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Interaction of silica in dichlorocarbene modified styrene butadiene rubber

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ABSTRACT

Hydrated silica imparts better physical properties to polar rubbers, compared to those of hydrocarbon rubbers. The interaction of silica on dichlorocarbene modified styrene butadiene rubber (DCSBR) was evaluated with reference to their processing characteristics, technological properties and resistance to vulcanizate towards thermal, flame and oil resistance. The result indicates that with increasing filler content ratio of silica, the properties such as tensile strength, modulus, tear resistance, hardness, compression set, heat build up and flame resistance increases whereas elongation at break and resilience decreases. The changes in technological properties had been correlated with variation in cross-link density estimated from stress strain and swelling behavior. The results of the studies showed that silica could be used as excellent reinforcing filler for DCSBR. The mechanical properties such as tensile strength, modulus and hardness of the silica filled DCSBR were also evaluated after immersion in ASTM oil. Variation of bound rubber content of silica filled DCSBR and the influence of the extracting temperature on the bound rubber content was investigated and its activation energy was also calculated from the Arrhenius plot.

KEYWORDS

Dichlorocarbene modified styrene butadiene rubber;
Silica;
Mechanical properties;
Flame resistance;
Oil resistance;
Bound rubber.

INTRODUCTION

Silica occupies an important position in the rubber industry as an indispensable material, because it had reinforcement effect and an excellent functionality for rubbers[1-4]. It imparts high tear strength, low heat build up and better compound adhesion characteristics in polar rubbers[5]. Further it was obtained from regenerating source, unlike carbon black, which was manufactured from fossil feed through high-energy demanding operations[6]. Hence reinforcement of rubbers with silica may be favored over carbon black on economic grounds. There is continuing interest to provide improved properties to non-black filled rubber goods. More recently, silica was found to exert a higher reinforcement over elastomers and to improve the tire durability and now used in place of carbon black filler[7]. Another reason was that silica filled passenger tires shows a low hysterisis in comparison with carbon black filled tire [8-10].

The chemical environment of silica particle is quite different from that of carbon black due to the existence of silanol group in the particles. Silica had number of hydroxyl group on the surface, which results in strong filler interaction and absorption of polar materials by hydrogen bonding[10]. Since inter molecular hydrogen bonding between hydroxyl groups on the surface of silica were very strong and it could form tight aggregate[11,12]. The way to avoid aggregation was to improve the compatibility between silica and rubber in order to reduce the silica migration. Hence hydrated silica imparts better physical properties to polar synthetic rubbers than it does not to nonpolar rubbers like natural rubber, styrene butadiene rubber and the like, and have used to produce colored articles that require high strength properties. We recently reported that in small amount of DCSBR could be used as a compatibiliser for SBR/NBR and SBR/CR blends and also studied the reinforcing nature of filler like carbon black and silica on these blend system[13-16]. The interaction between hydrocarbon rubber and silica can be improved by the introduction of polar group in the rubber or by some additives. Our previous work[17,18] showed that chemically modified SBR (DCSBR) have excellent resistance to oil, superior to CR and approaching to that of NBR. In addition to this dichlorocarbene modification also imparts better flame resistance and tensile strength than that of polar rubbers like CR and NBR. The processability and final properties of most elastomeric products could be best evaluated by appropriate test on gum elastomer over different filler concentration. Both the gum and filled compounds could provide significant insight into the microstructral understanding of the filler rubber interaction of a highly filled system. The present study, therefore aims to further improve the properties of modified rubber with different filler content of silica with reference to their cure characteristics, mechanical properties, flame and oil resistance of the composite. The reinforcing nature of the filler was also calculated using stress strain and swelling measurements. The variation of bound rubber content of silica filled DCSBR and the effect of temperature with the filler content ratio was evaluated. The influence of extacting temperature on the bound rubber content was investigated and the activation energy for loosely bound rubber was also calculated using Arrhenius plot.

EXPERIMENTAL

Dichlorocarbene modified styrene butadiene rubber with 15% chlorine content was synthesized by alkaline hydrolysis of chloroform with styrene butadiene rubber (SBR) in presence of phase-transfer catalyst[17]. Rubber additives were reagent grade obtained from local chemical suppliers. The filled DCSBR compounds were prepared by adding various amounts (10, 20, 30 and 40 phr) of precipitated silica in a two roll mixing mill and the basic formulation used in the study was given in TABLE 1.

TABLE 1: Basic formulation of silica filled DCSBR

Ingredients	Mix no. 1	2	3	4	5
DCSBR	100	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5.0	5.0	5.0	5.0	5.0
CBS	1.2	1.2	1.2	1.2	1.2
TMTD	0.8	0.8	0.8	0.8	0.8
TDQ	1.0	1.0	1.0	1.0	1.0
Aromatic oil	-	0.7	1.4	2.1	2.8
Silica	-	10	20	30	40
Sulphur	2.2	2.2	2.2	2.2	2.2

CBS is N-Cyclohexyl 1,2- benzothiazole sulphenamide; TMTD is Tetramethyl thiuram disulfide; TDQ is 2,2,4-trimethyl 1,2-dihydroquinoline

TABLE 2 : Details of the analysis of vulcanised samples

Physical properties	Equipments	Method
Tensile and tear strength	Zwick Universal Testing Machine (UTM)	ASTM D 412-80 and ASTM D 624-81
Compression set	Compressed to constant deflection	ASTM D 395 - 1982
Rebound resilience	Dunlop Tripsometer	ASTM D 1504
Abrasion resistance	DIN abrader	DIN No.5351
Hardness	Shore A type durometer	ASTM D-2240-81
Heat build-up	Goodrich flexometer	ASTM D 623
LOI	Stanton Redcroft FTA flammability	ASTM D 2843
Thermal ageing (70^{o}C for 5 days)	Conventional oven	ASTM D 573-88

Cure characteristics were studied using a Monsanto Rheometer R-100 at 150^{0}C according to ASTM D 2705. The samples were vulcanized to their respective cure time in a hydraulic press at 150^{0}C and a pressure of 4.4 Pa on the mould. The different physical properties of the vulcanised samples were analysed as per the relevant ASTM standard and details were given in TABLE 2.

The cross-link density of a rubber vulcanisate could be estimated from swelling measurement[19-20], or by a mechanical method involving stress strain measurement[21]. The cross-link density was determined from swelling data, the samples were allowed to swell in toluene and the equilibrium uptake was noted. From molecular weight between crosslinks Mc, the crosslink density ν was calculated using the following equation[22].

$$\nu = 1/2M_c \qquad (1)$$

On the basis of phenomenological theory of rubber elasticity and derived from the Mooney Rivlin equation[23], stress-strain measurement could be used for measuring the crosslink density of rubber. This can be obtained using Equations (2) and (3) below. From the plot of $\sigma_0/(\lambda - \lambda^{-2})$ and $1/\lambda$, the constants C_1 and C_2 can be determined, the intercept of the curve on the $\sigma_0/(\lambda - \lambda^{-2})$ axis corresponds to the C_1 value and its slope corresponds to the value of C_2.

$$F = 2A_0(\lambda - \lambda^{-2})(C_1 + C_2\lambda^{-1}) \qquad (2)$$

$$\sigma_0/(\lambda - \lambda^{-2}) = 2C_1 + 2C_2/\lambda \qquad (3)$$

Where F is the tensile extension force required for stretching a specimen, A_0 is the cross-sectional area of the unstretched specimen, σ_0 is identifiable with F/A_0 and C_1 and C_2 characteristic constant of the vulcanizate. C_1 is directly related to the physically effective crosslink density (ν_{phys}) by the equation,

$$C_1 = \rho RT\nu_{phys} \qquad (4)$$

Oil resistance of the composite was measured by immersing the specimens to in ASTM # 1, 2 and 3 oil at 25°C and at 100°C for 72 hrs. Thereafter, the test specimen was removed from the oil, quickly dipped in acetone, and blotted lightly with filter paper to remove excess oil from the surfaces. Finally, tensile and hardness of the samples (in ASTM # 3 oil at 25°C) were measured.

Bound rubber contents was determined by extracting the unbound material with toluene for seven days and in n-heptane for one day and drying for two days at room temperature. The experiments were conducted at 30, 50, 70 and 90°C using conventional oven. Weights of the sample before and after extraction was measured and bound rubber was calculated by following equation.

$$R_b\,(\%) = 100\times\{W_{fg} - W_t[m_f/(m_f+m_r)]\}/W_t[m_r/(m_f+m_r)] \qquad (5)$$

Where R_b is bound rubber content, Wf_g is the weight of filler and gel, W_t the weight of sample, m_f is the fraction of filler in the sample, m_r is the fraction of the rubber in the compound.

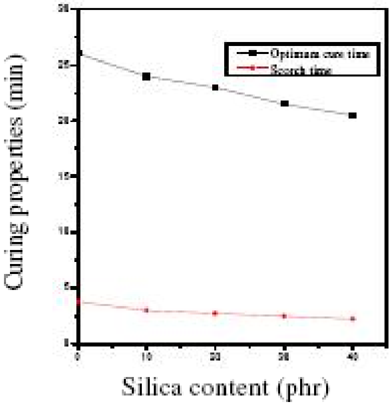

Figure 1: Optimum cure time and scorch time of different content of silica filled DCSBR

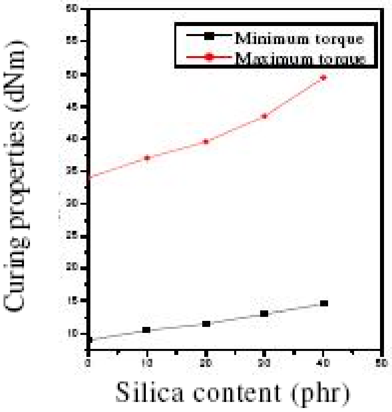

Figure 2: Maximum torque and minimum torque of different content of silica filled DCSBR

RESULTS AND DISCUSSION

Cure characteristics

The effect of silica on the cure characteristics of DCSBR with different content such as 10, 20, 30 and 40 phr of fillers are shown in figures 1 and 2. It is obvious from figure 1 that the scorch time and optimum cure time decreases with increase in concentration of filler in DCSBR. This clearly indicates that filler increases the rate of curing of DCSBR[14]. The reduction in optimum cure time may possibly due to the increased thermal conductivity of the composite system, resulting from the formation of conductive chain composed of filler particle[24]. The variation of torque given in figure 2 shows that, the maximum torque increases gradually as loading of filler in DCSBR increases. The increase in rheometric torque is attributed to the better polymer filler interaction that becomes more pronounced in 40 phr filler loading. It is already reported that maximum

TABLE 3 : Mechanical properties of DCSBR with different content of silica

Properties	Filler content (phr)				
	0	10	20	30	40
Tensile strength (MPa)	11.5	15.9	20.1	22.9	24.0
Modulus, 300 % (MPa)	3.3	4.5	5.9	8.1	10.3
Elongation at break(%)	510	459	430	400	365
Tear strength (kN/m)	41.8	47.8	52.3	56.3	59.0
Hardness (Shore A)	41.0	46.0	49.0	53.0	58.0
Resilience (%)	35.0	32.0	30.0	27.0	23.0
Heat build up (^{o}C)	15.0	19.0	22.0	25.0	27.0
Compression set (%)	14.0	17.0	19.0	24.0	26.0

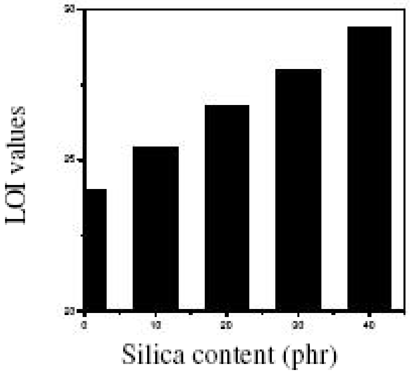

Figure 3: Variation of limiting oxygen index value (LOI) of different concentration of silica filled DCSBR

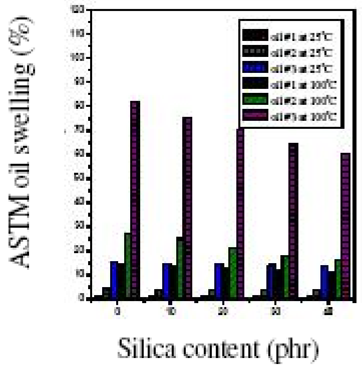

Figure 4: Change in ASTM oil resistance values of different content of silica filled DCSBR at 25^{0}C and at 100^{0}C

torque dependent on the cross-link density and chain entanglements, and for this system higher interaction is due to the silanol group of silica with chlorine group of DCSBR.

Effect of filler content ratio on mechanical properties

Effect of silica content on the physical properties of DCSBR is presented in TABLE 3. Modulus at 300 % is increased with increasing the loading of silica. The increased crosslink density resulting from polymer filler interaction might have contributed to the modulus enhancement. Improved tensile strength and reduced elongation at break (EB) are considered as the criteria for higher filler reinforcement[25]. From TABLE 2 it is also evident that as the content of filler increases the tensile strength increases where as the elongation at break decreases. These two properties are also related to the nature and number of crosslinks. It can also seen that the magnitude of increase in the tensile strength is higher up to 20phr, when the loading becomes 30 - 40 phr the magnitude is lower compared to 10 to 20phr. This means that the more uniform distribution of filler in DCSBR is up to 20 phr loading, in other words this loading provides a large interfacial area of contact, resulting in better interfacial adhesion. The variations in tear resistance abrasion loss for DCSBR with different filler loading are shown in TABLE 3. Improvement in tear and abrasion resistance is the measure of enhanced filler reinforcement[26]. Both tear and abrasion resistance increases with increase in loading of filler. Filler particles present at the crack propagation tip arrest the propagating cracks and thus increase the tear strength. The variation in resilience and hardness of silica filled DCSBR are given in TABLE 3. Resilience showed a continuous decrease, where as hardness increase. It can be seen from the TABLE 3 that the compression set increases with increase in loading of filler. Compression set data measures the ability of sample to recover from compression and provides information regarding the degree of cross linking that takes place during compression, a lower result indicates less cross linking (hardening) during compression.

Heat build up of an elastomer result from the internal friction in the sample. It can be seen from the TABLE 3 that heat build up increases with increasing loading of filler. This is due to the less effective interface, which leads to the increased friction between the filler and polymer.

The limiting oxygen index values of various loading of silica filled DCSBR are presented in figure 3. When the halogen containing elastomers are ignited, they could exhibit an intumescences effect, due to which the char formed thermally insulate the polymer from the flame and thus inhibits combustion. From the figure it is clear that flame resistance increases with increase in concen-

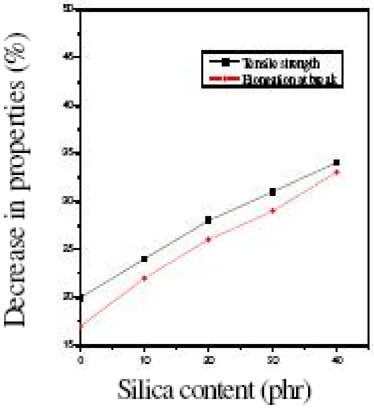

Figure 5: Decrease in percentage of tensile strength and elongation at break of silica filled DCSBR after aging at 72 hrs

TABLE 4: Crosslink density parameter C_1, C_2, ν_{phys} from stress strain measurement and from swelling data

Filler content (phr)	Mooney Rivlin equation $\times 10^{-3}$ (g molml^{-1})	$2C_2$ (Nmm-^{2})	$2C_1$ (Nmm-^{2})	Flory Rhener Equation $\times 10^{-5}$ (g molml^{-1})
0	1.41	3.25	0.736	2.50
10	1.50	3.38	0.750	3.05
20	1.56	3.47	0.761	3.20
40	1.61	3.53	0.770	3.31
30	1.65	3.57	0.778	3.40

tration of silica in DCSBR. Substances with LOI value above 20.8 are classified as relatively safe while substances with LOI less than 20.8, which continue to burn in oxygen deficient air, are not safe as building material[27]. DCSBR filled composite show better flame resistance, which is due to presence of two chlorine atoms in one unit of SBR, which leads to higher flame resistance. Hence the DCSBR composite considered being safe for indoor applications.

ATSM oil resistance properties at 25°C and at 100°C of silica filled DCSBR is given in figure 4. It is evident from the figure that oil resistance of DCSBR filled silica is increased with increasing concentration of filler. The ageing resistance of the vulcanizate, is assessed by determining the tensile properties and elongation at break before and after aging. The resistance of the rubber samples to thermal ageing was considered as an essential requirement for the long service life of products. The percentages of decrease in tensile strength as a result of aging are presented in figure 5. It can be see that after aging the change in tensile and elongation at break properties are decreases with increasing loading of filler.

Calculation of crosslink density from swelling and stress-strain behavior

The crosslink density values obtained from swelling data for silica filled DCSBR are given in TABLE 4. Generally, the presence of an active (reinforcing) filler reduces the extent of equilibrium swelling[28]. The crosslink density is found to be increasing with increase in concentration of silica filler. Higher crosslink density is observed for silica with 40 phr loading, this is because of the restriction of swelling which causes an increase in volume fraction, which in turn increases the crosslink density. It should be noted that studies on equilibrium swelling of filled rubber vulcanizate are usually conducted, assuming that the presence of filler does not alter the polymer solvent interaction considerably[29]. The crosslink density values(ν_{phys}) calculated using the Equation 4 is given in TABLE 4. It can be seen that the force and crosslink density is found to be maximum in 40 phr silica containing DCSBR and is in good agreement with the increase in rheometric toque. As the concentration of silica increases, the $2C_2$ value is found to be increasing (TABLE 4). In a paper[21], Mooney-Rivlin constant C_2 is observed to be associated with intermolecular forces and flexibility between polymer chains. This value increases with increase in proportion of rigid (such as the polymer filler interaction[30]) and increasing degree of crosslinking[31]. The higher 2C2 value noted for the 40 phr silica containing DCSBR, shows the presence of higher chain entanglement[32], a higher chain entanglement shows better molecular level mixing. The crosslink density increases with loading of DCSBR. Thus the observed tensile strength variation can be exactly correlated with the variation of νphys from Mooney-Rivlin equation and the crosslink density data from swelling studies. Moreover, the values of νphys are higher compared to that of crosslink density from swelling studies. In swelling studies of these samples, crosslinks are flexible to penetrants, but as the loading of filler increases they restricts the swelling. The discrepancy between crosslink density determined by chemical analysis and by the application of stress-strain equation is partly due to the entanglements of interpenetrating network chains, which behave as crosslinks and partly by the presence of elastically ineffective chain

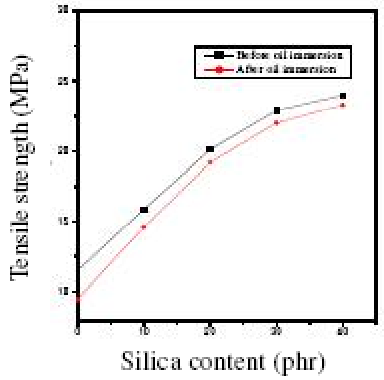

Figure 6: Change in tensile strength of silica filled DCSBR before and after oil immersion

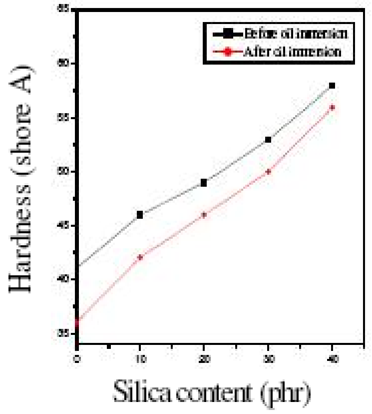

Figure 7: Change in hardness of silica filled DCSBR before and after oil immersion

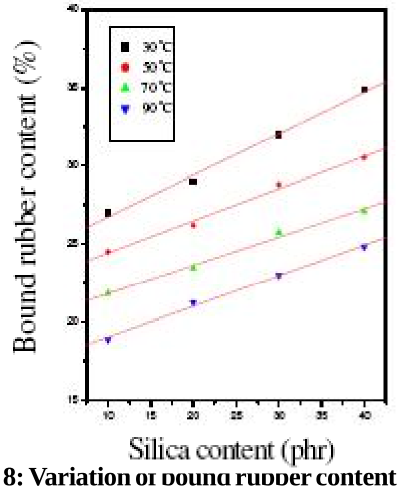

Figure 8: Variation of bound rubber content of silica filled DCSBR compound

ends.

The result of oil resistance based on the changes in tensile strength and hardness after oil immersion at room temperature for about 72 hrs is presented in figures 6 and 7. It is obvious from the figure 6 that the tensile properties of the compounds are decreases after oil immersion and the magnitude of decrease in tensile strength is decreased with increase in concentration of filler. The change in hardness of the filled DCSBR after oil immersion is shown in figure 7. The magnitude of decrease in hardness increases with increasing filler content in the matrix. DCSBR posses excellent resistance to hydrocarbon liquids due to the presence of two chlorine atoms in one unit of SBR, and the oil resistance is expected to increase with increase in polarity[18].

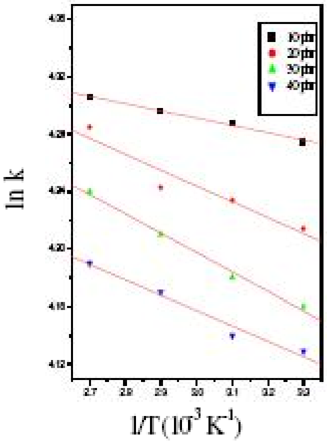

Figure 9: Arrhenius plots for the extraction of the unbound and loosely bound rubber of silica filled DCSBR compound

Estimation of bound rubber

Variation of bound rubber content of the silica filled DCSBR compounds with filler content ratio is given in figure 8. The bound rubber content of filled DCSBR increases linearly with increase in filler content ratio. This may be possibly due to the chemical bonds between the silanol group of silica and rubber by the polar interaction of both filler and DCSBR. The chemical bonds between DCSBR and silica enhance the bound rubber formation. The bound rubber content decreases as the extracting temperature becomes higher. This implies that the loosely bound rubbers start to extract as the temperature increases[33]. Bound rubbers consist of loosely and tightly bound ones. The loosely bound rubber exists in an outer shell around the filler while the tightly bound rubber is in the immediate vicinity of the filler particle. The loosely bound rubber can be extracted using the solvent at high a temperature because the binding energy of may be very low. The extraction rate can

TABLE 5 : Activation energy for extraction of loosely bound rubber in silica filled DCSBR

Slica content (phr)	Activation energy (KJ/mol)
10	1.40
20	1.48
30	1.59
40	1.67

be plotted using Arrhenius equation (6).

$$\ln k = \ln A - E\alpha/RT \qquad (6)$$

where k is the extraction rate, A is the Arrhenius parameter, $E\alpha$ is the activation energy, R is universal gas constant and T is the temperature. The Arrhenius plots for the silica filled DCSBR is presented in figure 9. The slope obtained from the plots indicates the sensitivity of the extraction rate to temperature, slope increases with increase in concentration of filler in the polymer matrix. The activation energy calculated from the Arrhenius plots is given in TABLE 5. The activation energy increases with increase in the concentration of filler. The extracting rubbers include the loosely bound one as well as the unbounded one. Energy to dissolve the unbound rubber from the filler gel is much lower than for the loosely bound rubber. Hence higher energy is required to extract the loosely bound rubber as the amount of loosely bound rubber increases, which can be attributed due to the occluded rubber. The filler aggregate in the filed rubber compound have tendency to associate to agglomerates, especially at higher loading of filler, leading to chain like filler structure or filler network or cluster. These are generally called secondary structure or filler network[34]. The filler network enhances the content of the occluded rubber, this occlude rubber includes large loosely bound rubber.

CONCLUSIONS

Studies on DCSBR with different loading of silica filler showed that there is a reduction in optimum cure time and increase in rheometric torque with increase in concentration of fillers. This clearly indicates that filler increases the rate of curing of DCSBR. Mechanical properties such as tensile strength, tear strength, compression set increases with increase in loading of fillers and this magnitude of effect is noted up to 30 phr loading. The improvement in mechanical properties is supported by data on the increased content of crosslinks in these samples obtained from swelling and stress strain data measurements. The mechanical property such as tensile strength, modulus and hardness decreases after oil immersion where as these properties are increased progressively with increasing concentration of filler. The bound rubber content is increased by increasing the temperature and also increases with increase in concentration of silica in DCSBR. Activation energy of the filled compounds also increases with increase in the silica content ratio.

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