Reclaiming of Rubber by a Renewable Resource Material (RRM). III. Evaluation of Properties of NR Reclaim

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ABSTRACT: Sulfur-cured filled natural rubber (NR) is successfully reclaimed by using a renewable resource material (RRM) and diallyl disulfide (DADS), which is the major constituent of RRM. Reclaiming of NR vulcanizate was carried out at 60°C for 35 min in an open two-roll mixing mill. Evaluation of the properties of NR reclaim was carried out by mixing it with virgin rubber in various proportions. The cure characteristics and mechanical properties of the virgin NR/ reclaim NR blend were studied. With increase in the proportion of reclaim rubber (RR) in virgin NR/ reclaim NR blend scorch time and optimum cure time decrease. To increase scorch time N-cyclohexylthiophthalimide as prevulcanization inhibitor (PVI) was added in NR/RR (50/50) blend. It was found that use of 40% NR reclaim with virgin rubber resulted 83% retention of tensile strength of that of the virgin NR vulcanizate. Effect of carbon black loading was studied in NR/RR (50/50) blends. Tensile properties and swelling value of different NR/RR blends were evaluated before and after aging. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1493–1502, 2000

Key words: recycling, reclaiming, reclaim rubber, devulcanization, sol fraction, renewable resource material, diallyl disulfide, mechanical properties, Mooney viscosity, prevulcanization inhibitor

INTRODUCTION

Reclaim rubber (RR) is a degraded mass obtained after reclaiming of vulcanized rubber by a suitable agent following a suitable process. All reclaim rubber samples contain a sol and a gel fraction. Almost in all commercial applications reclaim rubber is used as a component of a blend with fresh rubber. Incorporation and dispersion of reclaim rubber in virgin rubber play important roles towards the product quality, production economy, and market competition. Good and consistent dispersion of reclaim rubber in virgin rubber is essential for optimum vulcanizate properties. So it is necessary to evaluate the performances of such blends containing reclaim rubber. For a good quality of reclaim product sol fraction and molecular weight of sol fraction should be as high as possible and Mooney viscosity of reclaim rubber should be adequate for easy processibility.

Klingensmith[1] used cryoground butyl rubber with fresh virgin rubber in 5–15% level. Such small amount of reclaim rubber appeared to be incorporated as a filler with respect to virgin rubber. Studies by Chopey[2] and Burgogue et al.[3] showed that there was a significant drop in the tensile strength when powdered rubber was added to a conventional rubber compound. Accetta and Vergnaud[4,5] developed a process to improve the quality of the scrap rubber powder recovered from old tires. De et al.[6] studied the fractured surface of a vulcanizate containing reclaim rubber by scanning electron microscope (SEM). SEM photomicrograph of tensile fractured sur-

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face was found to be brittle. Decrease in matrix flow and appearance of cracks were also observed with the increase in the proportion of reclaim rubber. Thus this reclaim rubber is nothing but a nonreinforcing filler.

Kohler[7] reported a new technology for the devulcanization of sulfur cured scrap rubber using a material termed as "De-Vulc" developed by Sekhar.[8] Such technique of devulcanization was designated as De-Link process where they have mixed 30% devulcanized rubber with virgin rubber and determined the properties of the blend. This has increased the Mooney viscosity, tan δ, and 300% modulus, whereas decreased the tensile strength, elongation at break, and tear resistance of the blend compared with virgin rubber.

Menadue[9] has described a process where the crumb scrap from vulcanized tire scrap tread compound was masticated on a mill with the addition of 1% sulfur, 0.5% diphenyl guanidine, and 1% zinc oxide. The milled mass was revulcanized at 60 psig steam for 15 min resulting in a product with 15 MPa tensile strength. Twiss et al.[10] of Dunlop Ltd. have patented a process where the crumb rubber is softened with a plasticizer (such as pine tar) and devulcanized by the addition of 0.5–2% mercaptobenzothiazole and an organic acid as catalyst. Tire tread obtained by this devulcanization process gave about 75% of the properties of the original compounds. Hildebrandt,[11] Yamashita, [12,13] and Stalinski[14] have developed chemical devulcanization processes by using softening agent, amines, and a catalyst. They also patented their developments. Warner[15] has summarized different methods of devulcanization in his excellent review. Myhre and MacKillop[16] have used one or more liquid chemicals to the crumb for swelling as well as softening so that reactive chemicals can easily penetrate into the vulcanized rubber network. Plasticizers, such as terpenes and pine oil that have been used for devulcanization, are very compatible with natural rubber. A blend of 70% devulcanized rubber with natural rubber including additional carbon black, plasticizers, and various curatives exhibit hardness 57–65 Shore A, tensile strength 15 MPa with elongation at break 485%, and tear strength from 345 to 515 N/cm. In a recent paper Tapale and Isayev[17] have reported the mechanical properties of revulcanized natural rubber (NR) where devulcanization was carried out by ultrasound energy.[18–20] Here it has been found that with increasing the proportion of sulfur (4 phr) and decreasing the proportion of zinc oxide and stearic acid without any accelerator (N-cyclohexyl 2-benzothiazylsulfenamide [CBS]) show maximum mechanical properties. Tensile strength of this type of vulcanizate is 14.2 MPa, which is 70% of that of the virgin NR vulcanizate, and elongation at break is 670%, which is the same as that of the virgin NR vulcanizate.

In this communication we will report on the suitability of NR reclaim, as a blend with fresh NR, obtained by reclaiming with a vegetable product. Curing characteristic and tensile properties before and after aging of such rubber compounds containing reclaim rubber have been studied.

EXPERIMENTAL

Materials

A renewable resource material (RRM) that is a vegetable product having the major constituent diallyl disulfide (DADS) was used as reclaiming agent. Other constituents of RRM are cyclic monosulfides, polysulfides, different disulfides, and sulfone compounds. Being proprietary in nature and because of pending patent application the name of the RRM is not disclosed. Diallyl disulfide (Aldrich Chem., USA) was used without further purification. Natural rubber (RSS-1, Rubber Board, India), zinc oxide (SD Fine Chem., India), stearic acid (Loba Chemie, India), sulfur (SD Fine Chem., India), CBS (ICI, India), carbon black (N330, Phillips Carbon Black), spindle oil (MCI, India), acetone (SD Fine Chem., India), and toluene (SD Fine Chem., India) were used as received.

Preparation of RRM

The vegetable product (RRM) was crushed into an aqueous paste by compressive shearing followed by squeezing through cheese cloth to obtain a liquid mass. The water in the liquid mass was removed by desiccation over anhydrous calcium chloride and silica gel. This liquid having organic matter was used as such for reclaiming of rubber vulcanizate. Amount of the organic matter in the vegetable product extract was 40%.

Preparation of Vulcanized and Aged Rubber Sample for Reclaiming

Compounding of NR with various additives for reclaiming study was done in a two-roll mixing mill at a friction ratio 1.2. The rubber compound was vulcanized at 150°C for respective optimum cure time that was obtained from an Oscillating Disc Rheometer (Monsanto ODR R-100). The vulcanized rubber samples were then aged under a predetermined accelerated aging condition. Next, the aged vulcanized rubber sheet was ground in an open two-roll mixing mill for use in reclaiming studies.

Preparation of NR Reclaim Using RRM or DADS

One hundred grams ground rubber was milled in a two-roll mixing mill with simultaneous addition of either 10 g RRM or 2 g DADS with 10 g process oil (a mixture of aromatic and naphthenic) separately. Reclaiming was carried out for 35 min milling at 60°C.

Compounding of Reclaim Rubber With Virgin Rubber

Compounding of rubber formulations was carried out in a laboratory size two-roll mixing mill of roll size 6″ × 13″, with friction ratio of 1.2 as per ASTM D 15-54T (1954). Rubber was first masticated to form a band on the front roll of the mill and the compounding ingredients were sequentially added in the order ZnO, stearic acid, carbon black, CBS (accelerator), and sulfur. The mixed stock was finally sheeted off by passing through a small nip of the rolls.

Mooney Viscosity of Rubber Compound

Mooney viscosities of rubber compounds were determined by a Monsanto Mooney Viscometer 2000 at ML (1 + 4) 100°C as per ASTM D 1646.

Cure Characteristics of Rubber Compounds

Cure characteristics of rubber compounds were analyzed with the help of a Monsanto Oscillating Disc Rheometer, R-100 at 150°C. From the rheographs extent of cure, scorch time, optimum cure time, and cure rate index were obtained.

Molding of Rubber Stocks

About 35 g of the compounded rubber stock after 24 h of mixing were placed in a mold (15 cm × 10 cm × 0.2 cm) and pressed between the platens of a hydraulic press (Carver, Model 2518). The samples were cured at 150°C temperature and at applied pressure of 5000 psi for the respective optimum cure times ($t = t_{90}$) obtained from rheographs. After curing, the sheet was taken out of the mold and immediately cooled under tap water to restrict from further curing.

Tensile Properties

The dumb-bell shaped test specimens were punched out from the vulcanized sheet after 24 h of vulcanization by a tensile specimen cutter as per ASTM D15-54T (1954). Moduli at 100%, 200% elongation, tensile strength, and percentage elongation at break were measured following ASTM D412-51T (1957) in a tensile testing machine (KMI, Model 1.3 D) at room temperature (30 ± 2°C) at a uniform speed of separation 20 in./min. Hardness (Shore A) of the vulcanized samples was measured by Hirosima hardness tester as per ASTM D1415-56T.

Aging Characteristics

The dumb-bell shaped test specimens were aged in an air aging oven at 70 ± 2°C. After aging for 24, 48, and 72 h moduli at 100%, 200% elongation, tensile strength, and percentage elongation at break were measured following ASTM D412-51T(1957) in a tensile testing machine (KMI, Model 1.3D) at room temperature (30 ± 2°C) at a uniform speed of separation 20 in/min. Hardness (shore A) and swelling value of the aged specimen were also measured.

Swelling Value

The swelling value (Q) was determined with about 0.5 g of cured samples (accurately weighed). The sample was immersed in 250 mL toluene for 3 days to attain equilibrium swelling. After the equilibrium swelling the sample was taken out and the solvent was blotted from the surface of the sample and weighed immediately. It was then dried under vacuum at 100°C up to constant weight. The swelling value (Q) was calculated from the following equation.[5]

$$Q = (W_S - W_D)/(W_O \times 100)/W_F$$

Where, W_S, W_D, W_O and W_F are swollen weight, dried weight, weight of the original sample, and the formula weight, respectively. Formula weight (W_F) is the total weight of rubber plus compounding ingredients based on 100 parts of rubber.

RESULTS AND DISCUSSION

Compounding of Reclaim Rubber with NR

Compound formulations are presented in Table I. The amounts of the additives such as ZnO, stearic

Table I Mix Formulation of Rubber Compounds

	Formulation Code[a]												
Ingredients (phr)	1	2	3	4	5	6	7	8	9	10	11	12	13
Natural Rubber (NR) (RSS-1)	100	50	50	50	50	50	75	60	40	75	60	50	40
Reclaim Rubber (RR) (RRM as reclaiming agent) (15- and 35-min milled reclaim)	—	50	50	50	50	50	25	40	60	—	—	—	—
Reclaim Rubber (RR) (DADS as reclaiming agent) (15- and 35-min milled reclaim)	—	—	—	—	—	—	—	—	—	25	40	50	60
N-cyclohexyl thiophthalimide	—	—	—	—	0.10	0.25	—	—	—	—	—	—	—
Carbon black (N330)	40	20	30	40	30	30	35	32	28	35	32	30	28
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2
CBS	1	1	1	1	1	1	1	1	1	1	1	1	1
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
Curing characteristics (35-min milled reclaim)													
Optimum cure time, t_{90}, min	8.5	5.5	5.75	6.25	7.0	7.25	6.0	5.75	5.5	7.75	7.5	7.0	6.25
Scorch time, t_{s2}, min	3.5	1.5	1.5	1.5	2.0	2.25	1.5	1.25	1.0	2.5	2.0	1.5	1.25
Extent of cure, dNm	65.0	64.5	65.5	69.7	66.7	63.7	64.4	65.0	66.8	67.5	72.0	73.0	73.4
Cure rate index, min^{-1}	20.0	25.0	21.0	21.0	21.05	19.05	22.2	23.5	20.0	19.0	18.2	18.2	20.0
Curing characteristics (15-min milled reclaim)													
Optimum cure time, t_{90}, min	—	—	5.75	—	—	—	6.75	6.5	5.5	7.25	6.0	6.0	6.0
Scorch time, t_{s2}, min	—	—	1.5	—	—	—	2.5	1.75	1.0	2.0	1.5	1.5	1.25
Extent of cure, dNm	—	—	75.6	—	—	—	71.8	75.0	71.6	67.8	71.3	73.1	72.6
Cure rate index, min^{-1}	—	—	25.0	—	—	—	23.5	21.0	21.0	19.0	22.2	22.2	21.0

[a] Rubber compounds were cured at 150°C for respective optimum cure time.

acid, CBS, and sulfur were used based on 100 g rubber irrespective of the amount of reclaim rubber used in the compound, because it was observed that the additives in NR reclaim originated from parent compound were inactive.[21] Formulation 1, 2, and 4 contain 40 phr carbon black on the basis of 100 g fresh rubber and formulation 3, 5, and 6–13 contain 40 phr black per 100 g fresh rubber and 20 phr black per 100 g reclaim rubber. Formulations 1–4 were made to study the effect of carbon black on the performances of reclaim rubber in the blend and formulations 5 and 6 were made to see the influence of a retarder on the curing behavior. Effect of milling time and performances of reclaim rubber at varied proportions were studied with the formulations 7–13. Formulations 1–9 contain RRM reclaim and formulations 10–13 contain DADS reclaim. During compounding with the carbon black it has been observed that with the progressive loading of carbon black, its incorporation and dispersion become gradually difficult. With higher amounts of carbon black the compound becomes stiff and the temperature goes high because of higher shearing action required for better dispersion.

Effect of Milling Time on Properties of Reclaim

To study the effect of milling time during reclaim rubber preparation using specific amount of reclaiming agent (10 g RRM/2 g DADS) at 60°C, 15 min milled reclaim rubber and 35 min milled reclaim rubber were blended separately with fresh NR at different proportions. Mix formulations are shown in Table I.

It was discussed in our previous communication[21] that 15 min milling of vulcanized rubber for reclaiming produced lower sol fraction, lower molecular weight of the sol, and higher Mooney viscosity, whereas 35 min milling produced reclaim rubber with higher sol fraction, higher molecular weight of the sol, and lower Mooney viscosity. So it was decided to evaluate the performances of these two reclaim rubbers in a blend with fresh rubber. This paper compares the properties of two such reclaim rubbers for establishing their suitability in applications.

Curing Characteristics

Curing characteristics of the rubber compounds containing reclaim rubber as given in Table I show that with the increase in carbon black loading optimum cure time increases but scorch time remain unaltered in all the cases. Such low scorch time data shows the reclaim rubber to be scorchy in nature. The increase in the extent of cure is due to the higher proportion of carbon black used in such formulations.

It is found from Table I that inclusion of PVI has increased the scorch safety period (compare formulations 2, 3, and 4) but the increase in the proportion of PVI has marginally increased the optimum cure time (t_{90}). It appears from the results that increasing the level of PVI beyond 0.25 phr may increase the scorch safety. The increase in optimum cure time and scorch safety time by addition of PVI finds advantage in curing of thick items such as tires containing reclaim rubber so as to avoid over curing at surface and under curing at the inner bulk. So it is seen that inclusion of PVI in reclaim formulations would be useful for better effects on curing behavior.

Curing characteristics of NR/RR blend compounds containing 15-min milled reclaim rubber (formulations 3 and 7–13) are also shown in Table I. It is evident from the results that with increase in the proportion of reclaim rubber both optimum cure time (t_{90}) and scorch time decrease. The reason for such decrease in optimum cure time and scorch time may be due to the presence of active cross-linking sites in the reclaim rubber that accelerate the cross-linking reaction when the rubber compound is heated at 150°C. The increase in the value of extent of cure may be due to the presence of a rubber network and cross-link precursors in the reclaim rubber. Here the influence of carbon black on the extent of cure is assumed to be absent because these formulations contain same amount of black on the basis of 40 phr black per 100 g fresh rubber and 20 phr black per 100 g RR.

Effects of both 35-min and 15-min milled reclaim rubbers on the curing characteristics of NR/RR blends are also shown in Table I. It is found that formulations containing DADS reclaim showed higher values of optimum cure time (t_{90}) and scorch time (t_{s2}) than those of RRM reclaim formulations. But in both the cases optimum cure time and scorch time decrease with increase in the percent of reclaim rubber. But here the increase in the value of extent of cure is less for 35-min milled reclaim for both RRM and DADS than that for 15-min milled RR/NR blends because of the higher sol fraction present in 35-min milled reclaim rubber.

Evaluation of Tensile Properties of Rubber Compound

Tensile properties, Mooney viscosity, and swelling value of rubber compounds are shown in Table II. From the data in Table II it is seen that with increase in the proportion of carbon black 100% and 200% moduli increase in case of RRM reclaim rubber blends. This is also corroborated by corresponding decrease of swelling value data. From swelling value data it is evident that with increase in the proportion of carbon black swelling value decreases, i.e., cross-link density increases and hence 100% and 200% moduli increase. Tensile strength gradually decreases with increase in carbon black loading. This is because of the fact that when reclaiming was carried out by DADS molecular weight of the sol fraction (9.8×10^3) was found to be lower than that when reclaiming was carried out by RRM (10.5×10^3). The sol portion of the reclaim rubber is supposed to function as a continuous matrix whose molec-

Table II Vulcanizate Properties of NR/RR Blend

	Formulation Code												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Vulcanizate properties (35-min milled reclaim)													
100% Modulus, MPa	1.7	1.9	2.4	4.1	2.2	2.0	2.2	2.2	2.8	2.1	2.4	2.9	3.3
200% Modulus, MPa	4.9	4.3	7.5	10.9	5.3	6.2	5.7	7.8	9.1	6.2	6.5	8.3	8.3
Tensile strength, MPa	22.9	21.2	18.5	16.3	17.6	17.5	21.4	19.1	17.7	21.6	18.1	14.5	12.7
Elongation at break (%)	500	500	400	300	450	450	500	450	400	500	400	400	350
Hardness, Shore A	66	68.3	77.6	82.2	71.3	73.7	68.3	75.0	79.7	67.7	70.3	74.5	74.8
Mooney viscosity	31.3	34.9	45.9	76.1	44.5	45.5	30.4	44.3	52.7	32.5	40.8	45.2	50.9
ML (1 + 4) 100°C	3.0	2.7	2.3	2.0	2.5	2.5	2.7	2.5	2.1	2.9	2.7	2.3	2.2
Swelling value (Q)													
Vulcanizate properties (15-min milled reclaim)													
100% Modulus, MPa	—	—	2.5	—	—	—	1.8	2.4	2.8	2.1	2.3	2.3	2.3
200% Modulus, MPa	—	—	7.2	—	—	—	5.2	6.1	8.0	6.4	6.6	7.1	7.7
Tensile strength, MPa	—	—	15.4	—	—	—	17.9	16.4	14.8	21.5	19.7	17.4	15.4
Elongation at break (%)	—	—	350	—	—	—	450	400	320	450	400	350	320
Hardness, Shore A	—	—	78.2	—	—	—	67.5	73.5	79.2	72.5	74.7	77.0	78.7
Mooney viscosity	—	—	57.8	—	—	—	39.1	51.6	61.1	36.5	48.8	55.4	60.2
ML (1 + 4) 100°C	—	—	2.1	—	—	—	2.7	2.4	2.0	2.9	2.7	2.4	2.3
Swelling value (Q)													

ular weight becomes a determining factor in tensile properties. The reclaim rubber used in these formulations contains 28% sol (RRM) and 29% sol (DADS). So due to lower molecular weight of the sol tensile property may be less in case of DADS reclaim rubber. Elongation at break also decreases with increase in carbon black content. Hardness increases because when higher amount of carbon black was incorporated into rubber compounds vulcanizates become stiffer. Mooney viscosity data also increased when carbon black loading was increased as the rubber compound became stiffer by increase in carbon black loading and, therefore, processing of rubber compounds also became difficult.

From the data in Table I it is found that the presence of PVI puts very little influence on the ultimate properties. It is also true that the retarder functions by stopping the premature cure during processing but are neither supposed to influence the state of cure nor influence the tensile properties.[22,23]

From Table II it is apparent that with increase in the proportion of reclaim rubber 100% and 200% moduli increase but tensile strength and elongation at break decrease. The reason for higher 100% and 200% moduli may be due to higher cross-link density of rubber vulcanizates, arising out of the gel present in reclaim rubber, which is also corroborated by swelling value data. As cross-link density increases in the rubber matrix, chain mobility decreases and more load is required for 100% and 200% elongation. Tensile strength increases with increase in the cross-link density up to certain level and then decreases. When the swelling value (Q) is 3.0 for control (formulation 1) then the tensile strength is maximum. With further decrease in swelling value for other formulations containing reclaim rubber tensile strength gradually decreases.

There is another factor that is also responsible for decrease in the value of tensile strength. Because reclaim rubber contains cross-linked gel when this is blended with virgin rubber, much gel remains as such without dispersing as a continuous matrix with virgin rubber. Such gel remains present as weak sites for stress transmission to its surrounding (continuous matrix) resulting in a lower tensile stress. Elongation at break decreases with the higher percentage of reclaim rubber in both the cases. Hardness and Mooney viscosity increase in both the cases for vulcanizates containing higher amount of reclaim.

Here also 100% and 200% moduli increase with increase in the percent of reclaim rubber in both the cases. Here a peculiar behavior was observed. For RRM reclaim containing vulcanizates tensile strength value for 35-min milled reclaim is higher than that for the 15-min milled reclaim. But for DADS reclaim containing vulcanizate the reverse result is observed. Another direct proof of better compounding characteristics of NR/RR (35-min milled reclaim) blends is their lower Mooney viscosity data than that for the 15-min milled reclaim. Swelling value also decreases with increase in the proportion of reclaim rubber. But the swelling values of NR/RR (15-min milled reclaim) and NR/RR (35-min milled reclaim) are almost same, i.e., cross-link density in both the cases is almost equal.

Aging Characteristics of NR/RR Blends

Because aging characteristics of the rubber compounds containing reclaim rubber need attention, accelerated aging tests were also performed with the compounds as formulated in Table I. The results of aging studies with the formulations 2, 3, and 4 containing reclaim rubber have been compared with those of a control formulation 1 without reclaim rubber. Tensile properties, hardness, and swelling value of NR/RR blend vulcanizates were measured after 24, 48, and 72 h aging at 70 ± 2°C in an air aging oven. Percent retention of 200% modulus, tensile strength, and elongation at break after aging is shown in Figure 1. From Figure 1 it is seen that vulcanizate containing 20 phr carbon black shows lower retention of properties on 24 h aging, whereas after 72 h aging retention of properties increases; that means with aging 200% modulus continuously increases. Higher loading (30 phr) of carbon black has not affected the 200% modulus and the aging time has not shown a big difference in modulus value that is observed in the case of 20 phr loading. The same trend is also observed for retention of 100% modulus. A peculiar behavior in retention of tensile properties was observed for different carbon black loaded samples. It has been found from Figure 1 that retention of tensile properties is very less when 20 phr carbon black was added to the rubber compound. But for 30 phr carbon black loading retention of tensile strength value is the highest compared with 20 phr and 40 phr carbon black loaded vulcanizates. These results show the effectiveness of 30 phr carbon black in the 50:50 (NR/RR) blend to get better properties. In this connection it is interestingly observed that the aging performances of formulations containing reclaim rubber are better than the control formulation that does not contain any reclaim rubber. This phenomenon shows some antiaging characteristics of reclaim rubber. That is if such reclaim rubbers are used in any product formulation the use of antioxidants may be partially reduced or even altogether excluded. Such characteristics of this reclaim indicate a better future in its favor. Here also a higher percent retention value of elongation at break was observed for the 30 phr carbon black loaded NR/RR blend vulcanizate. Loading of 40 phr carbon black may not be effective because when such amount of carbon black was added to the rubber compound then compounding became difficult, temperature increased during processing, and rubber compound became stiffer.

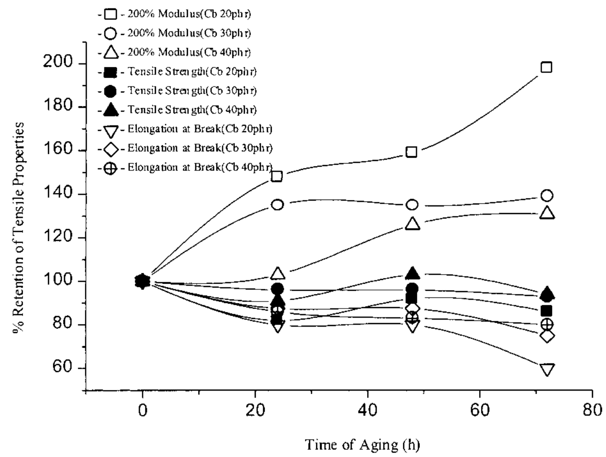

Figure 1 Effect of time of aging on vulcanizate properties of different carbon black loaded vulcanizate.

Aging characteristics of NR/RR blends containing 15-min milled reclaim rubber is shown in Figures 2–4. Tensile properties of NR/RR blends were measured after 24, 48, and 72 h aging at 70 ± 2°C in an air aging oven. Percent retention of 200% modulus, tensile strength, and elongation at break after aging are shown in Figures 2–4. During aging modulus at 200% elongation (Fig. 2) increases due to increase in cross-link density. For virgin NR vulcanizate (control formulation 1) tensile strength (Fig. 3) gradually decreases with aging. But for formulations containing reclaim

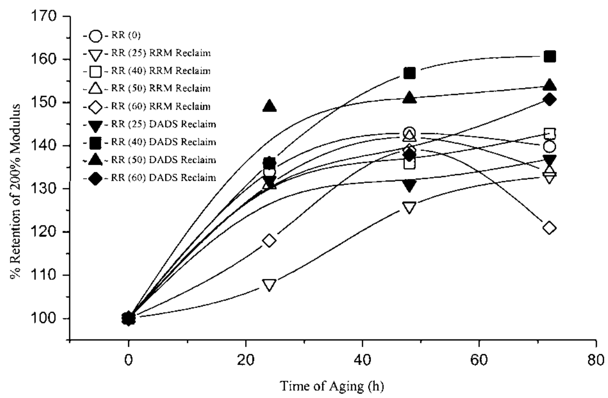

Figure 2 Effect of time of aging on % retention of 200% modulus of 15-min milled RRM and DADS reclaim containing vulcanizate.

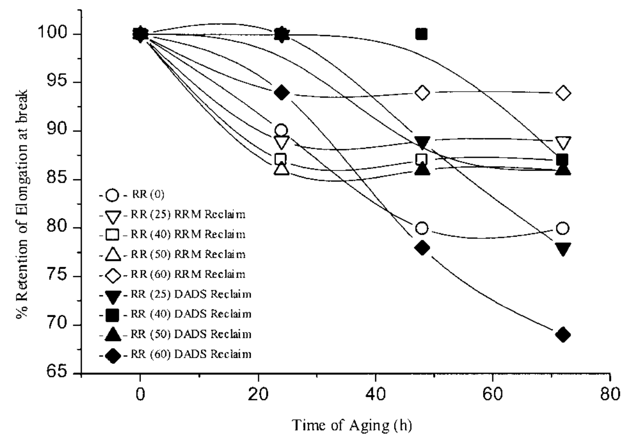

Figure 4 Effect of time of aging on % retention of elongation at break of 15-min milled RRM and DADS reclaim containing vulcanizate.

rubber with increase in the proportion of reclaim rubber percent retention of tensile strength increases with aging. Here RRM reclaim shows better aging properties than DADS reclaim. Percent retention of elongation at break (Fig. 4) decreases in both the cases with aging.

Tensile properties of NR/RR blends containing 35-min milled reclaim rubber were measured after 24, 48, and 72 h aging at 70 ± 2°C and the results are shown in Figures 5–7. It has been found that percent retention of 200% modulus (Fig. 5) increases with aging in all the blends both for RRM or DADS reclaim containing vulcanizates. This is because that during aging cross-link density increases. But the increase in the value of percent retention of 200% modulus is higher for 35-min milled reclaim rubber blends than 15-min milled reclaim rubber blends. This is because of the fact that 35-min milled reclaim rubber may contain some active cross-linking sites that form cross-link bonds during aging. Here also RRM reclaim rubber blends show better antiaging property than DADS reclaim rubber blends. Percent retention of tensile strength is shown in Figure 6. From the result it has been found that reclaim rubber containing vulcanizate shows better aging resistance than that of the virgin NR vulcanizate. Percent retention of elongation at break (Fig. 7) also shows better result for RRM reclaim rubber blends. Here on prolonged aging

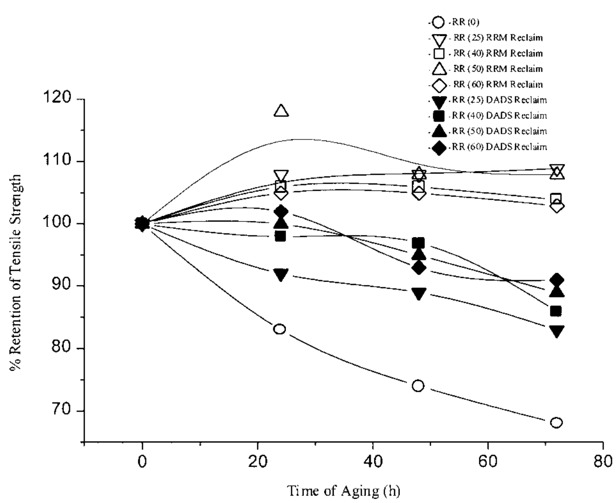

Figure 3 Effect of time of aging on % retention of tensile strength of 15-min milled RRM and DADS reclaim containing vulcanizate.

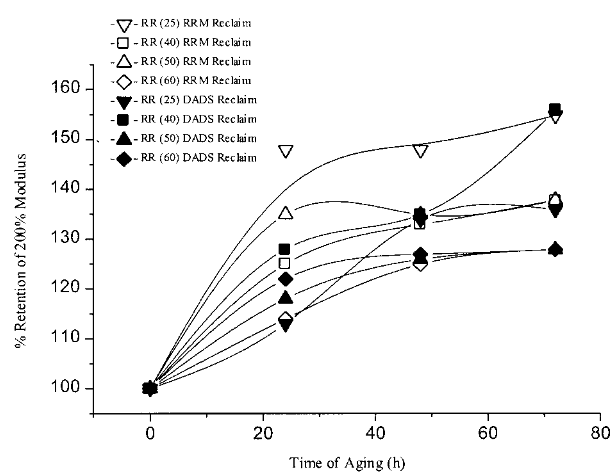

Figure 5 Effect of time of aging on % retention of 200% modulus of 35-min milled RRM and DADS reclaim containing vulcanizate.

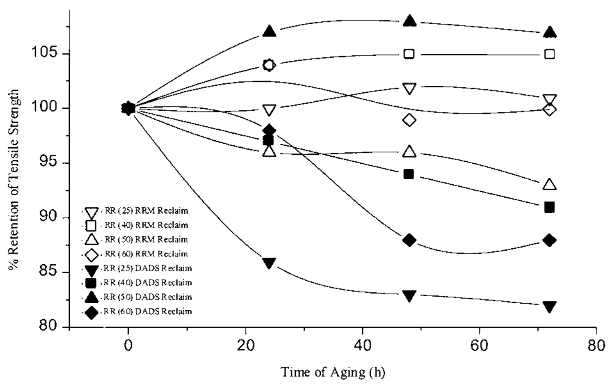

Figure 6 Effect of time of aging on % retention of tensile strength of 35-min milled RRM and DADS reclaim containing vulcanizate.

elongation at break marginally decreases or remains almost same.

Swelling Value

Changes of swelling value with time of aging are shown in Figure 8 for RRM reclaim rubber containing vulcanizates. Here it is found that swelling value gradually decreases with progressive aging. The reason for such behavior is due to the increase in cross-link density during aging.

CONCLUSION

The use of reclaim rubber, prepared in this investigation, when blended with virgin rubber has been found to reduce the tensile strength by about 6% for 25% reclaim containing vulcanizate and 16% for 40% reclaim containing vulcanizate. Reclaim rubber being scorchy in nature, the scorch safety of reclaim containing formulations has been found to be improved by the use of PVI. It is observed that the aging performances of rubber formulations containing reclaim rubber and having no antioxidant are better than the control formulation which does not contain any reclaim rubber.

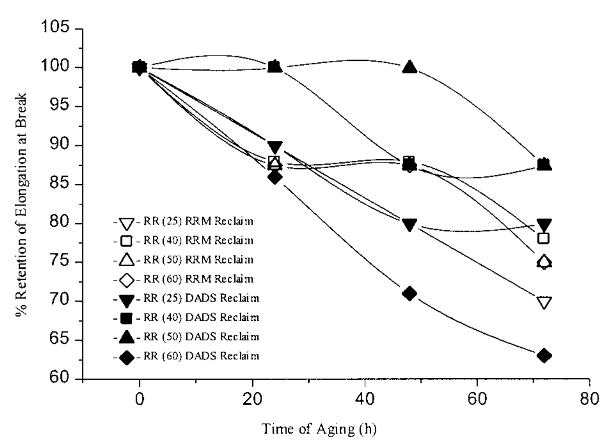

Figure 7 Effect of time of aging on % retention of elongation at break of 35 min milled RRM and DADS reclaim containing vulcanizate.

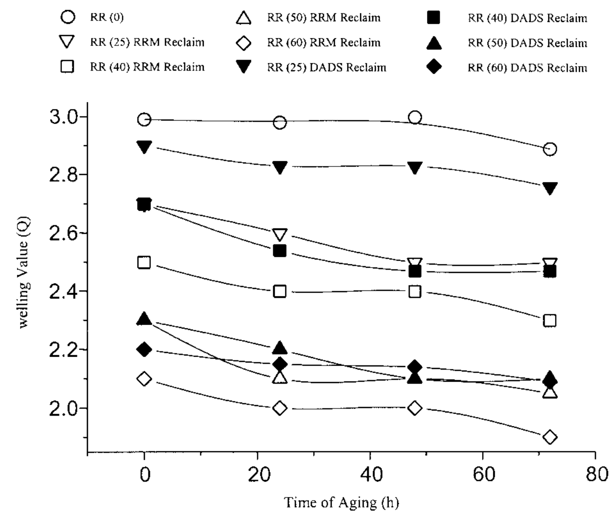

Figure 8 Effect of time of aging on swelling value of 35 min milled RRM and DADS reclaim containing vulcanizate.

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REFERENCES

1. Klingensmith, B. Rubber World 1991, 203 (6), 16.
2. Chopey, N. P. Chem Eng 1973, 80, 54.
3. Burgogue, M. D.; Leaker, G. R.; Kretic, Z. Rubber Chem Technol 1976, 49, 375.
4. Accetta, A.; Vergnaud, J. M. Rubber Chem Technol 1981, 54, 302.
5. Accetta, A.; Vergnaud, J. M. Rubber Chem Technol 1982, 55, 961.
6. Phadke, A. A.; Bhattacharya, A. K.; Chakraborty, S. K.; De, S. K. Rubber Chem Technol 1983, 56, 726.

7. Köhler, R.; O'Neill, J. Rubber World 1997, 216 (2), 32.
8. Sekhar, B. C. European Patent Application, EP 0690091 AL
9. Menadue, F. B. Rubber Age 1945, 56, 511.
10. Twiss, D. F.; et al. British Patent 577,868, 1946; and 578,482, 1946.
11. Hildebrandt, H. German Patent 1,244,390, 1967.
12. Yamashita, S.; Kawabata, N.; Sagan, S.; Hayashi, K. J Appl Polym Sci 1977, 21, 2201.
13. Kawabata, N.; Okuyama, B.; Yamashita, S. J Appl Polym Sci 1981, 26, 1417
14. Stalinski, E. France Patent 1,1517,694, 1968.
15. Warner, W. C. Rubber Chem Technol 1994, 67, 559.
16. Myhre, M. J.; MacKillop, D. A. Rubber World 1996, 214, 42.
17. Tapale, M.; Isayev, A. I. J Appl Polym Sci 1998, 70, 2007.
18. Isayev, A. I.; Chen, J.; Tukachinsky, A. Rubber Chem Technol 1995, 68, 267.
19. Tukachinsky, A.; Schworm, D.; Isayev, A. I. Rubber Chem Technol 1996, 69, 92.
20. Yu. Levin, V.; Kim, S. H.; Isayev, A. I.; Massey, J.; Von Meerwall, E. Rubber Chem Technol 1996, 69, 104.
21. De, D.; Maiti, S.; Adhikari, B. J Appl Polym Sci 1999, 73, 2951.
22. Stewart, S. J.; Leib, R. I.; Kerwod, J. E. Rubber Age (NY) 1970, 102, 56.
23. Leib, R. I.; Sullivan, A. B.; Trivette, Jr., C. D. Rubber Chem Technol 1970, 43, 1188.