
Effect of Silane Coupling Agent on Cure Characteristics and Mechanical Properties of Nitrile Rubber/Reclaimed Rubber Blend

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ABSTRACT

Blends of nitrile rubber and reclaimed rubber containing different levels of a coupling agent, Si 69 (bis(3-triethoxysilylpropyl)tetrasulphide) were prepared and the cure characteristics and mechanical properties were studied. Optimum loading of Si-69 was found to be a function of blend ratio. 3 phr of Si 69 in a 70:30. Blend was found to be the optimum combination with respect to the mechanical properties. The rate and state of cure were also affected by the coupling agent. Tensile strength, tear strength and abrasion resistance were improved in the presence of coupling agent. While the state of cure improved, the cure rate and scorch time decreased with increasing silane content. Ageing studies showed that the blends containing the coupling agent were inferior to the unmodified blends.

INTRODUCTION

Large-scale growth of transport sector has caused severe damage to environment in terms of solid and gaseous pollution. Worn out and discarded tyres constitute a major source of solid pollution. One way of recycling these is to convert them into reclaimed rubber - Whole Tyre Reclaim (WTR), which can be blended with virgin rubbers as a source of rubber hydrocarbon and filler. Several workers have explored these possibilities⁽¹⁻¹⁵⁾. Kim and Buford studied the utilization of waste tyres in polar and non-polar rubbers⁽¹⁶⁾. WTR when used with a polar matrix such as nitrile rubber the compatibility also has to be taken into account. One way to improve the compatibility of the components of the blend is to reduce the interfacial tension by using a coupling agent such as silane coupling agent (Si 69).

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Silanes are a group of organo functional compounds that have the ability to bond inorganic materials such as glass, mineral fillers, metals and metallic oxides to organic matrix. The silanes react chemically and promote adhesion between non polar the base polymer and polar fillers in the vulcanised rubber compounds. The Si (OR)₃ portion reacts with the polar components, while the organo functional (vinyl-, amino-, epoxy-, etc.) group reacts with the non polar matrix. It is expected that Si69 can also improve interaction between polar and non polar matrix. Ghosh *et al.* reported uses of silane coupling agent in blends of polyethylene and ethylene propylene rubbers⁽¹⁷⁾. Use of silane coupling agent in natural rubber was reported by Ismail H. *et al.*⁽¹⁸⁾. Use of silane coupling agent in styrene butadiene rubber was reported by Bokobza L. *et al.*⁽¹⁹⁾.

Nelson and Kutty have reported the use of Maleic anhydride to improve the properties of acrylonitrile butadiene rubber/reclaimed rubber blends⁽²⁰⁾. In this paper, we report the results of our study on the effect of Si-69 on the blends of NBR and WTR. The loading of Si69 varied from 0 to 4 phr in blends containing different loadings of WTR. The cure characteristics and mechanical properties of the blend were then investigated.

EXPERIMENTAL

Materials Used

Nitrile rubber (NBR) N553 grade used in this study with Mooney viscosity [ML (1+4) at 100 °C] 45 and an acrylonitrile content of 33%, was supplied by Apar Polymers Ltd. India. Reclaimed rubber (WTR) was obtained from Kerala Rubber and Reclaims, Mamala, Kerala, India. The characteristics of WTR used are given in the Table 1. Zinc oxide was obtained from Meta Zinc Ltd., Bombay, India. Sulphur was supplied by Standard Chemicals Pvt. Ltd., Chennai, tetramethylthiuramdisulphide (TMTD) was procured from NOCIL,

Table 1 Characteristics of WTR

Property	Value
Acetone extract (%)	15
Carbon black (%)	30
Gel content (%)	68
Mooney viscosity	24
Particle size	30 mesh

Mumbai, stearic acid was procured from Godrej Soaps Pvt. Ltd., Mumbai. Antioxidant 4020 [N(1,3 dimethylbutyl) N' phenyl p-phenylenediamine] and Mercaptobenzothiazole disulphide (MBTS) were obtained from Bayer India Ltd. Silane coupling agent, Si 69 i.e. (bis(3-triethoxysilylpropyl)tetrasulphide) was obtained from Degussa Corporation, Germany.

Preparation of blends

Formulations of the mixes are given in Table 2.

The blends were prepared on a laboratory size two-roll mill (150 x 330 mm) as per ASTM D 3184(1989). After completion of mixing, the compound was homogenized by passing six times endwise through a tight nip and finally sheeted out in a nip gap of 6 mm.

Cure characteristics were determined by using a Goettfert Elastograph model 67.85 at 150 °C. Vulcanization was carried out at 150 °C under a pressure of 180 kg/cm² in an electrically heated hydraulic press. For thicker samples, sufficient extra cure time was given to get the same extent of cure. The different mechanical properties of the vulcanizate were tested according to ASTM standards. Tensile and tear properties were measured using a tensile tester from Lloyd Instruments, LRX PLUS, according to ASTM D 412 (1987) and ASTM D 624 (1981) (die C), respectively. The abrasion resistance of the blend was measured using a DIN abrader as per DIN 53516 and values were expressed as volume loss per hour. Compression set at constant strain was measured according to ASTM D 395-86 method B. Resilience was measured according to ASTM D2832-88 using a vertical rebound resilience tester from Modex Industries. For ageing resistance studies, samples were aged in an air oven for 48 hours at 70 °C (ASTM D 573-88), and the tensile and tear properties were measured.

Determination of concentration of cross link density

The chemical cross-link density of the vulcanizate was evaluated as follows. Samples of unmodified WTR/NBR blends and modified WTR/NBR blends were used for the determination of cross link density. Samples of approximately 10 mm diameter and 2 mm thickness and 0.2 gm weight were punched out from the central portion of the vulcanizate and allowed to swell in methyl ethyl ketone. (MEK) for 48 hrs. The swollen samples were taken out and weighed again. The solvent was removed in vacuum and the samples were weighed again. Volume fraction of the rubber V_r in the swollen network was then calculated by following equation:⁽²¹⁻²²⁾

Table 2 Formulation of the mixes

Sample	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	B ₂	B ₃	B ₄	B ₅	B ₆	C ₂	C ₃
NBR	100	90	80	70	60	50	90	80	70	60	50	90	80
Reclaimed rubber	-	20	40	60	80	100	20	40	60	80	100	20	40
Si 69	-	-	-	-	-	-	1	1	1	1	1	2	2
Sample	C ₄	C ₅	C ₆	D ₂	D ₃	D ₄	D ₅	D ₆	E ₂	E ₃	E ₄	E ₅	E ₆
NBR	70	60	50	90	80	70	60	50	90	80	70	60	50
Reclaimed rubber	60	80	100	20	40	60	80	100	20	40	60	80	100
Si 69	2	2	2	3	3	3	3	3	4	4	4	4	4

Note: A₁ gum compound
A₂-A₆ NBR/WTR reclaim blend
B₂-B₆ = NBR/WTR in presence of 1 phr Si 69
C₂-C₆ = NBR/WTR in presence of 2 phr Si 69
D₂-D₆ = NBR/WTR in presence of 3 phr Si 69
E₂-E₆ = NBR/WTR in presence of 4 phr Si 69
All mix A₁ to E₆ contain ZnO 5 g Sulphur 2 g MBTS 0.8 g TMTD 0.4 g Antioxidant (4020) 1 g. From A1 to E6 amount of NBR and reclaimed rubber are taken in grams

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}}$$

where T is the weight of test specimen, D is the weight of deswollen test specimen, F is the weight of fraction of insoluble components. A_0 is the weight of absorbed solvent corrected for the swelling increment. Density of the rubber ρ_r is 1.018 g/cm³ and ρ_s is the density of the solvent MEK, (0.804 g/cm³).

Knowing the value of V_r , the total chemical cross link density was calculated using Flory-Rehner equation⁽²³⁻²⁴⁾

$$-\ln(1 - V_r) + V_r + \chi V_r^2 = \frac{\rho_r (V_s (V_r)^{1/3})}{M_c}$$

where V_s is the molar volume of the solvent χ is the parameter characteristic of the interaction between rubber and solvent and M_c is the number average molecular weight of rubber chains between the cross links. The value of the parameter χ taken for NBR-MEK system was 0.21⁽²⁵⁾.

RESULTS AND DISCUSSION

Cure characteristics

Figure 1 shows the minimum torque values of the mixes A1 to E6 containing different levels of silane coupling agent. All the blends containing silane-coupling agent show higher minimum torque, indicating higher viscosity of the blends. This can be attributed to improved interaction between the matrix and filler particles in the blend. The effect of silane coupling agent on the stock viscosity is best reflected at higher reclaim content. At 10 parts reclaim loading, the values are almost the same. Since at higher WTR loading the higher filler content and hence the chance of matrix-filler interaction are higher, the effect of silane coupling agent is more pronounced at higher WTR content. In the 20-30 parts WTR loading range, higher viscosity is shown by mixes containing 1 phr of silane coupling agent. However, in the 40-50 range the higher viscosity is obtained with 2 phr of silane coupling agent. Beyond this further incorporation of the coupling agent seems to have no positive effect on the viscosity. At 3 and 4 phr of silane loading, the viscosity remains more or less constant for all mixes.

Figure 2 shows the variation of (maximum-minimum) torque (ΔT). In all the

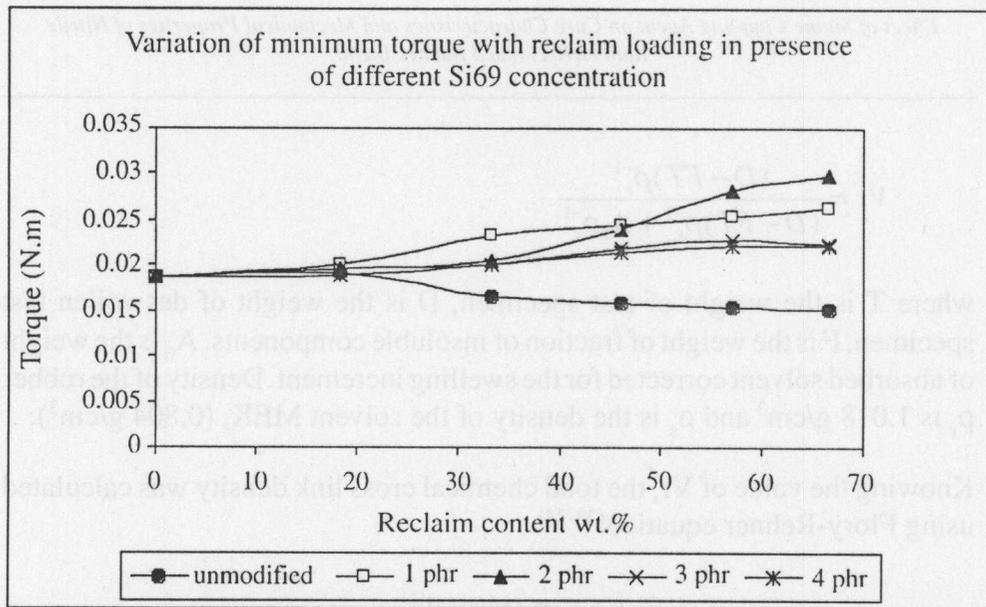


Figure 1. Variations of minimum torque with reclaim loading in presence of different levels of coupling agent

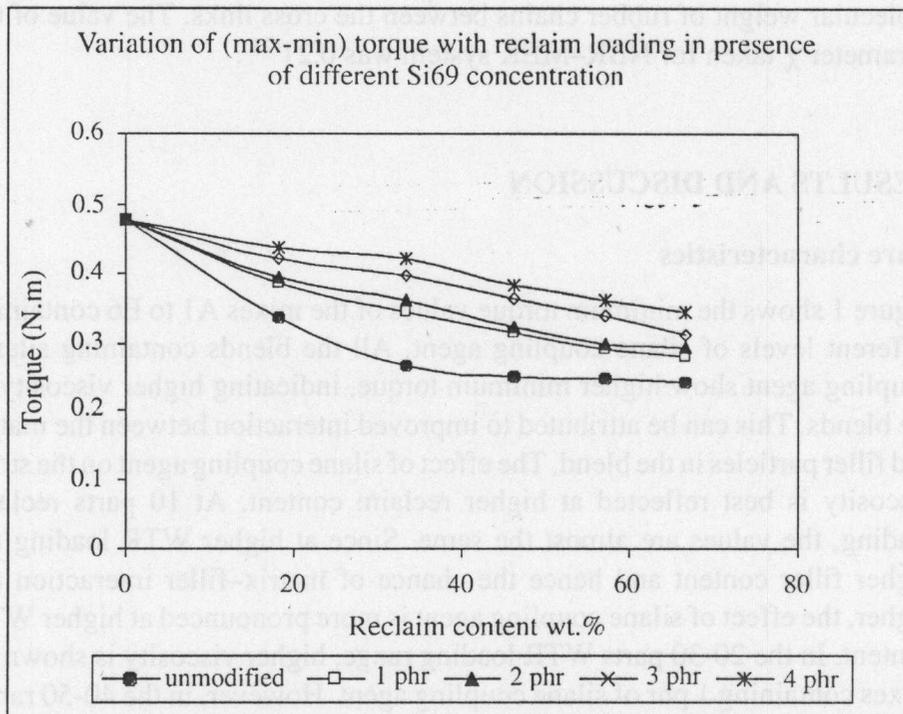


Figure 2. Variations of (maximum-minimum) torque with reclaim loading in presence of different levels of coupling agent

cases the (ΔT) of the blends containing silane coupling agent shows higher torque values compared to that of the control compound (mix A) indicating a relatively more restrained matrix resulting from the combined effect of higher interaction between blend components and higher levels of cross links formed. Table 3 shows that the cross-link density is higher at higher loading of coupling agent. Accordingly all blends containing 4 parts of Si69 show the highest loading torque values. With increasing reclaim content in the blends, the (ΔT) is found to be gradually decreased, the effect being less significant in the presence of silane coupling agent. The lower level of cross link at higher reclaim loading may be attributed to the fact that the reclaim is already partially cross linked matrix and hence there is relatively less reaction sites available for further cross linking. However, the improved matrix interaction compensates for this and hence (ΔT) for the blends containing silane-coupling agent is higher.

Figure 3 shows the variation of cure time with blend ratio at different loadings of Si69. For the unmodified blend the cure time decreases gradually with increasing WTR content. This may be attributed to the presence of sulphur and accelerator relics in WTR. All the blends containing the coupling agent show higher optimum cure time compared to the unmodified blend. The effect of Si69 loading on the cure time is dependant on the blend composition. At low WTR level, the cure time almost the same at all loading of Si69. Where as at higher blend ratios, the Si69 content seems to have very marked effect on the cure time. From 0 to 4 phr of Si69 there is a gradual increase in cure time, suggesting an adverse effect on the rate of cure. Figure 4 shows there indeed is a drop in cure rate at higher WTR and Si69 loadings. The relatively lower scorch time (Figure 5) coupled with higher (Max-Min) torque (Figure 2) for Si69 containing samples indicates that the delay in completion of cure is only temporary and complete cure does take place within the extended cure time.

Table 3 Cross link density measurement

No	Blend ratio NBR:WTR	Silane coupling agent in phr	Cross link density in m. mole/kg of rubber hydrocarbon
1	80:20	0	23.0
2	80:20	1	29.7
3	80:20	2	30.5
4	80:20	3	31.6
5	80:20	4	37.6

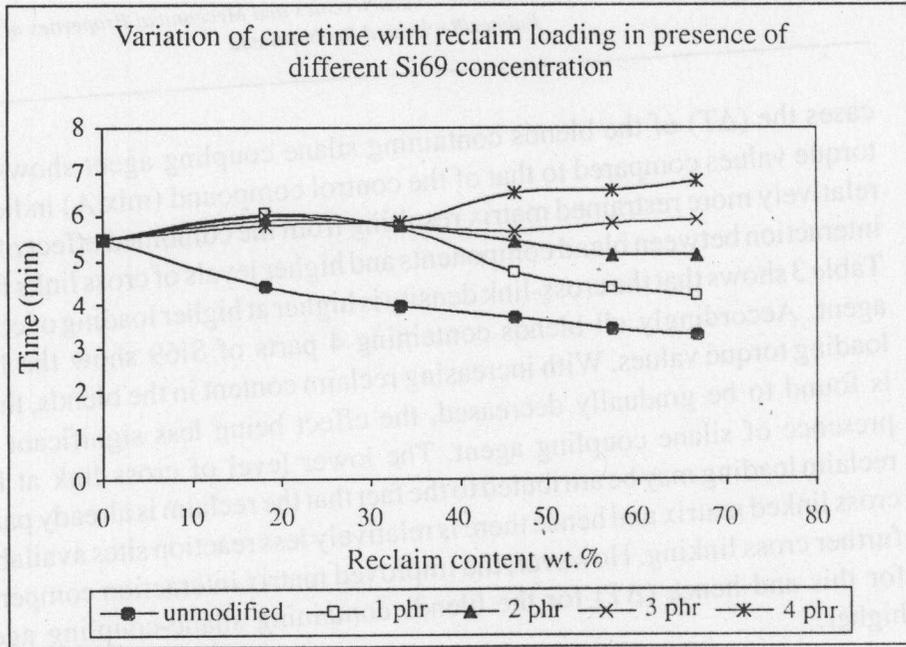


Figure 3. Variations of cure time with reclaim loading in presence of different levels of coupling agent

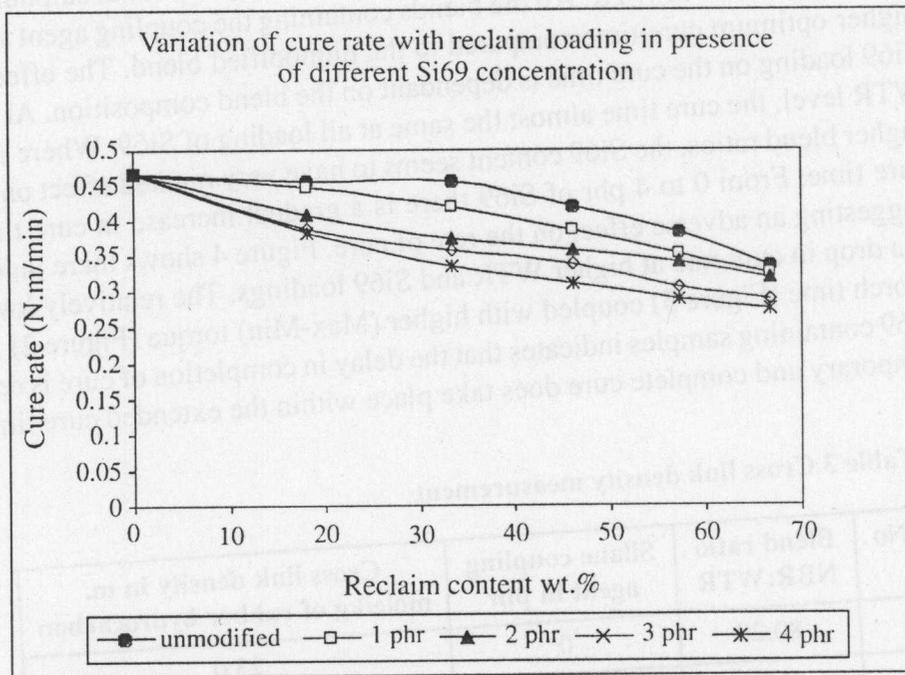


Figure 4. Variations of cure rate with reclaim loading in presence of different levels of coupling agent

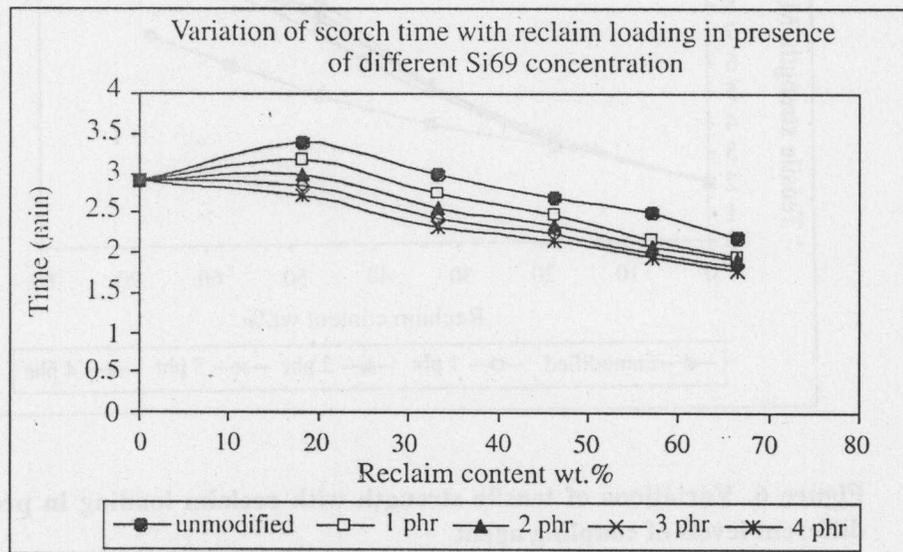


Figure 5. Variations of scorch time with reclaim loading in presence of different levels of coupling agent

Mechanical properties

Figure 6 shows variation of tensile strength of different blends containing 0 to 4 phr of Si69. With increasing WTR content the tensile strength is found to increase for all the blend. This may be attributed to the presence of reinforcing filler contained in the WTR. Table 1 shows that WTR contains about 30 phr of carbon black filler. All the blend containing Si69 show improved tensile strength, the effect being more pronounced at higher WTR content. At 20 parts of WTR incorporation of more than 1 phr of Si69 does not have a much effect on the tensile strength. At 30 parts of WTR the optimum loading of the coupling agent is 3 phr. At still higher WTR loading again there is not much difference in the tensile strength of the samples containing different levels of coupling agent. The improved tensile strength of the blends in the presence of Si69 may be attributed to the improved interaction between the blend component and filler, apart from the higher extent of cure of the modified blends.

Figure 7 shows the ultimate elongation values of the blends at different Si69 loadings. All the blends containing the coupling agent show higher elongation than the unmodified blend. The maximum elongation is obtained for the blend containing 40 parts of WTR with 3 phr of coupling agent. With 4 phr of the coupling agent the highest elongations obtained for blend containing 20 parts of WTR. The higher elongation of the samples containing coupling agent indicates that the coupling also has a plasticizing effect also on the blends.

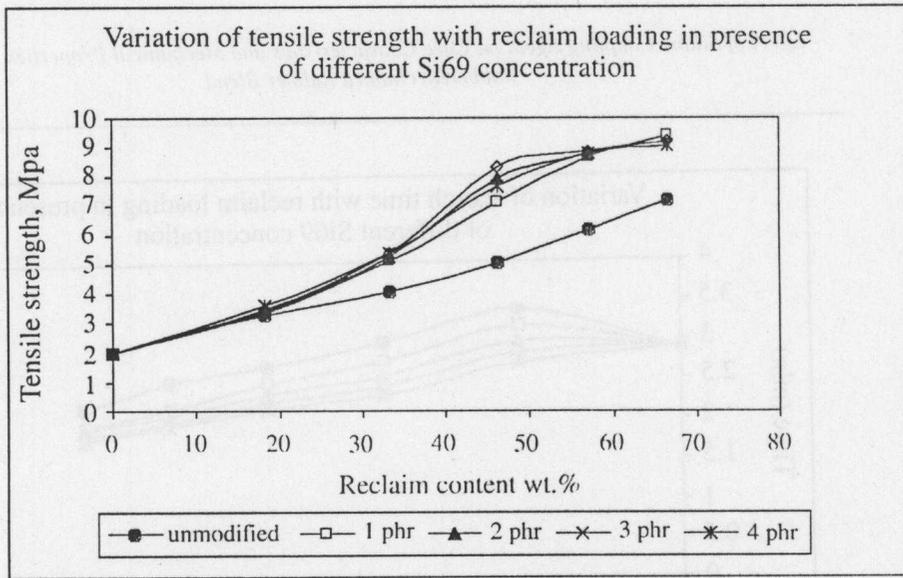


Figure 6. Variations of tensile strength with reclaim loading in presence of different levels of coupling agent

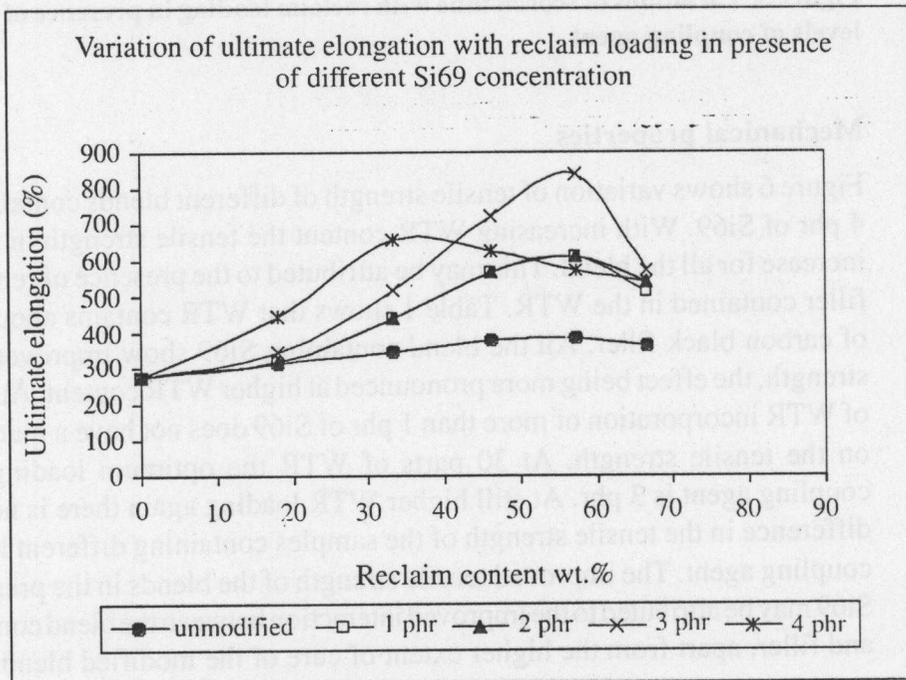


Figure 7. Variations of ultimate elongation with reclaim loading in presence of different levels of coupling agent

Figure 8 shows tear strength of the blends at different loading of the coupling agent. All the blends show similar trend with a marked improvement in the tear strength beyond WTR content of 10 parts. This may be attributed the reinforcing effect of the filler present in the WTR (Table 1). In the presence of the coupling agent, the tear strength is found to be higher. This may be attributed to the improved matrix filler interaction through the coupling agent.

Figure 9 shows the variations of compression set of the blends containing different levels of the coupling agent. The compression set is found to increase with the WTR content⁽²⁶⁾. This may be attributed to the poor strength of the low molecular weight WTR. At the test temperature under load, the blends containing higher WTR flows more, resulting in higher compression set. With increasing coupling agent loading, compression set is also found to be more. This may be arising from the type of additional cross links formed in the presence of Si69. The higher compression set values indicates that the cross links formed are predominately poly sulfide which are prone to break down and rearrangement under elevated temperature and stress.

The abrasion loss is increased with WTR loading in the absence of a coupling agent (Figure 10). In the presence of coupling agent all the blends containing

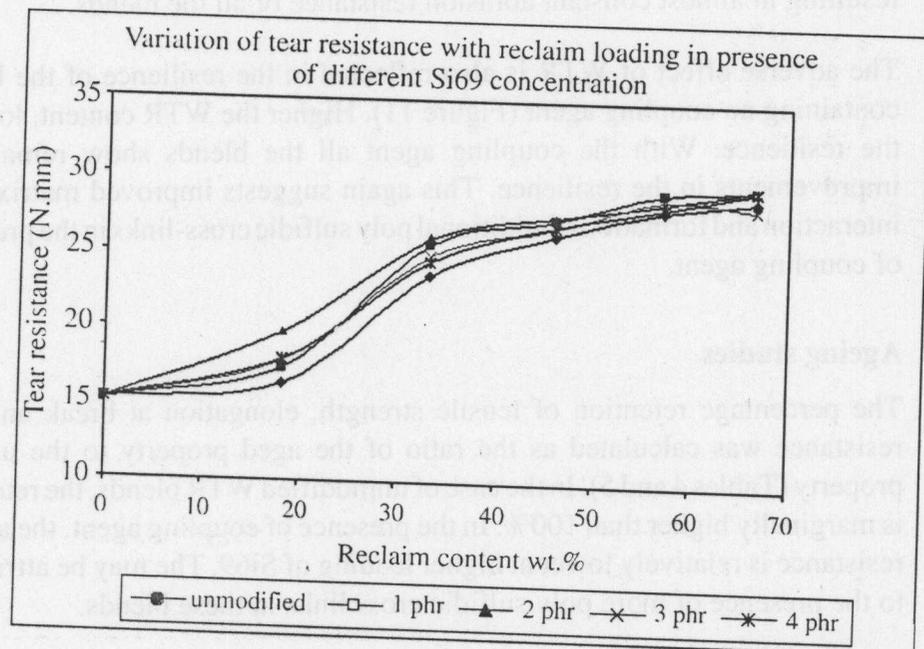


Figure 8. Variations of tear resistance with reclaim loading in presence of different levels of coupling agent

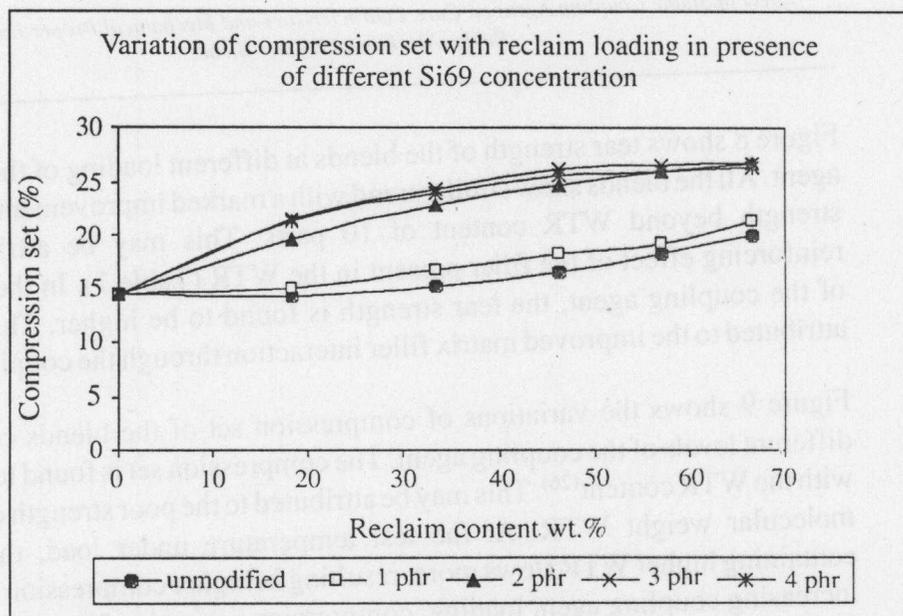


Figure 9. Variations of compression set with reclaim loading in presence of different levels of coupling agent

different levels of WTR show significantly lower abrasion loss. The detrimental effect of WTR on the abrasion resistance of the blends seems to be compensated for by the improved filler–matrix interaction in the presence of coupling agent resulting in almost constant abrasion resistance of all the blends.

The adverse effect of WTR is also reflected in the resilience of the blends containing no coupling agent (Figure 11). Higher the WTR content, lower is the resilience. With the coupling agent all the blends show remarkable improvements in the resilience. This again suggests improved matrix–filler interaction and formation of additional poly sulfidic cross-links in the presence of coupling agent.

Ageing studies

The percentage retention of tensile strength, elongation at break and tear resistance was calculated as the ratio of the aged property to the unaged property (Tables 4 and 5). In the case of unmodified WTR blends, the retention is marginally higher than 100%. In the presence of coupling agent, the ageing resistance is relatively lower at higher loading of Si69. This may be attributed to the presence of more poly sulfidic cross links in these blends.

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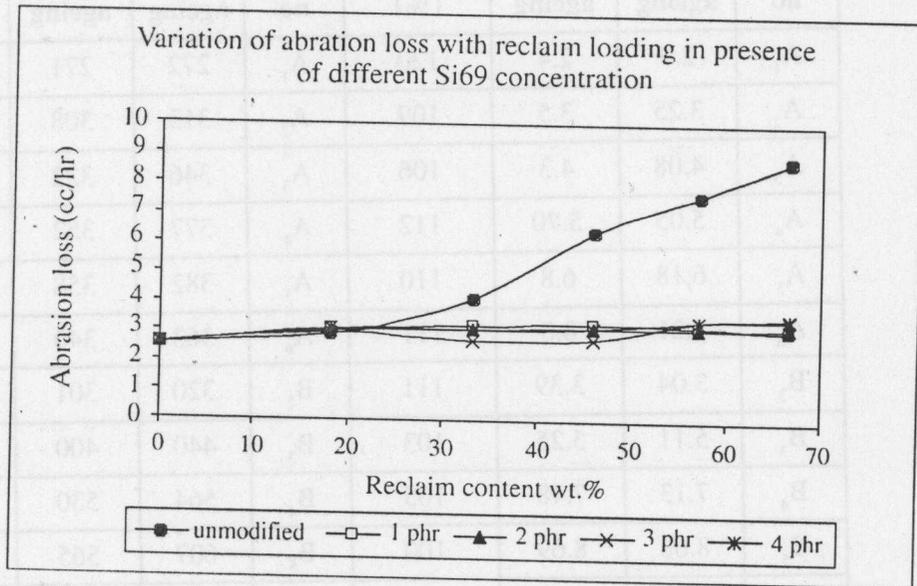


Figure 10. Variations of abrasion loss with reclaim loading in presence of different levels of coupling agent

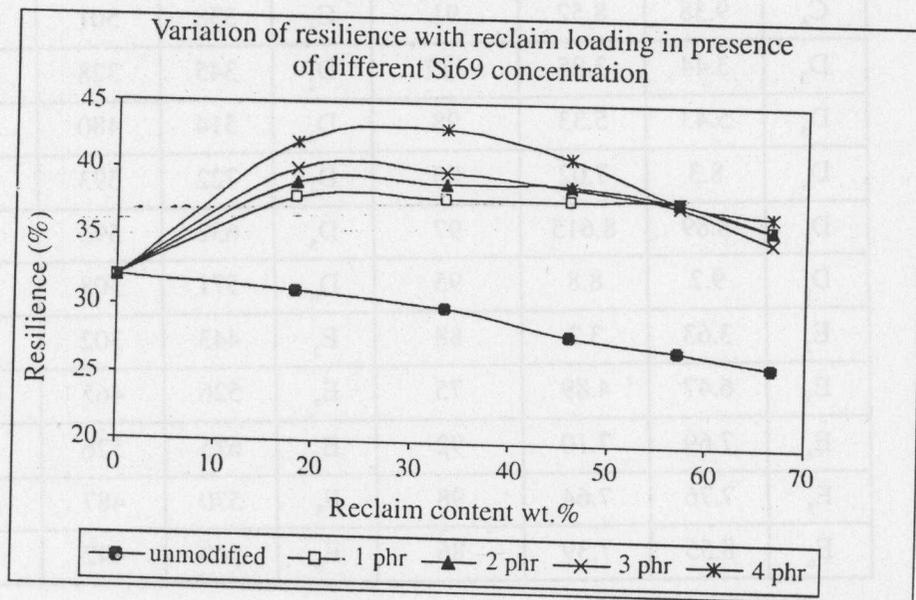


Figure 11. Variations of resilience with reclaim loading in presence of different levels of coupling agent

Table 4 Retention values of tensile strength and ultimate elongation after ageing

Tensile strength (MPa)				Ultimate elongation (%)			
Mix no	Before ageing	After ageing	Retention (%)	Mix no	Before ageing	After ageing	Retention (%)
A ₁	2.0	2.4	120	A ₁	272	271	100
A ₂	3.25	3.5	109	A ₂	313	308	98
A ₃	4.08	4.3	106	A ₃	346	322	93
A ₄	5.05	5.70	112	A ₄	377	352	93
A ₅	6.18	6.8	110	A ₅	382	358	94
A ₆	7.21	8.0	111	A ₆	363	340	93
B ₂	3.04	3.39	111	B ₂	320	301	94
B ₃	5.11	5.25	103	B ₃	440	400	91
B ₄	7.13	7.48	105	B ₄	564	530	94
B ₅	8.68	8.69	100	B ₅	607	565	93
B ₆	9.38	9.28	99	B ₆	509	482	95
C ₂	3.04	3.6	117	C ₂	320	318	95
C ₃	5.24	5.84	111	C ₃	440	406	92
C ₄	7.96	7.9	99	C ₄	565	510	90
C ₅	8.78	8.69	99	C ₅	608	551	91
C ₆	9.38	8.52	91	C ₆	538	501	93
D ₂	3.44	3.85	112	D ₂	345	328	95
D ₃	5.43	5.33	98	D ₃	514	480	93
D ₄	8.3	7.02	85	D ₄	722	593	95
D ₅	8.89	8.615	97	D ₅	632	593	94
D ₆	9.2	8.8	95	D ₆	571	508	89
E ₂	3.63	3.2	88	E ₂	443	302	84
E ₃	6.47	4.89	75	E ₃	526	465	88
E ₄	7.69	7.10	92	E ₄	625	526	84
E ₅	7.76	7.64	98	E ₅	570	487	86
E ₆	8.55	7.39	86	E ₆	540	442	82

Table 5 Retention values of tear strength after ageing

Tear strength retention (N.mm)							
Mix no	Before ageing	After ageing	Retention (%)	Mix no	Before ageing	After ageing	Retention (%)
A ₁	15.24	15.19	100	C ₄	27.54	24.50	92
A ₂	16.37	16.00	98	C ₅	28.50	26.2	92
A ₃	23.60	23.15	98	C ₆	29.60	26.5	89
A ₄	26.25	25.09	95	D ₂	19.9	16.9	94
A ₅	28.03	27.5	98	D ₃	24.9	22.95	92
A ₆	28.74	28	97	D ₄	26.8	24.3	90
B ₂	17.4	16.70	96	D ₅	28.70	25.6	89
B ₃	25.6	24.20	94	D ₆	28.20	26.2	92
B ₄	27.3	24.80	91	E ₂	18.0	17.8	98
B ₅	29.1	25.90	89	E ₃	24.50	22.80	93
B ₆	29.4	26.72	91	E ₄	26.90	24.6	92
C ₂	19.72	18.80	95	E ₅	28.20	25.60	91
C ₃	26.0	23.69	91	E ₆	29.40	25.60	87

CONCLUSIONS

From the above study, following conclusions are drawn. Optimum concentration of the silane-coupling agent is 3 phr at a blend ratio 70:30, of Acrylonitrile butadiene rubber and WTR. Addition of coupling agent to the acrylonitrile butadiene/whole tyre reclaim blend improves mechanical properties such as tensile strength and abrasion resistance. Tear strength has no such improvements in presence of coupling agent. Compression set values of the blends containing silane-coupling agent are higher than the unmodified blend. In the presence of coupling agent, cure time is higher, where as scorch time and cure rate are lesser than the control mix. Cross link density is increased in presence of coupling agent. In the Ageing studies percentage retention values of tensile strength, tear strength and ultimate elongation has a marginal decrease, when compared to unmodified blends.

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