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

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ABSTRACT

Chloroprene rubber was blended with whole tire reclaimed rubber (WTR) in presence of different levels of a coupling agent Si69 [*bis*-(3-(triethoxysilyl)propyl)tetrasulfide] and the cure characteristics and mechanical properties were studied. The rate and state of cure were also affected by the coupling agent. While the cure time was increased, the cure rate and scorch time were decreased with increasing silane content. Tensile strength, tear strength, and abrasion resistance were improved in the presence of coupling agent. Compression set and resilience were adversely affected in presence of silane-coupling agent.

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Aging studies showed that the blends containing the coupling agent were inferior to the unmodified blends.

Key Words: Silane coupling agent Si69; Whole tire reclaimed rubber; Chloroprene rubber; Mechanical properties.

INTRODUCTION

Large-scale growth of the transport sector causes severe damage to the environment in terms of solid and gaseous pollution especially from used and scrap tires. One way of recycling tires is to convert them into whole tire reclaimed rubber (WTR). WTR can be blended with virgin rubber as a source of rubber hydrocarbon and filler. Several workers have explored these possibilities.^[1-14] Kim and Burford studied the utilization of waste tires in polar and nonpolar rubbers.^[15] When WTR is used with a polar matrix such as chloroprene rubber, the compatibility 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 a silane based coupling agent, Si69.

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 the polar base polymer and nonpolar fillers in the vulcanized rubber compounds. The Si(OR)₃ portion reacts with the polar components, while the organo-functional (vinyl-, amino-, epoxy-, etc.) group reacts with the nonpolar matrix. Si69 is a silane coupling agent that can improve the interaction between polar and nonpolar matrix. Ghosh et al. reported the uses of silane coupling agent in blends of polyethylene and ethylene propylene rubbers.^[16] Use of silane coupling agent in natural rubber was reported by Ismail et al.^[17] Use of silane coupling agent in styrene butadiene rubber was reported by Bokobza et al.^[18] Nelson and Kutty reported grafting of maleic anhydride on WTR to improve the compatibility of blend components in NBR/WTR blends.^[19]

In this article we report the results of our study on the effect of Si69 as a coupling agent on the blends of CR and WTR. The loading of Si69 was 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

Chloroprene rubber (neoprene) used in this study was of W type with Mooney viscosity [ML (1 + 4) at 100°C] 47. The rubber was supplied by Du Pont, USA. 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. MgO was supplied by Merck India Ltd. Stearic acid was procured from Godrej Soaps Pvt. Ltd. Mumbai. Antioxidant 4020 [*N*-(1,3 dimethylbutyl) *N'*-phenyl *p*-phenylenediamine] was obtained from Bayer India Ltd., silane coupling agent Si69, [*bis*-(3-(triethoxysilyl) propyl tetrasulfide)] was obtained from Degussa Corporation, Germany, and NA 22 was obtained from Akrochem Corporation, USA.

Preparation of Blends

Formulation of the mixes is given in Table 2.

The blends were prepared on a laboratory-size two-roll mill (150 × 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 at 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 so as to get the same extent of cure. 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

Table 1. The characteristics of WTR.

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

Table 2. Formulation of mixes.

Mix no.	A	B	C	D	E	A1	B1	C1	D1	E1	A2	B2	C2	D2	E2	A3	B3	C3	D3	E3	A4	B4	C4	D4	E4
Chloroprene	90	80	70	60	50	90	80	70	60	50	90	80	70	60	50	90	80	70	60	50	90	80	70	60	50
Reclaimed rubber	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100
Si69	—	—	—	—	—	1	1	1	1	1	2	2	2	2	2	3	3	3	3	3	4	4	4	4	4

Mixes A to E₄ contain ZnO 5 g, MgO 4 g, stearic acid 0.5 g, NA 22 0.5 g, and antioxidant 4020 1 g.

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 D 2832-88 using a vertical rebound resilience tester. For aging resistance studies, samples were aged in an air oven for 48 h at 70°C (ASTM D 573-88) and the tensile and tear properties were measured.

Determination of Crosslink Density

Samples of WTR/CR blend and WTR/CR blends in presence of silane coupling agent were used for the determination of crosslink 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 benzene for 48 h. The swollen samples were taken out and weighed again. The solvent was removed under vacuum and the samples were weighed again. Volume fraction of the rubber V_r in the swollen network was then calculated by the following equation^[20,21]:

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

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, ρ_r is density of the rubber, and ρ_s is the density of the solvent benzene.

Knowing the value of V_r , the total chemical crosslink density was calculated using the Flory-Rehner equation^[22,23]

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

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 crosslinks. The value of the parameter χ taken for CR-benzene system was 0.26.^[24]

RESULTS AND DISCUSSION

Cure Characteristics

Figure 1 shows the minimum torque values of the mixes containing different levels of silane coupling agent. All the blends containing

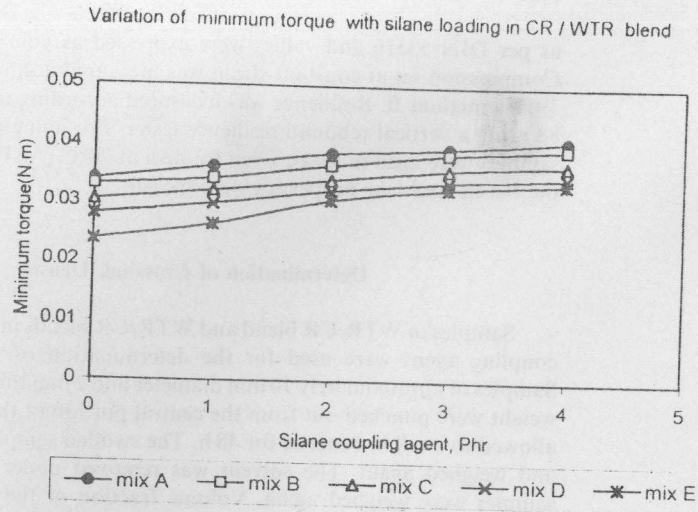


Figure 1. Variation of minimum torque with reclaim loading in presence of different levels of coupling agent.

silane-coupling agent show higher minimum torque, indicating higher viscosity of the blends. This can be attributed to the improved interaction between the matrix and filler in presence of coupling agent. The improvement of stock viscosity is found to be more pronounced in blends containing higher proportions of WTR. This may be attributed to the fact that higher WTR levels contain higher filler concentrations and hence better chance of interaction with the coupling agent. There also seems to be a leveling off beyond 2-3 phr of Si69. At any silane concentration with the increase in the reclaim content, the probability of crosslinking decreases due to the partially crosslinked nature of WTR.

The Fig. 2 shows the variation of (maximum-minimum) torque (Δt). In all cases, the (Δt) gradually increases with the increase in concentration of silane-coupling agent, indicating a relatively more restrained matrix resulting from improved interaction between the blend components. The improved interaction between the blend components is also indicated by the increase in crosslink density of the matrix (Table 3). It is also observed that after 3-phr silane concentration there is no significant improvement in the (Δt). There is also a progressive decrease in (Δt) values with increasing the WTR content. The lower level of crosslinking

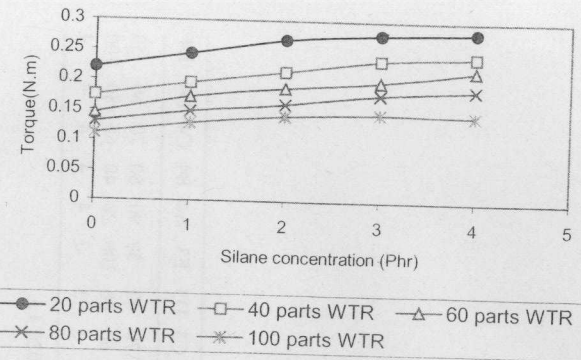


Figure 2. Variation of (maximum-minimum) torque with reclaim loading in presence of different levels of coupling agent.

Table 3. Crosslink density of reclaim blends (mixes B, B1, B2, B3, B4).

No.	Blend ratio CR:WTR	Silane coupling agent in phr	Crosslink density in mmol/kg of rubber hydrocarbon
1	80:40	0	30.6
2	80:40	1	40.9
3	80:40	2	42.8
4	80:40	3	44.6
5	80:40	4	44.1

at higher reclaim loading may be attributed to the fact that the reclaim is already partially crosslinked matrix and hence there is relatively less reaction sites available for further crosslinking. However, the improved matrix interaction compensates for this and hence (Δt) for the blends containing silane-coupling agent is higher.

Figure 3 shows variation of cure time in the presence of different levels of silane-coupling agent. The cure time registers a gradual increase with increasing silane loading. The delayed completion of the cure coupled with reduced cure rate (Fig. 4) and extended scorch time (Fig. 5) suggests that the silane-coupling agent not only delays the onset of cure but also slows down the rate of cure reaction.

Variation of cure time with silane loading in CR / WTR blend

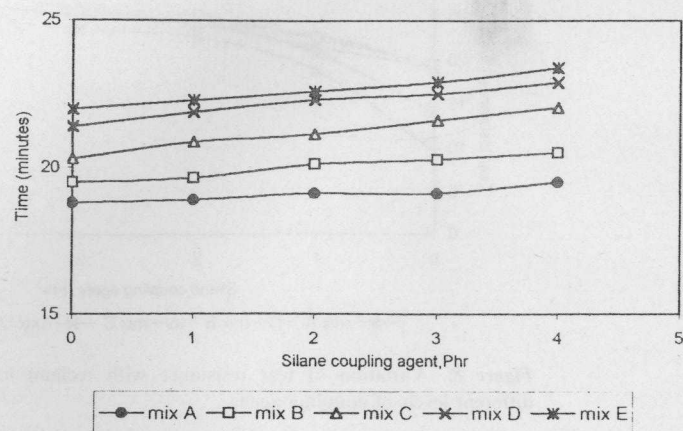


Figure 3. Variation of cure time with reclaim loading in presence of different levels of coupling agent.

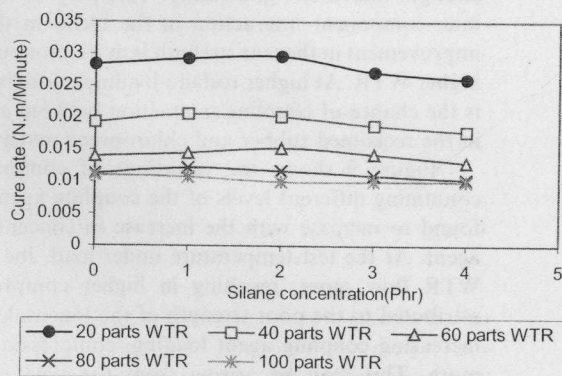


Figure 4. Variation of cure rate with reclaim loading in presence of different levels of coupling agent.

Variation of scorch time with silane loading in CR / WTR blend

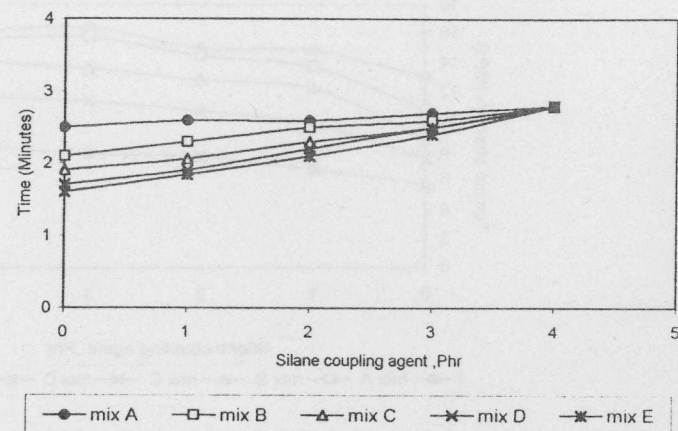


Figure 5. Variation of scorch time with reclaim loading in presence of different levels of coupling agent.

Mechanical Properties

Figure 6 shows the tensile strength of different blends, containing 0–4 phr of Si69. It is observed that tensile strength is gradually increased by the addition of silane-coupling agent. The increase in tensile strength is accounted for on the basis of increased interaction between the blend components in presence of the coupling agent. At any silane concentration, increase in reclaim content reduces the tensile strength, which may be attributed to the dilution effect produced by the addition of reclaim to the chloroprene matrix. Since the whole tire reclaim is predominately natural rubber, addition of reclaim to the chloroprene reduces the crystallizability of the matrix and hence results in lower tensile strength.

Figure 7 shows the variation of ultimate elongation with the silane-coupling agent at different mixes A to E4. Here the ultimate elongation increases with the addition of Si69 and levels off beyond 1 phr. The increased extensibility of the matrix in the presence of the coupling agent point to its minor plasticizing effect. Similar reports have been reported by Ismail et al.^[17]

Variation of tensile strength with silane loading in CR / WTR blend

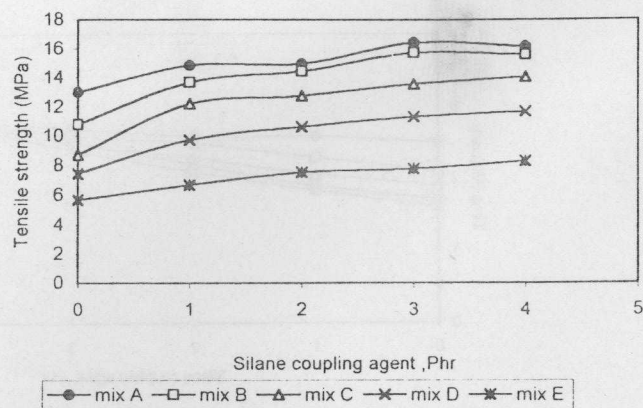


Figure 6. Variation of tensile strength with reclaim loading in presence of coupling agent.

Variation of ultimate elongation with silane loading in CR/WTR blend

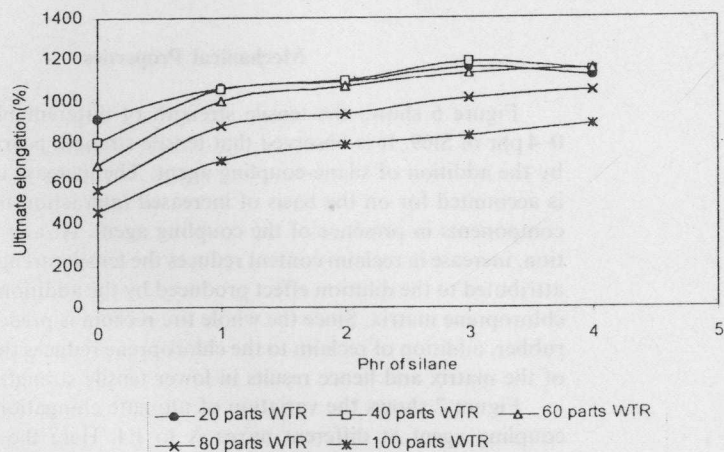


Figure 7. Variation of ultimate elongation with reclaim loading in presence of different levels of coupling agent.

Variation of tear resistance with silane loading in CR / WTR blend

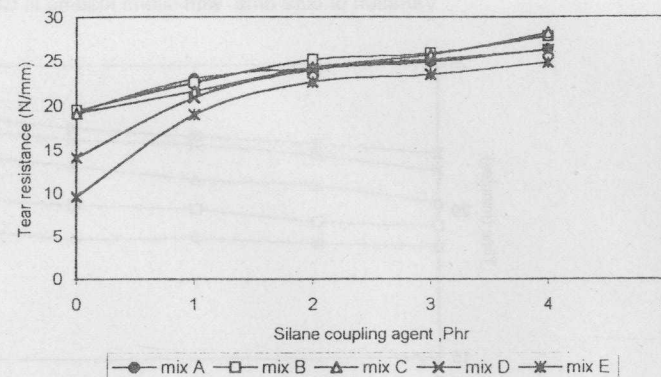


Figure 8. Variation of tear resistance with reclaim loading in presence of different levels of coupling agent.

Figure 8 shows comparison of tear strength with the addition of coupling agent in different mixes A to E₄. In the chloroprene/reclaim blend, with the increase in reclaim concentration, the tear strength decreases because of the dilution effect produced by the low molecular weight reclaimed rubber. But in presence of coupling agent, the tear strength increases significantly. This may be attributed to the increased inter-component interaction in the blend in the presence of Si69. The improvement in the tear strength is more pronounced in blends containing higher WTR. At higher reclaim loading, more is the filler and hence more is the chance of coupling interaction between carbon black filler present in the reclaimed rubber and chloroprene matrix.

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 increase in concentration of silane-coupling agent. At the test temperature under load, the blends containing higher WTR flow more, resulting in higher compression set. This may be attributed to the poor strength of the low molecular weight WTR. With increasing coupling agent loading, compression set is also found to be more. This may be arising from the type of additional polysulfidic crosslinks formed in the presence of Si69. The higher compression set values indicate that the crosslinks formed are predominately polysulfidic.

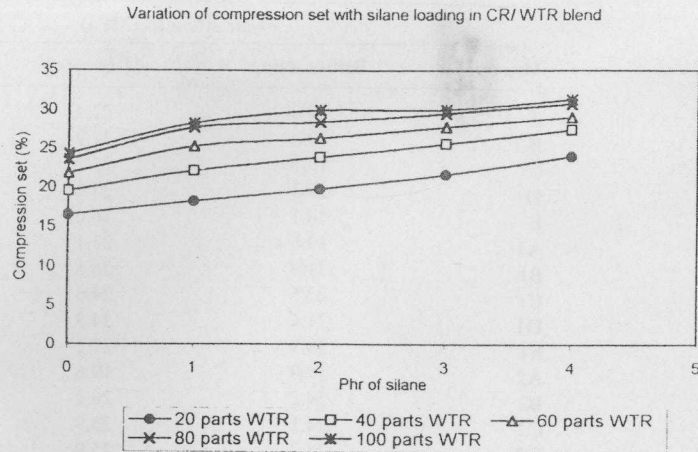


Figure 9. Variation of compression set with reclaim loading in presence of different levels of coupling agent.

which are prone to break down and rearrange under elevated temperature and stress. Similar results have been reported by Phadke et al.^[25]

Figure 10 shows the variation of abrasion loss with increase in concentration of silane-coupling agent in mixes A to E4. It is observed that abrasion loss decreases with the addition of silane-coupling agent. Decreased abrasion loss, i.e., increased abrasion resistance in the presence of coupling agent, is accounted for on the basis of improved interaction between the blend components. The effect is more predominant at higher reclaim concentration.

Figure 11 shows the variation of resilience with the addition of coupling agent in different mixes A to E4. The resilience decreases with the addition of Si69, the effect being more prominent at higher reclaim loading. Introduction of more filler by way of adding more WTR increases chances of energy loss at the interfaces leading to the lower resilience. The improved intercomponent interaction is not reflected as improved resilience in the case of blends containing coupling agent. This may be attributed to the extent of strain involved. The level of strain on sample subjected to a resilience test is very small compared to a hysteresis or compression set tests.

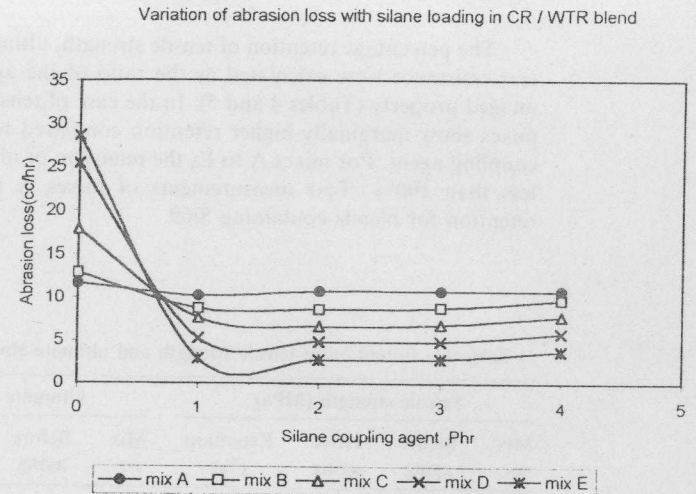


Figure 10. Variation of abrasion loss with reclaim loading in presence of different levels of coupling agent.

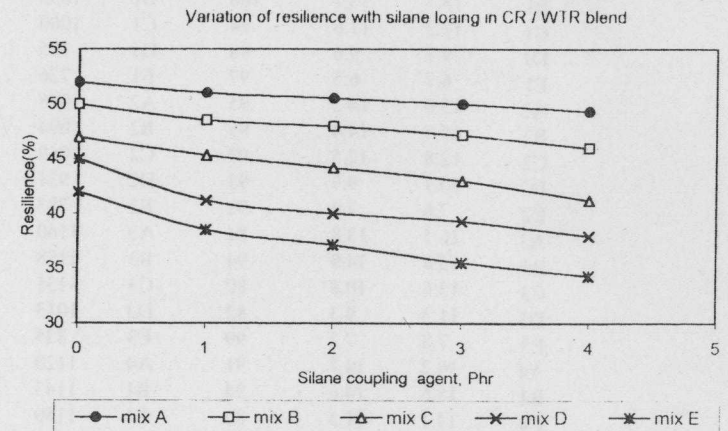


Figure 11. Variation of resilience with reclaim loading in presence of different levels of coupling agent.

Aging Studies

The percentage retention of tensile strength, ultimate elongation, and tear resistance were calculated as the ratio of the aged property to the unaged property (Tables 4 and 5). In the case of tensile strength, control mixes show marginally higher retention compared to blends containing coupling agent. For mixes A to E₄ the retention of ultimate elongation is less than 100%. Tear measurements of mixes A to E₄ shows lower retention for blends containing Si69.

Table 4. Retention of tensile strength and ultimate elongation after aging.

Mix no.	Tensile strength (MPa)			Mix no.	Ultimate elongation (%)		
	Before aging	After aging	Retention (%)		Before aging	After aging	Retention (%)
A	13.0	13.7	106	A	912	877	96
B	10.8	11.7	108	B	802	750	94
C	8.7	9.6	110	C	684	750	91
D	7.5	7.9	107	D	566	462	82
E	5.7	5.9	103	E	456	437	96
A1	14.9	14.5	97	A1	1064	1045	98
B1	13.7	13.7	100	B1	1056	1000	95
C1	12.2	11.6	94	C1	1000	980	98
D1	9.7	9.6	98	D1	785	820	94
E1	6.7	6.5	97	E1	726	623	88
A2	15.0	14.2	95	A2	1088	1075	99
B2	14.5	14.4	99	B2	1094	1080	99
C2	12.8	12.5	97	C2	1069	993	93
D2	10.7	9.9	93	D2	931	848	91
E2	7.6	7.0	92	E2	783	685	87
A3	16.5	13.8	84	A3	1160	1046	90
B3	15.8	14.9	94	B3	1188	1029	87
C3	13.6	10.8	80	C3	1131	990	88
D3	11.3	9.3	82	D3	1013	862	85
E3	7.8	7.7	99	E3	825	788	96
A4	16.2	14.7	91	A4	1120	963	86
B4	15.6	14.6	94	B4	1143	923	81
C4	14.1	11.5	82	C4	1150	920	80
D4	11.7	9.9	85	D4	1150	887	84
E4	8.3	7.3	88	E4	883	768	87

Table 5. Retention of tear strength after aging.

Mix no.	Tear strength (MPa)		Retention (%)
	Before aging	After aging	
A	19.3	22.4	116
B	19.4	22.9	118
C	19.5	23.2	119
D	19.1	23.2	121
E	14.1	16.6	118
A1	19.6	22.1	113
B1	21.9	26.5	115
C1	22.5	24.6	109
D1	21.6	24.3	112
E1	20.9	22.2	106
A2	19.0	19.6	103
B2	24.2	26.2	108
C2	24.1	25.9	103
D2	24.3	25.9	107
E2	23.9	24.6	103
A3	22.6	24.4	108
B3	24.9	27.5	111
C3	25.9	28.6	111
D3	25.7	27.6	107
E3	25.2	24.2	104
A4	23.5	24.2	103
B4	23.6	27.8	106
C4	27.8	28.2	101
D4	28.2	29.1	103
E4	22.3	27.3	104

CONCLUSIONS

From the above study, the following conclusions were drawn. Introduction of Si69 coupling agent to the CR/WTR blend increases cure time and reduced scorch time and cure rate. Addition of Si69 improves the mechanical properties such as tensile strength, ultimate elongation, tear resistance, and abrasion resistance. Crosslink density is improved in presence of coupling agent. Aging studies showed that the blends containing the coupling agent have lower resistance toward aging.

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Radiation Polymerization of Hydrophilic Monomers for Producing Hydrogel Used in Waste Treatment Processes

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ABSTRACT

Co⁶⁰- γ radiation was used in the synthesis of bipolymer hydrogel, using acrylamide (AAm), acrylic acid (AAc), and sodium acrylate. The parameters affecting preparation of these hydrogels such as monomer ratio, crosslinking agent ratio, and irradiation dose have been studied. The swelling behavior of these hydrogels was studied under different preparation conditions. The experimental results showed that the gel fraction of the produced hydrogel depends mainly on the irradiation dose, and the degree of swelling was intimately related to irradiation dose and blending ratio of the two monomers. Characterization of the obtained hydrogel was carried

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