condition, in comparison to dispersion of silica generated in-situ by sol-gel process for similar blend. From, Si mapped SEM EDS image (Fig. 5(b)), large sized silica agglomerates into rubber matrix are also noted. Moreover, two distinct rubber phases are evident in the SEM image of composite **11** indicating heterogenous morphology and incompatibility of the blends for externally silica filled composite. Heterogeneous distribution of silica is further confirmed from the SEM EDS (energy dispersive spectroscopy) studies of this composite. Elemental distribution in two different regions as analysed by EDS is shown in Fig. 6. Intensities of silicon (Si) and oxygen (O) peaks are found to vary widely at different region indicating heterogeneous distribution of filler into rubber blend matrix.

Fig. 5 (a) Scanning electron microscopy (SEM) image and (b) Silicon mapped SEM EDS image of externally silica filled composite at 40/60 blend ratio (**11)**

Fig. 6 Scanning electron microscopy (SEM) image with energy dispersive spectroscopy (EDS) pattern for externally silica filled composite at 40/60 blend ratio (**11)**

3.4 Stress-strain studies

Mechanical properties of all the NR/CR composites were evaluated by stress-strain studies (Table 4 and Fig. 7.) It is observed that modulus, tensile strength and elongation at break of all the unfilled blends (**1-4**) increase with increase in CR content in the blend. This is attributed to the increased crosslinking density (determined by swelling studies), in moving from **1** to **4** as shown in Table 2.[37] Significant improvement in modulus and tensile strength for all the in-situ silica filled composites (**5-8**) is observed in comparison to unfilled (**1-4**) and externally silica filled (**9-12**) composites of similar composition. Among the in-situ silica filled composites, highest mechanical property is achieved for composite **7** with NR/CR at 40/60 blend ratio. It may be recalled here that highest improvement in thermal property as well as highest torque value were shown by this particular composite in earlier studies. It is noteworthy that the filler content of this composite is less than that in composite **5** and **6** with NR/CR blend ratio at 80/20 and 60/40 respectively. However, the level of improvement, in comparison to respective unfilled composite of same blend ratio, is highest for composite **5** that contain highest in-situ silica. So, it is quite reasonable to conclude that not only the filler content but blend ratio can also play an important role in governing the ultimate properties of the composites. Improvement in mechanical properties for the in-situ silica filled composites is attributed to the homogeneous dispersion of silica, strong rubber-filler interaction and enhanced compatibility of the blends brought by in-situ silica loading.

In case of externally silica filled composites **(9-12)**, although improvement in modulus compared to respective unfilled composites is observed but it is inferior if one compares that with respect to the improvement achieved for in-situ silica filled composites **(5-8).** However, fall in tensile strength (except composite **9**) as well as in elongation at break for this group of composites compared to unfilled one show that reinforcement effect brought by externally added silica is of less significance. This is due to severe agglomeration of silica particles into rubber matrix, as revealed in SEM study, in addition to lower crosslinking density values in this case.[5] Unlike in-situ filled composites, this group of composites, irrespective of silica loading, shows same trend in modulus and tensile strength values as shown by unfilled blend composites. This shows contribution of silica towards mechanical property is not so significant when added externally.

For comparison purpose, one composite (**13**) was prepared with externally filled carbon black (HAF) at same blend ratio and same filler content as those of composite **7** (Fig. 7(b)). Composite **13** shows better modulus value at 100% and 300% strain but tensile strength and elongation at break are much less than those of composite **7**.

Hardness values of the unfilled composites (**1-4**) are found to increase consistently along the series with increasing CR content as it contributes higher viscosity and greater crosslinking density in the blends. Hardness values of the composites become significantly higher by incorporation of silica by 8-12 point in shore A scale. The highest value is shown by composite **7** where the tensile properties are found to be best.

Table 4 Mechanical properties of NR/CR blend composites

Fig. 7 (a) Stress-strain curves of unfilled composites (**1-4**) and in-situ silica filled composites (**5-8**); (b) Stress-strain curves of unfilled composite **(3),** in-situ silica filled composite (**7**)**,** precipitated silica filled composite (**11**) and carbon black filled composite **(13)**

3.5 Dynamic mechanical properties

Dynamic mechanical analysis (DMA) of all the composites have been done to assess the effect of filler incorporation on the dynamic response of the composites as this can deliver many important information about the blend compatibility, viscoelastic property and rubber-filler interaction.[17, 37-40] The dependency of storage modulus on temperature is shown in Fig. 8. The storage modulus values of the composites can be regarded as a direct measure of the reinforcement effect of filler which is very much dependent on the state of filler dispersion, rubber-filler interaction and compatibility of the blend. In the present case, storage modulus in the rubbery region increases for unfilled composites (**1-4**) with increase in CR content in the blends (Fig. 8(a)) which is in accordance with the increased crosslinking density as discussed in earlier sections. For the in-situ silica filled composites (**5-8**), incorporation of silica results in significant reinforcement as shown by the higher storage modulus values in the rubbery region (above T_g) for all the blend ratios as expected (Fig. 8(a)). Comparison of storage modulus among the in-situ silica filled composites (**5-8)** reveals highest value for composite **7** that shows best mechanical properties. The value is also high for blend composite **5** that shows maximum level of improvement in comparison to respective unfilled blends in stress-strain study. Another notable obsevation here is low storage modulus values of **8** relative to other in-situ filled composites which is due to distribution of silica mostly in NR phase of the blend as found in SEM micrograph (Fig. 3 and supplementary Fig. S1). It is also worthwhile to note here that this improvement is very significant for in-situ silica filled composites in comparison to externally filled composites of similar composition which is in accordance with the observation made in stress-strain studies (Fig. 8(b)). This is primarily attributed to the homogeneous dispersion of in-situ silica in the rubber matrix and strong rubber-filler interaction between CR and silica. In addition, improved compatibility between NR and CR brought by the incorporation of in-situ silica, can further enhance the reinforcement effect. The improvement in blend compatibility is achieved by accumulation of silica at the NR/CR interphase, during its diffusion from NR to CR phase in curative mixing stage. Carbon black filled composite (**13**) at same filler loading and at same blend ratio as those in composite **7**, shows lower storage modulus value than **7** (Fig. 8(b)). However, its viscoelastic behaviour is found to be more or less same as that of corresponding externally silica filled composite **11**.

Fig. 8 (a) Storage modulus versus temperature curves of unfilled composites (**1-4)** and in-situ silica filled composites (**5-8);** (b) Storage modulus versus temperature curves of unfilled composite **(3),** in-situ silica filled composite (**7**), precipitated silica filled composite (**11)** and carbon black filled composite **(13)**

Improvement in blend compatibility is confirmed by analysing the glass transition temprature (T_g) of the constituent rubber phases in the blends, for all the composites obtained from temperature versus tanδ curves (Fig. 9, Table 5). Two distinct tanδ peaks corresponding to characteristic T_g of the individual rubber phases ($T_{g(NR)}$ and $T_{g(CR)}$) are observed in Fig. 9. In general, T_g value is influenced by polymer-filler interaction and extent of compatibility in a blend. Strong polymer-filler interaction causes positive shift in T_g. On the other hand, enhancement in compatibility in an elastomer blend results in shifting of T_g of two individual phases towards each other.[17,18] Among the unfilled composites (**1-4**) analysis of Δ T_g (Separation of T_g between two individual phases) shows that compatibility of the blends depends on blend ratio and it is highest for composite **3** (NR/CR: 40/60) having minimum ΔT_g value. Careful analysis of T_g values for individual rubber phase and ΔT_g values have been done for unfilled, in-situ filled and externally filled composites for each NR/CR blend ratio and the results are tabulated in Table 5. Results in Table 5 show that individual T_g and ΔT_g values for all the composites have been influenced by incorporation of silica. In case of externally filled composites (**9-12**), both $T_{g(NR)}$ and $T_{g(CR)}$ values show postive shift in comparison to those in respective unfilled composite (**1-4**). This is attributed to polymer-filler interaction in both the NR and CR phases brought by filler incorporation. Interestingly, for all the in-situ filled composites (**5-8**) $T_{g(NR)}$ is shifted in postive direction but $T_{g(CR)}$ is moved in oppostie direction for each composite with reference to respective unfilled composite. Positive shift of $T_{g(NR)}$ is as much as expected due to increased polymer-filler interaction while reverse trend of $T_{g(CR)}$ is resulted due to enhancement in blend compatibility as revealed by morphology study in earlier section. This clearly shows that influence of blend compatibility enhancement brought by in-situ silica dominates over the effect of CR–silica intereaction and as a result negative shift of $T_{g(CR)}$ takes place. Furthermore, comparison of ΔT_g values among the three groups of composites shows that ΔT_g values are comparable for unfilled composites (**1-4**) and externally filled composites **(9-12)** whereas it significantly decreases for in-situ filled composites (**5-8**) (supplementary Fig. S2). This results confirms the enhancement in compatibilty of this immiscible blend brought by silica when incorporated in-situ into rubber matrix and the effect is insignificant when silica is added externally. Best compatibility effect exhibited by in-situ filled composite **7** (NR/CR at 40/60 blend ratio), with minimunm ΔT_g, offers a rationale for the best mechanical, thermal and curing properties observed for this particular composite.

A comparative study has been done for unfilled, in-situ silica filled, externally silica filled and carbon black filled composites for NR/CR at 40/60 blend ratio and is presented in

Fig. 8. The lowering of tanδ peak is evident in both the phases for the in-situ filled composite (**7**). This clearly indicates that better rubber-filler interaction is acheived for in-situ filled composite compared to that in others.

Table 5 Glass transition temperature, T_g (ºC) of the composites

Fig. 9 Temperature versus tanδ curves of the unfilled composite (**3**)**,** in-situ silica filled composite (**7**)**,** precipitated silica filled composite (**11**) and carbon black filled composite (**13**) at 40/60 blend ratio

4 Conclusions

Reinforcing efficiency and compatibilizing effect of in-situ silica, generated by soaking sol-gel method, have been evaluated for the NR/CR blends. Amount of silica generation into rubber matrix is mostly governed by the blend composition owing to different solvent uptake capability of the constituent rubber phases. SEM images show more uniform dispersion of nano silica throughout the rubber matrix in in-situ silica filled composites that in externally filled composite. Significant improvement in modulus and tensile strength are observed for all the in-situ silica filled composites in comparison to unfilled and externally silica filled composites of same blend ratio and at same filler loading. This is attributed to the uniform filler dispersion and enhanced compatibility of the blends achieved by the generation of silica in-situ into rubber blends. Significant reinforcement and compatibilization effect of in-situ silica for the NR/CR blends are also strongly supported by the DMA studies. It is proposed that a concentration gradient of filler in the blend matrix may arise due to difference in solubility parameter of NR, CR and silica. This leads to migration of silica from less polar NR to more polar CR during physical mixing of curatives which is associated with the accumulation of silica at the interphase of the blends. This results in enhancement in compatibility for such immiscible blends and overall improvement in mechanical properties. Among the in-situ silica filled composites, best mechanical properties are achieved for NR/CR at 40/60 blend ratio. But, the level of improvement is maximum for the composite with NR/CR at 80/20 blend ratio, containing highest in-situ silica, with respect to the unfilled composite of same blend ratio. This clearly shows that not only the filler content and it's nature but blend composition and blend compatibility can also play significant role in governing the ultimate properties of a composite. Present study thus reveals the potential of in-situ silica as a reinforcing filler as well as a compatibilizer for as such immiscible rubber blend composed of polar and non polar constituents. This study is expected to open up further exploration on the role of in-situ silica that can be of great importance for other systems too if proper formulation and filler loading technique are adopted.

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Table 1 Formulation of rubber composites in phr (parts by weight per hundred parts of rubber by weight)

Samples	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
Natural rubber	80	60	40	20	80	60	40	20	80	60	40	20	40
Chloroprene rubber	20	40	60	80	20	40	60	80	20	40	60	80	60
In situ silica	-	-	-	-	30	28	20	15	-	-	-	-	-
Precipitated silica (VN3)	-	-	-	-	-	-	-	-	30	28	20	15	-
Carbon black (HAF)	-	-	-	-	-	-	-	-	-	-	-	-	20

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

Table 2 Curing characteristics of NR/CR blend compounds

Curing characteristics	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
Minimum torque (dNm)	9.29	9.73	10.29	11.3	30.63	23.09	17.02	13.31	37.14	29.77	24.38	22.01	14.81
Maximum torque (dNm)	61.8	61.8	44.44	41.93	90.6	79.6	123.8	72.1	80.9	70.6	89.1	93.0	79.9
Δtorque (dNm)	52.51	52.07	34.15	30.63	59.97	56.51	106.78	58.79	43.76	40.83	64.72	70.99	65.09
Cure time t_{90} (min)	5.27	8.22	11.07	13.15	19.45	18.02	12.6	11.07	26.52	21.65	15.65	10.92	14
Scorch time (min)	1.75	2.4	2.7	2.88	1.21	1.56	1.95	1.97	1.58	1.46	1.35	1.22	1.50
Cure rate index (min^{-1})[a]	28.40	17.18	11.94	9.73	5.48	6.07	9.38	10.98	4.009	4.95	6.99	10.30	8.00
Crosslinking density ($\nu \times 10^3$)	2.19	2.28	4.1	4.32	7.75	5.61	6.29	10.9	3.41	5.85	7.48	11.6	8.86

a: Cure rate index (CRI) = 100/(cure time – scorch time)

Table 3 Thermogravimetric data of NR/CR blend composites

	Unfilled blends				**In-situ silica filled composites**				**Externally silica filled composites**			
			T_{max} (^{0}C)				**T_{max} (^{0}C)**				**T_{max} (^{0}C)**	
NR/CR ratio	**Composite**	**Onset (^{0}C)**	**NR**	**CR**	**Composite**	**Onset (^{0}C)**	**NR**	**CR**	**Composite**	**Onset (^{0}C)**	**NR**	**CR**
80/20	**1**	337.8	352.9	430.0	**5**	343.0	354.6	438.1	**9**	343.0	354.0	433.3
60/40	**2**	322.6	340.1	437.0	**6**	335.5	345.5	440.6	**10**	334.5	344.3	436.2
40/60	**3**	310.0	316.0	438.0	**7**	329.4	335.9	441.0	**11**	324.2	334.4	438.0
20/80	**4**	300.0	310.0	434.0	**8**	317.0	324.9	435.0	**12**	317.0	324.9	434.3

T_{max}- temperature at maximum weight loss

Table 4 Mechanical properties of NR/CR blend composites

Composite	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
$\sigma_{100\%}$ (MPa)	0.55	0.57	0.69	0.75	1.51	1.14	1.53	1.38	1.20	1.29	1.34	1.76	1.33
$\sigma_{300\%}$ (MPa)	1.09	1.13	1.30	1.27	4.33	3.39	4.39	3.39	2.98	3. 39	3.49	4.34	5.56
Tensile strength (MPa)	6.80	7.74	18.55	22.65	16.35	14.65	22.19	20.09	7.52	7.63	10.99	11.33	11.6
Elongation at break (%)	684	655	826	953	667	667	798	690	552	513	559	506	421
Hardness (Shore A)	39.4	43	45.6	48.6	60.2	60	61.2	58.6	51.6	54.8	56.2	62.2	54.4

Table 5 Glass transition temperature, T_g (ºC) of the composites

	Unfilled blends				In-situ silica filled composites				Externally silica filled composites			
NR/CR ratio	**Composite**	$T_{g(NR)}$	$T_{g(CR)}$	ΔT_g	**Composite**	$T_{g(NR)}$	$T_{g(CR)}$	ΔT_g	**Composite**	$T_{g(NR)}$	$T_{g(CR)}$	ΔT_g
80/20	**1**	-60.4	-35.5	24.9	**5**	-59.3	-36.5	22.8	**9**	-58.8	-33.5	25.3
60/40	**2**	-61.8	-36.8	25	**6**	-59.5	-37.5	22	**10**	-59.9	-34.9	25
40/60	**3**	-58.9	-37.5	21.4	**7**	-56.9	-39.4	17.5	**11**	-55.5	-34.4	21.1
20/80	**4**	-63.3	-35.9	27.5	**8**	-60.2	-36.0	24.2	**12**	-58.9	-31.8	27.1

$T_{g(NR)}$: Glass transition temperature of NR phase; **$T_{g(CR)}$:** Glass transition temperature of CR phase; **ΔT_g :** Separation of T_g