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LATEX SERUM COATED SILICA FILLED NATURAL RUBBER COMPOSITES

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In this study, an attempt was made to reduce the incompatibility between silica and natural rubber by coating the silica particles with the non-rubber constituents present in natural rubber latex serum. The presence of various non rubber constituents like proteins, carbohydrates and lipids on silica surface were confirmed from TGA, UV and FTIR spectroscopy. RPA studies showed improved processability and cure characteristics for composite prepared from coated silica compared to the unmodified silica. The Payne effect studies of uncured compound showed that the filler-filler interaction ($\Delta G'$) decreased by 70 per cent than the control at 2 per cent serum coating on silica. The better processability of the modified rubber-silica compound is further evident from the lowering of the elastic torque and minimum rheometric torque (M_L) of the respective vulcanizates. The serum modification on silica reduced the viscous shear modulus (G'') and loss factor (tan δ) by 36 and 33 per cent respectively, compared to the control. The physical properties of the coated system were comparable with that of the control compound.

Keywords: Latex, Natural rubber, Payne effect, Processability, Silica

INTRODUCTION

The combination of silica as the major filler with synthetic polymers for making radial tyres is well established due to its technological advantages and the green tyre concept (Rauline, 1992). The incorporation of silica to natural rubber is really challenging due to the incompatibility and other processing problems. The poor adhesion between the polar silica surface functionality and the nonpolar polyisoprene molecules, leads to reduced filler–polymer interactions. The surface silanol groups of silica particles results in strong filler–filler hydrogen bonding interactions, which results in aggregation of silica and reduces the dispersion of silica within the rubber matrix. Modification of natural rubber polymer backbone through epoxidation (Varkey *et al.*, 1998; Manna *et al.*, 1999; Cataldo, 2002; Kaewsakul *et al.*, 2012; 2014) and silica surface modification (Meng-Jiao *et al.*, 1991; Meng-Jiao and Siegfried, 1992; Meng-Jiao, 1998; Chonkaew *et al.*, 2014) to improve the compatibility between the polar filler and the non polar polymer are the two approaches attempted as solutions for the above problems. Several studies of surface modifications of silica with both covalent modifications of silanol groups by silane coupling agents (Meng-Jiao and Siegfried, 1992; Udo *et al.*, 1997; Sarkawi *et al.*, 2014a) surface grafting with vinyl, acrylic

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monomers (Luna-Xavier *et al.*, 2002), and the non covalent polymer coatings have been studied (O'Haver *et al.*, 1996; Somaratne *et al.*, 2014). Among these, the use of silane coupling agents has been the most successful. But in natural rubber system, controlling the vulcanisate properties, due to the limited control over the in-situ silanization process and its variability with temperature have been really challenging. (Sarkawi *et al.*, 2014b).

In the present paper, we have attempted the coating of commercial silica (precipitated silica) with non rubber constituents in the rubber latex serum obtained from the conventional rubber making process. The transition of natural rubber industry from conventional dry mixing of polymer and filler towards polymer-filler masterbatches from rubber latex is gaining momentum due to the benefits of the latter process (Meng-Jiao *et al.*, 2002; Alex *et al.*, 2013). The latex masterbatch process when compared to the conventional dry mixing of polymer and fillers incorporates more non-rubber constituents into the rubber compounds, as the process initiates from the latex itself. Hence understanding the role of non-rubber constituents on processing properties of rubber compounds and technological properties of rubber vulcanizates is essential for further exploration in the field. The incorporation of serum modified silica into natural rubber through dry mixing introduces non-rubber constituents and its effect on various processing and technological properties of rubber-silica composites have been studied. The filler – filler interactions in the uncured green compounds and cured vulcanizates with both modified and unmodified silica have been studied.

MATERIALS AND METHODS

Indian standard natural rubber (ISNR) 5 and natural rubber field latex obtained from Rubber Research Institute of India was used in the present study. Precipitated silica (Ultrasil VN3) from Evoniks was used for the study. All other chemicals of commercial grade were used for preparing the rubber formulations. Potassium bromide (KBr) of Infra Red spectroscopy grade was used for the Fourier Transform Infra Red (FTIR) studies of silica samples.

Preparation of rubber serum coated silica

Fresh natural rubber latex with a DRC of 30 per cent (1.5 L) diluted with 1.5 L water was acidified using 400 mL of 0.5 per cent formic acid and kept for 4 h in aluminium dishes. The acidified rubber serum (pH 4.6), after removal of the rubber coagulum, was used for the surface modification of silica VN3. A 20 per cent w/w dispersion of precipitated silica in Millipore grade water was prepared in a high speed mixer and treated with varying volumes of acidified rubber serum and stirred for one hour using a magnetic stirrer. The silica to serum coating (w/v) ratios of 1:0.5, 1:1, 1:2, 1:3 were prepared and the whole dispersion was dried in a laboratory oven (Memmert, Switzerland) at 70 °C to constant weight. The dried mass was then pulverised to fine powder using a mixer grinder.

Characterisation of rubber serum coated silica

The total weight loss during the heating of the silica samples from 35 to 900 °C at a heating rate of 10 °C min^{-1}, with hold time each at 110 °C and 900 °C for 5 minutes was carried out using a Thermo Gravimetric Analyser (TGA 50 - Shimadzu, Japan). The temperature ramp was carried out in N_2 atmosphere from 35 to 550 °C and in O_2 atmosphere from 550 to 900 °C. The weight percentage of serum components coated on the silica was calculated from the weight loss studies. Characterisation of coated silica was further done using UV- Visible and FTIR spectroscopy. FTIR spectra in the transmittance mode were taken in the mid IR region of 400 to 4000 cm^{-1} using FTIR spectrophotometer (Varian 660 -Agilent, USA). Samples of silica (Ultrasil VN3), serum modified silica and the oven dried methanol extract of the rubber serum modified silica were analysed by preparing corresponding KBr disc using a pellet making hydraulic press. The methanol extract of the serum modified silica was obtained by conventional soxhlet extraction of the modified silica for 4 h followed by the concentration of the methanol extract in a rotary evaporator and drying of the residue in a vacuum oven. The U. V-Visible spectrum of the methanol extract of the serum modified silica was scanned using a, UV-Visible Spectrophotometer (Biotek, USA).

Preparation of rubber-silica compounds

The rubber-silica compounds were prepared using a laboratory two-roll mixing mill having friction ratio of 1:1.25 (Bridge Castleton, England) as per the formulation given in Table 1. Rubber compounds prepared with coated silica, obtained by varying the amount of silica to serum coating ratios (w/v) from 1:0.5, 1:1, 1:2 and 1:3 are designated as A-RS-0.5, A-RS-1, A-RS-2, and A-RS-3 respectively and with unmodified silica is designated as A-control with S/CBS/DPG cure systems.

Evaluation of processability, cure and physical properties

The cure characteristics of the compounds and the variation of the rheological properties with respect to the cure were measured using a Rubber Process Analyser (Table 2).

Table 1. **Rubber compound formulation**

	A-control	A-RS-0.5	A-RS - 1	A-RS - 2	A-RS - 3
Natural rubber	100	100	100	100	100
Silica VN3	50	-	-	-	-
RS- Silica 1:0.5	-	50	-	-	-
RS- Silica 1:1	-	-	50	-	-
RS- Silica 1:2	-	-	-	50	-
RS-Silica 1:3	-	-	-	-	50
Stearic acid	2	2	2	2	2
ZnO[1]	4	4	4	4	4
Mernox 6c[2]	1	1	1	1	1
Naphthenic oil	5	5	5	5	5
Sulphur	2.5	2.5	2.5	2.5	2.5
CBS[3]	0.7	0.7	0.7	0.7	0.7
DPG[4]	1.5	1.5	1.5	1.5	1.5

ZnO[1]- Zinc oxide, Mernox 6C[2]- N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine, CBS[3]- N-cyclohexyl-2-benzothiazole sulfenamide and DPG[4]-Diphenyl guanidine

Table 2. **Rubber compound test methods**

Property	Test method	Instrument
Cure characteristics (Maximum and Minimum torque, dNm; TC90 and ts2, min, S″, dNm; G′, G″, kPa and Tan ′) at 0.5 degree strain , 150 ^{0}C, 1.67 Hz.	ASTM D 2084-92	RPA 2000 Alpha Technologies
Tensile (elongation at break, %; tensile strength, MPa; Modulus, MPa)	ASTM D 412-87	UTM, Instron 3365
Tear strength, N mm^{-1}	ASTM D 624	UTM, Instron 3365
Hardness test, (Shore A)	ASTM D 2240	Hardness Tester
Payne effect uncured (ΔG′, kPa) at 70 ^{0}C, 0.1 Hz, Strain sweep from 0.1 to 500 %		RPA 2000 Alpha Technologies

The compounds were then compression moulded to its optimum cure time (T_{90}) using a hydraulic press (Fontijne Presses, Netherland). The physical properties of the corresponding vulcanizates were measured using ASTM methods as given in Table 2. The processability of the uncured rubber compounds ('Payne effect') was measured using the Rubber Process Analyser in the strain sweep mode at 70 °C, 0.1 Hz frequency, and strain per cent from 0.1 to 500.

RESULTS AND DISCUSSION

Characterisation of rubber latex serum coated silica

The characterisation of serum components coated silica was initially carried out using thermo gravimetric analysis (TGA). The major non-rubber constituents of rubber latex serum have been listed in Table 3 and it mainly constitutes of proteins, lipids, carbohydrates and small molecules with polar functional groups (Salomez *et al.*, 2014). The percentage weight loss of silica VN3 and that of serum coated silica were calculated (Table 4) from the TGA curves. For the unmodified silica this was around 11.48 per cent. For the serum coated silica the percentage weight loss increased from 11.87 to 14.86 per cent and the maximum weight loss was observed in the range of 250 to 350 °C. The total weight loss in the temperature range of 35 to 900 °C includes the contribution from moisture, dehydroxylation of silanol as well as the degradation of serum components. Hence for each silica sample, the percentage of moisture loss was obtained from 35 to 111 °C. It was found that the moisture content on unmodified silica was 6.9 per cent and for the serum coated silica it varied from

Table 3. **Composition of latex and dry rubber (Salomez *et al.*, 2014)**

Components*	Percentage by weight in latex (w/v)	Percentage by weight in dry rubber (w/w)
Water	60	0
Polyisoprene	34	94
Proteins	1.5	2.2
Carbohydrates (total)	1.5	0.4
Lipids (total)	1.36	2.3
Free fatty acids	0.02	0.55
Minerals	0.5	n.d
Organic acids	0.4	-
Amino acids	0.2	n.d

*n.d-not determined, Lipid (total) includes neutral lipids, glycolipids and phospholipids and carbohydrates (total) includes quaebrachitol, sucrose and glucose

Table 4. **Weight loss studies of serum modified silica and unmodified silica by TGA**

	Silica VN3	Si:serum 1:0.5	Si:serum 1:1	Si:serum 1:2	Si:serum 1:3
Percentage weight loss b/w 35-900 °C	11.48	11.87	12.77	13.81	14.86
Percentage weight loss b/w 35-111 °C (weight due to moisture and volatile components)	6. 0	6.86	7.38	7.95	8.27
Percentage weight loss b/w 111-900 °C	4.57	5.01	5.39	5.86	6.59
Percentage weight due to the loss of serum components	0	0.44	0.82	1.29	2.02

6.86 to 8.27 per cent, which increased with the serum coating. During the heating of silica from 111 to 900 °C, dehydroxylation of silanol groups has been reported (Zhuravlev, 2000). In the present study the weight loss for silica VN3 due to dehydroxylation was 4.57 per cent. For the serum coated silica, the weight loss from 111 to 900 °C has contributions from the silanol dehydroxylation and the degradation of serum components. Thus the difference between the percentage weight loss of silica VN3 and that of the serum component coated silica in the same temperature range gives the percentage of the rubber latex serum components. It was found that as the silica to serum (w/v) loading increased from 1:0.5 to 1:3, the weight of the serum components on silica increased linearly (Fig. 1) from 0.44 to 2 per cent w/w.

The further characterisation of the serum coated silica was done using UV-visible and FTIR spectroscopy. The UV-visible spectra of the methanol extract of serum coated silica and the control methanol is given in figure 2. Strong absorbance in the UV region from 400 to 200 nm with maximum absorbance around 270 and 210 nm was clearly observed in the UV spectrum of coated silica, whereas the control shows lesser absorbance in the same region. The absorbance at 205-210 nm could be attributed to the possible absorbance of the amide group of proteins (Scopes, 1974) and that at 270 nm could be attributed to the aromatic residues of the serum components.

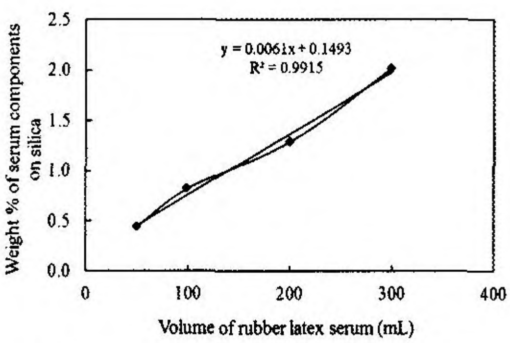


Fig. 1. Percentage weight of serum components on silica versus the rubber serum volume

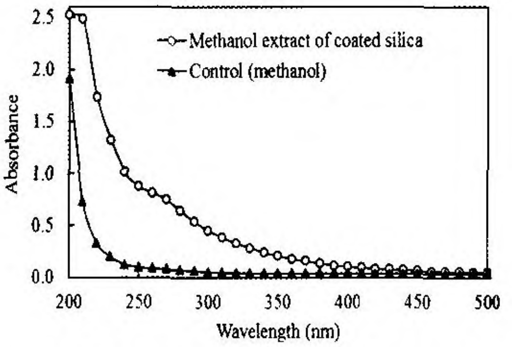


Fig. 2. UV-Visible spectra of methanol extract of the rubber serum modified silica and the control

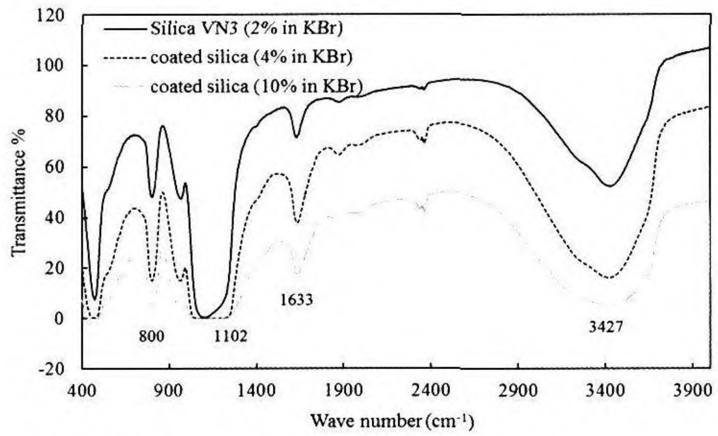


Fig. 3. FTIR spectra of silica VN3 and rubber serum components coated silica

FTIR was used to identify the functional groups of the various serum components coated on the modified silica (Fig. 3 and Fig. 4). For the unmodified silica (2 per cent silica in KBr powder (w/w)) the transmittance spectra shows (Fig. 3), a broad band between 3000 and 3600 cm^{-1},which is assigned to the O-H stretching vibration of *the silanol groups (Si-OH), while a strong* band centred at about 1100-1200 cm^{-1} corresponds to the Si-O-Si antisymmetric stretching vibration of the siloxane groups and peak at 800 cm^{-1} corresponding to Si-O-Si bending vibrations. For the serum coated silica, the transmittance spectra (both at 5 and 10 per cent coated silica in KBr powder

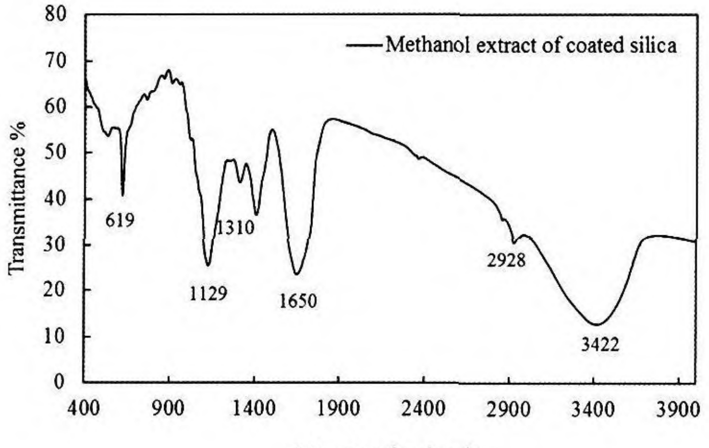


Fig. 4.FTIR spectra of dried methanol extract of the rubber serum components coated silica

(w/w), shows only the characteristic silica peaks with the expected peak broadening whereas the peaks of the serum components were not observed. This has to be attributed to the small loading of the individual serum components and the possible overlapping of the component peaks with that of the silica peaks, resulting in the detection of the individual serum components difficult using the coated silica. Hence alternately, the methanol extract of the coated silica was taken, dried and mixed with KBr powder. This clearly showed (Fig. 4) the presence of different NR latex serum components. The strong peak centred at 1650 cm^{-1} could be attributed most likely to C-O stretch of amide-I of proteins. The peak at 1129 cm^{-1} has overlapping contributions from C-C stretch of lipids, C-N stretch of proteins and C-O stretch of carboxyl. The presence of hydroxyl of carbohydrates at 3422 cm^{-1}, C-H stretch and C-C stretch of aliphatic hydrocarbons from proteins, fatty acid and lipids at 2928 and 1310 cm^{-1} respectively were also observed in the FTIR spectra.

Evaluation of the processing properties of uncured rubber-silica compounds

The surface modification of silica using rubber serum components should alter the filler–filler network interactions within the green or uncured rubber-silica compounds. The amide groups of the proteins, the hydroxyl group of carbohydrates and the polar head groups of the phospholipids could easily form hydrogen bonds with the silanol functionalities on the silica surface and an overall hydrophobation of the surface is expected. The variation in the silica filler- filler network interactions within the uncured compound was studied from the 'Payne effect' using the strain sweep mode of RPA. The plot of variation in G' with strain per cent of each compound is given in Figure 5 from which the ΔG' (G'_{max} - G'_{min}) of each curve was calculated (Table 5). The breakage of the filler-filler network due to the increase in the strain, results in the decrease in G'. The rubber compound with unmodified silica (A-control , Fig. 5) possess higher ΔG' (Table 5) indicating the higher flocculation of silica aggregates as previously reported (Ewe-Hong *et al.*, 1993). When compared to the control compound, all the rubber compounds with coated silica, showed lower ΔG' (A-RS-0.5 to A-RS-3 in Fig. 5). The plot of variation in the filler network (ΔG') against the per cent of serum coating on silica at 8, 23, 65 and 180 per cent strain is given in Figure 6. The magnitude of ΔG' (Fig. 6) decreased with increase in the serum coating on the silica. It was noted that the introduction of serum loading (0.5 to 1%) reduced the filler network (ΔG') by 48 per cent, and further reduced to 70 per cent at two per cent serum loading on silica. Also the breakage of filler network was nearly completed at 65 per cent strain. This clearly indicates that the non covalent interaction possibly the H-bonding, between the silanol

Table 5. **Rheological behaviour of the uncured rubber–silica compounds**

Processing property	Sample				
	A-control	A-RS-0.5	A-RS-1	A-RS-2	A-RS- 3
ΔG' uncured, kPa (70°C, 0.1 Hz, strain 0.1 to 180%)	1482	780	718	741	457
S' uncured, dNm (70°C, 0.1 Hz, 0.5 degree strain, 1 min.)	9.1	5.26	4.98	4.82	3.32

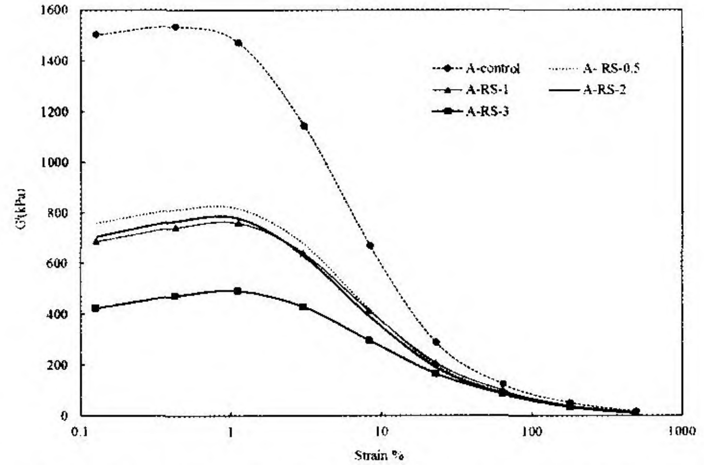


Fig. 5. Payne effect plot of uncured rubber-silica compounds with both unmodified and serum modified silica, (70°C, 0.1 Hz, strain 0.1 to 500%)

groups in the silica filler and the amide groups of the serum proteins, the hydroxyl group of carbohydrates and the polar head groups of the phospholipids is strong enough and hence the serum coating on the silica particles remains intact even after the high shearing during the compounding. This study highlights the benefit of multiple H-bonding interactions of the silanol groups of silica with the serum components in reducing the unwanted silanol-silanol interaction of silica fillers in

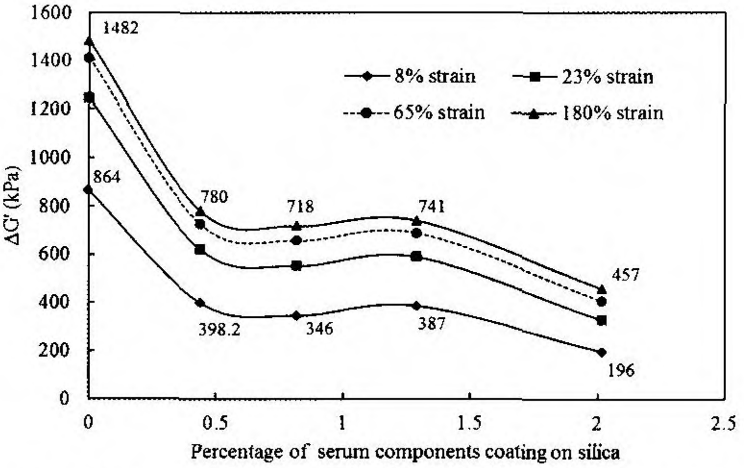


Fig. 6. Variation of Payne effect of uncured rubber-silica compounds with percentage serum components coating on silica at various strain percentage of 8 to 180 per cent. (70°C, 0.1 Hz)

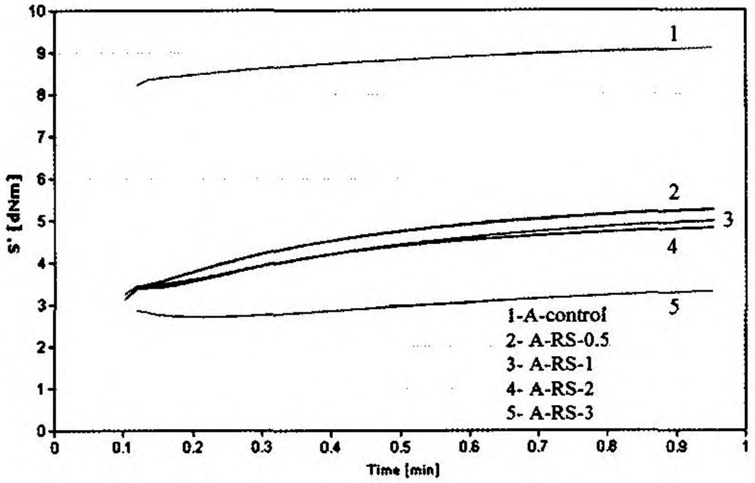


Fig. 7. Variation of elastic torque (S') with time of uncured rubber-silica compounds in serum modified and unmodified silica (70 °C, 0.1 Hz, 0.5 degree strain)

rubber compounds. In the control compound DPG is used both to minimise the surface activity of silanol (passivation) and as a secondary accelerator for sulphenamide cure. A higher filler-filler network is observed in the control compound in spite of the passivation of silica surface by DPG. This clearly indicates that the serum components coated on the silica surface could more effectively reduce

Table 6. **Cure properties of the rubber-silica compounds with S/CBS/DPG cure**

Property	Sample				
	A-control	A-RS-0.5	A-RS - 1	A-RS - 2	A-RS - 3
Cure time, TC90, min	11.08	8.19	8.50	8.05	8.05
ts2, min	2.43	3.05	3.34	2.95	2.73
S'rate @30%cure, dNm/min	5.53	6.47	6.23	7.42	7.61
Maximum torque, M_H, dNm	25.63	24.71	25.17	25.13	23.91
Minimum torque, M_L, dNm	5.9	4.4	4.52	4.04	3.45
M_H-M_L, dNm	19.73	20.3	20.65	21.09	20.47
S" at M_L, dNm	5.048	4.22	4.15	3.87	3.28
S" at M_H, dNm	9.624	8.13	7.347	6.79	6.01
tanδ at M_L	0.856	0.953	0.92	0.96	0.951
tanδ at M_H	0.375	0.329	0.292	0.270	0.251
G" at M_H Kpa	744.4	634.9	573.4	529.8	469.2

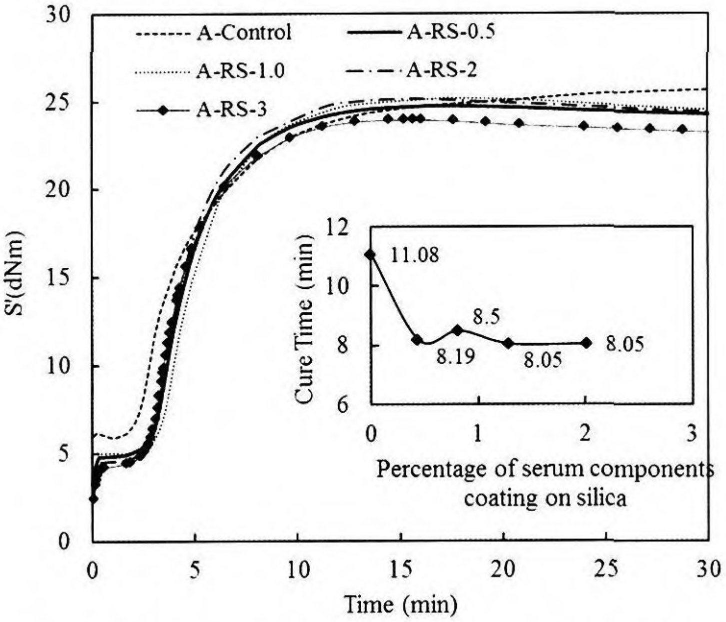


Fig. 8. Cure curves of natural rubber-silica compounds with both unmodified and serum modified silica from RPA, 150°C, 1.67 Hz. and 0.5 degree strain. Inset shows the variation in cure time (TC90) with percentage of serum coating on silica

the filler-filler networks within the uncured compounds than the DPG used in the control silica compound.

The processing properties of the uncured rubber-silica compounds were further evaluated using the RPA. The plot of variation in elastic torque (S') with time of the uncured compound at 70 °C and 0.1 Hz is given in Figure 7. The control compounds having commercial silica (curve 1 in Fig. 7) possess higher S' indicating the higher aggregation of silica and consequent stiffness. The serum coated silica compounds (A-RS-0.5 to A-RS-3) shows a lower S'. The magnitude of S' (Table 5) decrease with increase in the serum coating on the silica surface. This indicates lesser aggregation of the silica network, lower viscosity and better processability of the compounds.

Evaluation of cure properties of rubber-silica compounds

The S/CBS/DPG combination is a conventional silica specific cure system used for natural rubber-silica compounds. Though the DPG is identified as a toxic material, it is found to be effective in passivating the surface silanol activity of silica fillers, thus minimising the loss of accelerator by adsorption to the silica surface. Hence the same cure system was used in the present study. The cure curve obtained is shown in Figure 8. The variation of cure time (TC90) with per cent serum coating on the silica is shown in the

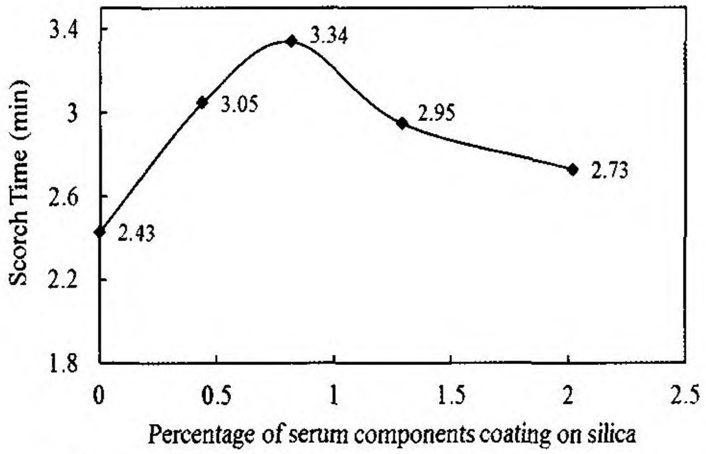
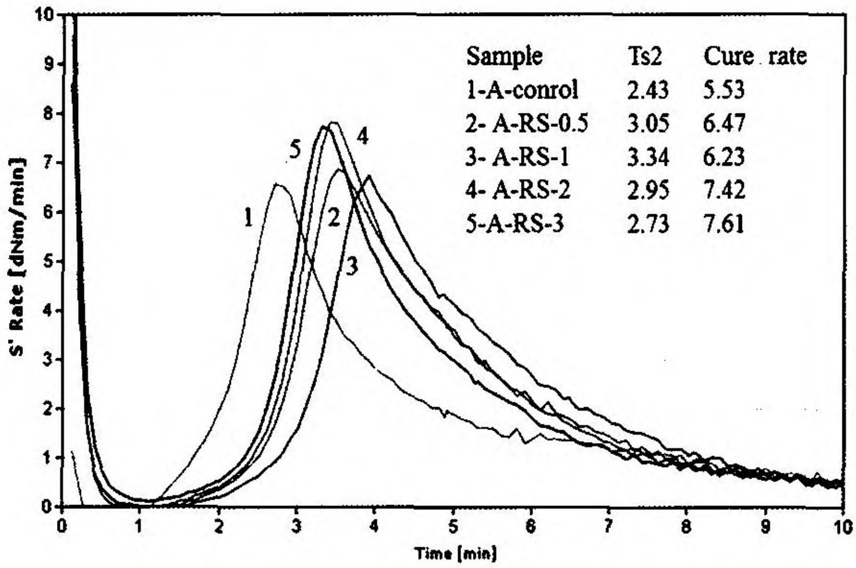


Fig.9. The variation in scorch time (ts2) with percentage of serum coating on silica

inset of Figure 8. Cure characteristics of the rubber compound with and without serum modified silica are tabulated in Table 6.

The cure time (TC90) changes significantly between the serum modified and unmodified silica compounds, but remains comparable between the serum



Sample	Ts2	Cure rate
1-A-conrol	2.43	5.53
2- A-RS-0.5	3.05	6.47
3- A-RS-1	3.34	6.23
4- A-RS-2	2.95	7.42
5-A-RS-3	2.73	7.61

Fig. 10.Cure rate curves of natural rubber-silica compounds with both unmodified and serum modified silica from RPA, 150°C, 1.67 Hz. and 0.5 degree strain

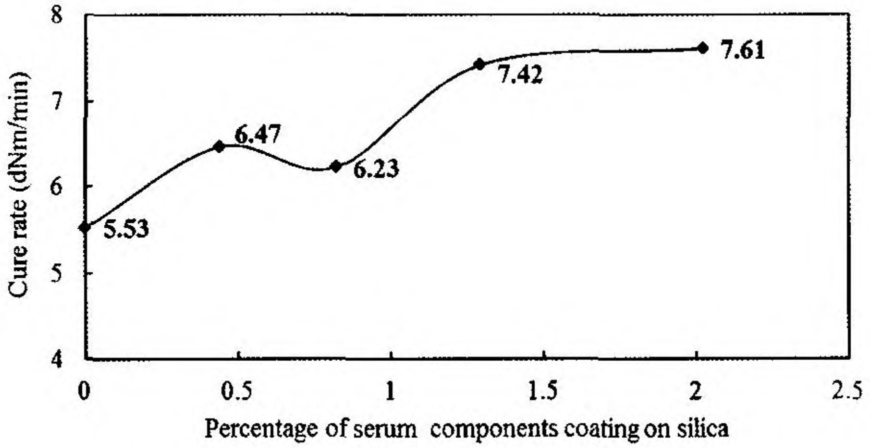


Fig.11. The variation in cure rate with percentage of serum coating on silica

modified compounds. A closer analysis shows that it decreases by 27 per cent (3 min.) from 11.14 (unmodified silica control) to 8.19 and 8.50 minutes with introduction of the serum coating (A-RS-0.5 and A-RS-1) and then stabilises at 8.05 minutes with further increases in the serum coating on the silica surface (A-RS-2 and A-RS-3). The decrease in cure time is probably due to the cure activation by proteins as previously reported (Gregg and Macey, 1973) and also due to the more effective coverage of silica surface by serum components than the DPG in the control compound, which minimizes the adsorption/ desorption of accelerators on the silica surfaces.

The variation in scorch time (ts2) with per cent of serum coating on silica is plotted in Figure 9. The scorch time increases for the serum modified silica compounds than the control. ts2 increases by 1 min from 2.43 (unmodified silica control) to 3.05 and 3.34 with the introduction of serum coating (A-RS-0.5 and A-RS-1), then decreases to 2.95 and 2.73 minutes with further increase in the serum components (A-RS-2 and A-RS-3). Generally it is accepted that the scorch time decreases in natural rubber composites with increase of the non-rubber constituents due to the basic character of the non rubber constituents (Alex and Nah, 2006). In contradiction here the scorch time increased for the rubber compounds with serum modified silica than the control. The general retardation in the initial phase of the

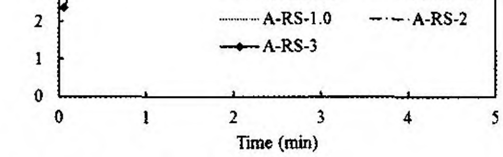


Fig. 12. The variation in M_L in the cure curve

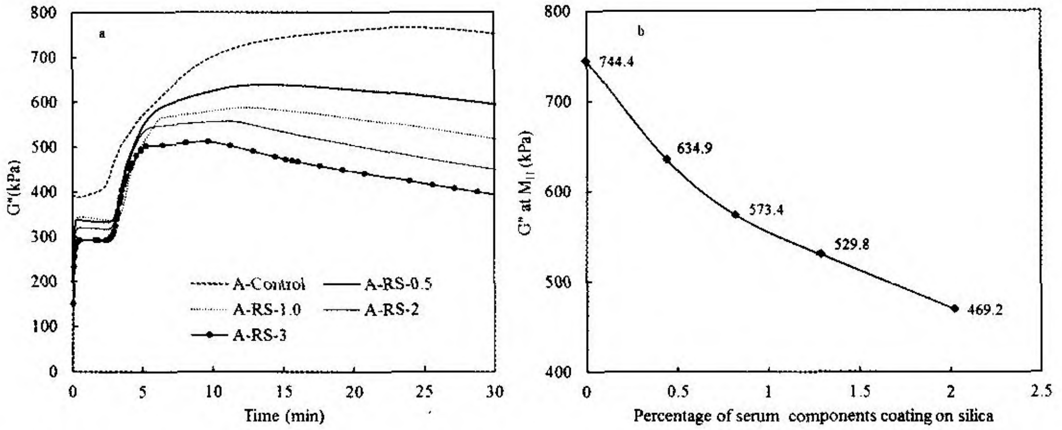


Fig.13 a. Plot of viscous shear modulus (G″) of natural rubber-silica compounds during vulcanisation at 150°C, 1.67 Hz. and 0.5 degree strain. b.The variation in G″ at M_H with percentage of serum coating on silica.

cure, specifically at the lower serum loading on silica, might be attributed to the presence of amide groups from the serum proteins. This could be correlated to the previous report of increase in scorch time (ts2) due to the amide based processing aids (Hergenrother and Lin, 2003). At higher serum loading the retardation offered by amide might be overtook by the basic functionality in the serum proteins leading to a further speeding up of cross-linking. The increase in scorch time will certainly help in better flow of the coated silica composites in the mold cavity, especially during the cure for thicker articles.

The cure rate curve is shown in Figure 10 and the variation of cure rate with the serum content on silica in Figure 11. The typical cure rate @ 30 per cent cure (S′, dNm/ min @ 30% cure) is generally found to be

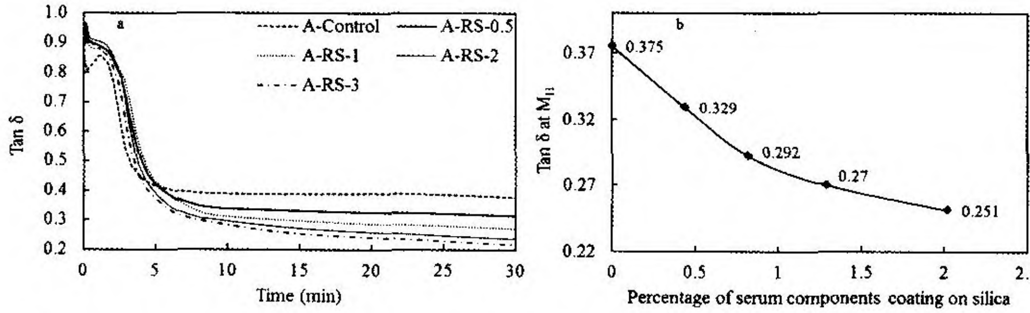


Fig.14a. The plot of loss factor (tan δ) of natural rubber-silica compounds with both unmodified and serum modified silica during vulcanisation at 150°C, 1.67 Hz. and 0.5 degree strain. b.The variation of loss factor at $M_H$with percentage of serum coating on silica.

Table 7. **Physical properties of the vulcanizates of rubber–silica composites**

Properties	Sample No.				
	A-control	A-RS -0.5	A-RS- 1	A-RS- 2	A-RS- 3
Tensile strength, mPa	21.5	20.78	21.5	21.5	22.4
Elongation at break, %	731	739	690	686	674
100 % modulus, mPa	1.83	1.77	1.83	1.88	1.89
300 % modulus, mPa	4.40	4.22	4.61	4.65	4.58
Ratio M300/M100	2.38	2.38	2.52	2.47	2.42
Tear strength, N/mm	86.5	89.4	84.85	79.0	81.1
Hardness, Shore A	76	76	75	75	74

increasing with respect to the serum modification from 5.53 (A- control) to 7.6 dNm/min at 2 per cent serum modification on silica (A-RS-3). The shift in the cure rate curve toward the right and its further re-tracking at higher coating on silica is also reflected in the scorch time.

The maximum torque attained in the cure system (M_H) remains almost comparable with a slight decrease at the highest coating (A-RS-3). From the cure curve (Fig. 12) it is again evident that the minimum elastic torque S′ (M_L) decreases with the increase in the coating on silica. The decrease in M_L (RS-0.5 to A-RS-3 in Fig. 12) with that of control (A-control), clearly indicates the lower viscosity of the rubber compounds with serum modification on silica, which has significant advantage with respect to the processability of the rubber compound.

The variation in the viscous shear modulus (G″), during the cure for the rubber-silica compounds containing unmodified and the coated silica is given in Figure 13a. The plot of G″at M_H against the percentage of serum coating on silica is shown in Figure 13b. The magnitude of G″ decreased with increase in the serum coating and 36 per cent reduction was obtained at 2 per cent serum loading on silica. Same trend in G″ was noted at M_L for the unmodified and serum modified silica filled compounds.

The variation in the loss factor (tan δ) of the rubber-silica compounds during the cure is given in Figure 14a. The plot of tan δ at M_H versus the percentage of serum coating on silica is given in Figure 14b. The magnitude of loss factor (tan δ) at M_H decreases from 0.329 (A-control) to 0.251 (A-RS-3) with increase in serum coating. This correspond to a 33 per cent reduction in loss factor at 2 per cent serum modification on silica, which too highlights the possible better dynamic property of the vulcanizate. This shows that the beneficial effects of serum components on the rheological properties obtained in the uncured rubber-silica compounds remains in the vulcanizates even after the cure at 150 °C. Hence the serum components coated on the silica surface has thermal stability in the same cure temperature range. The filler-filler interaction in uncured compounds and cured vulcanizates decreased significantly with increase in the serum coating on the silica as evident from the various studies mentioned above. The serum coating on the silica particles remains intact in spite of the high shearing during the compounding stage. This indicates that the non covalent interactions, possibly the *multiple H-bonding between the silanol* groups and the amide groups of the serum proteins, hydroxyl of carbohydrates and the polar head groups of the phospholipids are fairly strong. This reduces the unwanted filler–filler interaction of silica fillers in rubber compounds. This resulted in the lower elastic torque of uncured compounds, lower viscous shear moduli and loss factor of the cured vulcanizate for the composites with serum modified silica.

Evaluation of physical properties of the rubber-silica compounds

In the present study, the M_H-M_L of the natural rubber vulcanizates with serum modified silica and unmodified silica were almost comparable, which shows comparable cross-linking. The physical properties of the vulcanizates from different silica filled systems were evaluated and are given in Table 7. The physical properties were comparable for the serum modified and unmodified rubber–silica composites.

CONCLUSION

The silica particles could be effectively coated with 0.4 to 2 per cent of non-rubber constituents of the natural rubber latex serum. The UV and FTIR spectroscopy studies showed that major contribution of the coating on the silica surface is from serum proteins, carbohydrates and lipids. The Payne effect studies revealed that the silica filler-filler interaction ($\Delta G'$) within the uncured compound could be significantly reduced by 70 per cent at 2 per cent serum coating on silica compared to the control with unmodified silica. It is also noted that the *serum coating on the silica particles* could withstand high shearing during compounding. This is possibly due to the strong non-covalent H-bonding interaction between the silanol groups and the amide groups of the serum proteins, hydroxyl of carbohydrates and ionic moieties of lipids, which over ruled the silanol-silanol filler networking. The better processability of the rubber-silica compounds prepared with modified silica is evident from the lower elastic torque of the uncured compounds. This is also evident from the M_L values which decrease with increase of the serum components on the silica surface. Serum modification reduced the filler flocculation during the initial phase of the cure in compounds with modified silica, when compared to the unmodified one. The scorch time and cure rate increased while the cure time decreased with increase in the serum coating on the silica. In the cured vulcanizates, serum modified silica composites exhibited a decrease of viscous shear modulus (G″) by 36 per cent and loss factor by 33 per cent at two per cent of *serum coating on silica than the control* with unmodified silica. Both serum modified and unmodified vulcanizates exhibited comparable vulcanizate properties. Hence coating of silica surface with natural rubber serum components is an effective method to reduce the silica filler-filler networks and thus improving the processability of natural rubber-silica compounds, while maintaining the mechanical properties intact.

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