Reclaiming of Rubber by a Renewable Resource Material (RRM). II. Comparative Evaluation of Reclaiming Process of NR Vulcanizate by RRM and Diallyl Disulfide

DEBAPRIYA DE, SUKUMAR MAITI, BASUDAM ADHIKARI

Materials Science Centre, IIT Kharagpur 721302, India

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ABSTRACT: Sulfur cured natural rubber vulcanizates were reclaimed by a vegetable product and diallyl disulfide under various reclaiming conditions. Progress of reclaiming was monitored by estimating the sol and gel portions, molecular weight determination of sol portions, and Mooney viscosity of reclaimed rubber. Tensile properties and swelling characteristics of revulcanized reclaim rubber were studied. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2951–2958, 1999

Key words: renewable resource; reclaiming agent; diallyl disulfide; Mooney viscosity; reclaiming

INTRODUCTION

One of the various problems that humankind faces as it enters the 21st century is the problem of waste utilization and management. Since polymeric materials do not decompose easily, disposal of waste polymers including rubbers is an important environmental problem. Recycling of waste/scrap rubber not only solves the waste disposal problem and maintains environmental quality, but also saves the valuable and limited resource of fossil feedstock. It is reported that approximately three to five billion tires are piled up across America and the volume is increasing every year by 250 to 275 million a year.¹ Of the 49% being recycled, 30% is burnt for energy recovery and 13% is used for retreading. Only 2% are being used for civil engineering application and 2% for crumb rubber.²

Considerable attention has been given to reclaiming of scrap rubber by physical and chemical reclaiming processes. Different types of physical reclaiming processes reported so far are mechanical,^{3–5} thermomechanical,⁶ cryomechanical,⁷ microwave,⁸ and ultrasound^{9,10} methods.

In the chemical reclaiming process, a large number of chemical reclaiming agents—viz., diphenyl disulfide, dibenzyl disulfide, diamyl disulfide, ^{11,12} bis(alkoxy-aryl) disulfides, ¹³ butyl mercaptans, thiophenols, ^{14–16} xylene thiol, ^{15–17} other mercaptans, ^{18–21} phenol sulfides and disulfides, ^{22–27} iron oxide phenyl hydrazine based catalyst, ^{28–31} and copper chloride-tributyl amine catalyst³² have been used for treatment of scrap ground rubber crumbs or powders at elevated temperatures. In a recent review Warner³³ has nicely summarized the action of various chemical probes on vulcanized rubber and the use of various chemicals as well as wave methods as a means of rubber reclaiming.

Nevertheless, in all the above physical or chemical reclaiming processes except the ultrasound method the extent of reclaiming has not been evaluated or reported. In addition, the product of such reclaiming processes was a soft and weak mass that was neither characterized nor analyzed for the composition of reclaim. Probably because of a biased concept that reclaiming occurs by scission of sulfur crosslink bonds, the incidence

Correspondence to: B. Adhikari.

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Ingredients	Phr
Natural rubber (RSSI)	100
Zinc oxide	5
Stearic acid	2
CBS	1
Sulfur	1.75
N330 Carbon black (HAF)	40

of carbon chain scission and retaining of carbon black polymer gel during reclaiming were not investigated. It is either apparent or appropriate to believe that both the physical and chemical reclaiming processes involve polymer chain scission due to mechanical shearing at low or high temperatures, chemical action at high temperature, thermal scission, or ultrasound energy at high temperatures. The chain scission of vulcanized rubber during reclaiming is, therefore, supposed to increase plasticity as well as the sol content.

The monitoring of the Mooney viscosity of reclaim rubber will give an idea about the extent of breakdown of the rubber chains and hence the extent of reclaiming. A few workers^{34,35} reported the Mooney viscosity of reclaim rubber, but they did not determine the amount (percentage) of the sol fraction of the reclaim rubber and its molecular weight. However, it was reported that the ultrasound treatment of SBR resulted in low molecular weight $[M_n = 2-4 \times 10^3]$ of the sol fraction. These workers also reported the effect of various processing conditions on reclaiming.

In the present investigation we have reclaimed vulcanized rubber by mechanical milling in the presence of reclaiming agent and studied the extent of reclaiming action through measurement of sol-gel fraction, molecular weight of the sol fraction and Mooney viscosity of reclaim rubber as a function of milling time, reclaiming temperature and concentration of reclaiming agent. The tensile properties and swelling characteristic of the revulcanized reclaim sample were evaluated. The effects of reclaiming action of RRM and those of diallyl disulfide,³⁶ which is the major constituent³⁷ of RRM, have been compared while monitoring the progress of reclaiming.

EXPERIMENTAL

Materials

The renewable resource material (RRM), which is a vegetable product having the major constituent diallyl disulfide, was procured from the local market. Other constituents of RRM are cyclic monosulfides, polysulfides, different disulfides, and sulfone compounds. Being proprietary in nature and for patent application, the name of RRM is not disclosed. Natural rubber (NR) (RSSI), diallyl disulfide (DADS) (Aldrich Chem, USA), zinc oxide (S. D. Fine Chem), stearic acid (Loba Chemie), sulfur (S. D. Fine Chem), *N*-cyclohexyl-2-benzothiazylsulfenamide (CBS) (ICI Ltd.), N330 carbon black (Phillips Carbon), and toluene (S. D. Fine Chem) were used as received.

Preparation of RRM

RRM was made into an aqueous paste by compressive shearing followed by squeezing through cheesecloth to obtain a liquid mass. The water in the liquid mass was removed by desiccation over anhydrous calcium chloride. This liquid having organic matter was used as such for reclaiming of natural rubber vulcanizate. The vegetable product extract contains 40% organic matter.

Preparation of Vulcanized and Aged Rubber Sample for Reclaiming

Compounding of NR with various additives (Table I) for the reclaiming study was done in a two-roll

 Table II Composition of Reclaiming Agents per 100 g Vulcanized NR at Different Milling

 Temperatures

Ingredients			Compos	itions at Mil	ling Tempera	ature (g)		
		60)°C			40	0°C	
RRM ^a	10	20	_	_	10	20	_	_
DADS	_		2	4	_		2	4
Spindle oil (Process oil)	10	10	10	10	10	10	10	10

^a Containing 40% organic matter.



Figure 1 Effect of RRM and DADS on percent sol fraction at 40° C.

mixing mill at a friction ratio 1.2. This rubber compound was vulcanized at 150°C for optimum cure time (8.5 min), which was obtained from an Oscillating Disc Rheometer. 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.

Reclaiming Process

Vulcanized and aged ground natural rubber was milled in a two-roll mixing mill with simultaneous addition of the RRM or DADS solution in process oil (Table II). The reclaiming was carried out with different concentrations of reclaiming



Figure 2 Effect of RRM and DADS on percent sol fraction at 60°C.



Figure 3 Effect of RRM and DADS on molecular weight of sol at 40°C.

agents for different milling times at different temperatures (40 and 60°C).

Monitoring of Reclaiming

Sol-Gel Determination

After reclaiming by the above milling process at different milling times, small pieces of samples were cut and placed in toluene for 5 days at 30°C for sol-gel determination. Gel was filtered, washed with toluene, and dried to constant weight.

Molecular Weight of Sol Fraction

The molecular weight of the sol fraction was determined by the solution viscosity method. Viscosity of sol fraction of reclaimed rubber in toluene was measured with a Ubbelohde Capillary Viscometer at 25°C. Viscosity average molecular weight of the sol polymer was determined by using the equation³⁸ $[\eta] = 50.2 \times 10^{-5} (M_v)^{0.667}$.

Mooney Viscosity of Reclaim Rubber

Mooney viscosities of reclaim rubber samples were determined by a Monsanto Mooney Viscometer 2000 at $ML(1 + 4)100^{\circ}C$ as per American Society for Testing and Materials D1646.

Revulcanization Characteristics

The rubber after reclaiming was revulcanized at its respective optimum cure time ($t_{90} = 7 \text{ min}$) at similar vulcanization conditions followed for fresh rubber vulcanization. Swelling values of the fresh vulcanizate and revulcanized samples were mea-

		Milling at 40°C						Milling at 60°C					
	15 Minute Milling			35 Minute Milling		15 Minute Milling			35 Minute Milling				
Reclaiming Agent	% Sol	${f Mol} {Wt imes 10^{-4}}$	Mooney Viscosity	% Sol	$egin{array}{c} { m Mol} \ { m Wt} imes \ { m 10}^{-4} \end{array}$	Mooney Viscosity	% Sol	${f Mol} {Wt imes 10^{-4}}$	Mooney Viscosity	% Sol	$egin{array}{c} { m Mol} \ { m Wt} imes \ { m 10}^{-4} \end{array}$	Mooney Viscosity	
10 g RRM 20 g RRM 2 g DADS 4 g DADS	21.0 19.8 24.5 23.0	$0.28 \\ 0.27 \\ 0.49 \\ 0.49$	200.0 200.0 107.2 145.5	26.5 27.0 31.0 32.0	$0.80 \\ 0.83 \\ 1.35 \\ 1.41$	83.5 85.6 58.5 62.4	$18.0 \\ 22.4 \\ 25.0 \\ 23.0$	0.51 0.50 0.38 0.94	$97.9 \\ 200.0 \\ 54.1 \\ 89.9$	28.0 29.0 29.0 32.3	$1.05 \\ 1.68 \\ 0.98 \\ 1.38$	61.5 76.7 26.2 51.8	

Table IIIEffects of Concentration of Reclaiming Agent, Milling Time, and Temperature on SolContent, Mol Wt of Sol, and Mooney Viscosity

sured. The tensile strength, elongation at break, and Shore A hardness of the revulcanized samples were also measured. temperature, and concentration of the reclaiming agent. Compositions of reclaiming agents at different milling temperatures are shown in Table II.

RESULTS AND DISCUSSION

The composition of the rubber vulcanizate used for reclaiming is shown in Table I. Vulcanized rubber sheets were aged for 72 h at 70°C in order to maintain the analogy with aged scrap rubber products. In order to know the mechanism of the reclaiming processes occurring during milling of vulcanized and aged rubber with RRM and DADS, it was necessary to examine the sol-gel fractions, molecular weight of the sol fraction, and Mooney viscosity of reclaim rubber as functions of the treatment parameters such as milling time,

Effects of Reclaiming on Sol Content

Figures 1 and 2 show the percentage of sol fraction as function of milling time at varied concentration of reclaiming agents (RRM and DADS) and temperature. When reclaiming is carried out either by RRM or by DADS at 40° or 60°C, the sol fraction gradually increases with the increase in milling time. It is found from Table III that in all the cases the highest sol fraction is obtained at 35 min milling, showing a major dependence of sol percent on milling time because during milling vulcanized rubber samples undergo tremendous mechanical shearing, resulting in random poly-



Figure 4 Effect of RRM and DADS on molecular weight of sol at 60°C.



Figure 5 Effect of heating on molecular weight of sol with and without the addition of RRM and DADS.

mer chain breakdown. Then the RRM, the major constituent of which is diallyl disulfide, also breaks into radicals as the temperature rises due to mechanical shearing. Such radicals combine with the broken polymer chain radical and thereby prevent the recombination of these polymer radicals, which explains the increase of sol fraction with increase in milling time.

Effects of Reclaiming on Molecular Weight of Sol

Figures 3 and 4 show the molecular weight of sol fraction as a function of milling time at varied concentration of reclaiming agents and temperature. In Figures 3 and 4 it is found that the molecular weight of the sol fraction obtained at lower milling time is lower than that obtained at lower milling time. The reason for such an effect was thought to be due to the mechanical shearing of the vulcanized rubber network and due to the action of RRM or DADS present during reclaiming by milling.

To verify the above observation, the sol fraction obtained after 25 min milling during reclaiming at 60°C was separately heated (at 60°C) with or

without RRM (10 g/100 g rubber) and DADS (2 g/100 g rubber) and the molecular weights of the heat treated sols were measured. It is seen from Figure 5 that when RRM or DADS was added to the sol fraction of 25 min milled sample, the molecular weight of the sol fraction increases with increase in heating time. But when the sol fraction was heated without the reclaiming agent, first molecular weight increases and reaches a maximum, but it then attains almost a constant value. It should be noted also that in the former case, although a continuous rise of molecular weight is observed, the maximum molecular weight is always lower than the latter case (without DADS or RRM). Thus from Figures 3 and 4 it is clear that in presence of reclaiming agents the molecular weight of the sol fraction increases with the milling time. The reasons for such behavior are explained with the help of the proposed reaction schemes.

Scheme 1: Mechanical Milling in Presence of Reclaiming Agent



Radical capping (Molecular weight reduction)

The above steps represent the formation of low molecular weight sol fraction. This may also be supported by the findings of Watson and co-workers³⁹ by mastication of a radioactive labeled disulfide with natural rubber in an attempt to prove the peptizing action of the disulfide and the formation of a C-S bond. Furthermore, since RRM or DADS is added at the beginning of milling, the concentration of RRM or DADS gradually decreases with progressive milling. As a result, end capping of the shear generated low molecular weight radicals (I, II, III, and IV) by the RS radical gradually decreases with milling time. Therefore, such fragmented uncapped polymer radicals of the sol fraction may couple themselves, leading to chain extension (molecular weight increase) during the final part of the milling.

Scheme 2: Heating of Sol Fraction Without RRM or DADS at 60°C

In order to verify the phenomenon of increasing molecular weight of sol fraction with the progress of milling, in a separate experiment the sol fraction was heated at 60°C in absence of RRM or DADS. We propose the following reactions,

which supports the increase in molecular weight of the sol up to a certain maximum value without further increase.

Scheme 3: Heating of Sol Fraction with RRM or DADS at 60°C

On continued heating, the sol fraction containing the species V–VIII in the presence of RRM/DADS may subsequently undergo decomposition followed by chain extension and gradual increase in molecular weight. This also explains the lower molecular weight of sol when heated up to 150 min in the presence of RRM/DADS than that in absence of the same (Figure 5). This may also be logically explained by the lower bond energy of the C—S (65 kcal/mole) bond than that of the C—C bond (83 kcal/mole). So on prolonged heating, breaking of the C—S bond takes place and molecular weight increases by forming C—C bonds in presence of a reclaiming agent on heating.

Staudinger and Bondy^{40,41} suggested that cold mastication is not a conventional thermal reaction. But the required energy is supplied directly as mechanical energy. The molecules are ruptured by the shearing forces imposed during the deformation of the bulk rubber. This hypothesis was expressed more specifically by Kauzman and Eyring⁴² as the direct breakage of C—C bonds of the polymer backbone into free radicals as shown in the following scheme.Bateman⁴³ demonstrated that when two polymers of the types R-R and S-S are masticated together in the absence of radical acceptors, one or both may be mechanically ruptured.



The polymeric radicals R^{\cdot} and S^{\cdot} may then undergo further reactions exemplified by the following reactions:



Such types of reactions were termed "interpolymer formation." Angier and Watson^{44,45} also showed polymer interlinking when pairs of polymers like natural rubber with styrene butadiene rubber and acrylonitrile-butadiene rubber with polychloroprene were masticated together. Thus these reports also show increase in molecular weight during milling through grafting.

Effect of Reclaiming on Mooney Viscosity

Figures 6 and 7 show the Mooney viscosity of reclaimed rubber as a function of milling time at varied concentrations of reclaiming agent and temperatures. It is observed in Figures 6 and 7 that Mooney viscosity of reclaim rubber decreases



Figure 6 Effect of RRM and DADS on Mooney viscosity of reclaimed rubber at 40°C.

with increase in the milling time at both 40 and 60°C, and also in the case of RRM and DADS. The lowest Mooney viscosity was achieved at 35 min milling time at 60°C. Such an effect is more pronounced in the case of diallyl disulfide as the reclaiming agent. It is also observed that the lowest Mooney viscosity is obtained by adding lower concentration of RRM or DADS at 60°C than at 40°C. It has been found that the Mooney viscosity of virgin NR unvulcanized compound is 31.3 units, which is comparable with that of devulcanized NR reclaim by 2 g DADS at 60°C after 35 min milling (Table III), whereas, using 10 g RRM as reclaiming agent after 35 min milling at 60°C the reclaimed mass has shown a Mooney viscosity of 61.5 units (Table III). In a separate experiment when the same reclaim rubber was blended with 60% virgin rubber, the Mooney viscosity of such compound was 44.3 units. This data compares well with that of a tire compound.⁴⁶

Effect of Reclaiming on Tensile Properties

Table IV shows the tensile properties and swelling values of fresh vulcanizate, revulcanized NR reclaim obtained by reclaiming with RRM and DADS and a blend of NR reclaim and fresh rubber. It is observed that tensile strength, elongation at break, and Shore A hardness are less in the case of revulcanized sample compared to those of fresh vulcanizates. The reason for such a decrease in tensile properties may be explained from the swelling value (Q). It has been found that, in the case of the revulcanized sample, the swelling value is much higher, which means the crosslink density is very low. Since tensile strength is a function of crosslink density, tensile strength of revulcanized NR reclaim is lower due to its low crosslink density (high swelling value). The percent retention of tensile strength of revulcanized NR reclaim with respect to fresh vulcanizate is 19 and 15.4% when reclaimed by RRM and DADS, respectively. Similarly, the percent retention of elongation at break of the revulcanized reclaim is 57 and 60% when reclaimed by RRM and DADS, respectively. But when such reclaim rubber is blended with fresh rubber (60%) along with sulfur, accelerator, and carbon black, tensile properties increase over that of revulcanized NR and is close to that of fresh NR (Table IV). Detailed study for the use of reclaim rubber will be published in a article.

CONCLUSION

The results of this investigation have revealed a definite influence of reclaiming agent and milling conditions on the molecular weight of the sol, sol content, and viscosity of the reclaim rubber. Achievement of higher fraction of the sol as well as higher molecular weight of the sol after reclaiming will increase the quality of reclaim rubber.

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Figure 7 Effect of RRM and DADS on Mooney viscosity of reclaimed rubber at 60°C.

Nature of the Vulcanizate	Tensile Strength (MPa)	Elongation at Break (%)	Shore A Hardness	Swelling Value (Q)	Weight Loss After Eq. Swelling (%)
Vulcanized NR	22.88	500	66	2.99	1.79
Revulcanized NR reclaim by RRM	4.34	283	34	5.52	2.98
% Retention	19.00	57.0	51.5	184.0	_
Revulcanized NR reclaim by DADS	3.52	300	33	6.60	3.31
% Retention	15.40	60	50	220.7	
Reclaim NR, fresh NR blend ^a (RR : NR = $40 : 60$)	19.13	450	75	2.5	3.57
% Retention	83.60	90	114	84	

Table IV Tensile Properties of Revulcanized NR Reclai	m
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^a Formulation (phr): RR: 40; NR (RSSI): 60; Zno: 5; stearic acid: 2; CBS: 1; sulfur: 1.75; carbon black: 32; vulcanized at 150°C for 5.75 min.

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