

Recycling of NR Based Cured Latex Material Reclaimed with 2,2'-Dibenzamidodiphenyldisulphide in a Truck Tire Tread Compound

V. V. Rajan,¹ W. K. Dierkes,¹ R. Joseph,² J. W. M. Noordermeer¹

¹Faculty of Science and Technology, Department of Rubber Technology, University of Twente, 7500 AE Enschede, The Netherlands

²Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi - 22, Kerala, India

Received 27 October 2005; accepted 12 February 2006

DOI 10.1002/app.24563

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: It is observed that reclamation of natural rubber latex based rubber using 2,2'-dibenzamidodiphenyldisulphide as reclaiming agent is an optional methodology for recycling of waste latex rubber (WLR). For progressive replacement of virgin natural rubber by the reclaim, two alternatives curing system were investigated: adjustment or reduction of the curing system with increasing reclaim content, to compensate for the extra amount of curatives brought along by the reclaim. For fixed curing system, as if the reclaim were equivalent to virgin NR. The cure behavior, final crosslink density and distribution, mechanical properties, and dynamic viscoelastic properties of the blends with reclaimed WLR are measured and compared with the virgin compound. The

morphology of the blends, sulfur migration, and final distribution are analyzed. The mechanical and dynamic viscoelastic properties deteriorate for both curing systems, but to a lesser extent for fixed curing system compared to adjusted curing system. With the fixed cure system, many properties like tensile strength and compression set do still deteriorate, but $\tan \delta$ and M_{300}/M_{100} , representative for the rolling resistance of tires are improved. On the other hand, with the adjusted cure system both mechanical and dynamic properties still deteriorate. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4194–4206, 2006

Key words: recycling; rubber; compounding; tire tread; diphenyldisulphides

INTRODUCTION

In almost all commercial applications, the reclaimed rubber is used in a blend with virgin rubber. Incorporation and dispersion of reclaim rubber into the virgin rubber plays important roles in product quality and production economy. Good and consistent dispersion is essential for optimum vulcanizate properties.

Myhre and MacKillop¹ describe a reclaiming process based on mixing of plasticizers, reactive chemicals that can break sulfur bonds and a catalyst to speed up the process with powdered rubber. Using this process, a material with moderate properties was produced. This process bears a close resemblance to another technique known as the Trelleborg cold reclaim (TCR) process.² In this process, cryogenically ground rubber is mixed in a stirred device with plasticizers and a reactive agent. A powder is produced, which compacts easily upon milling and has a Mooney viscosity of 50–80 MU. Phenylhydrazine metal oxide is mentioned as a possi-

ble reactive agent and diphenylguanidine as a less efficient but milder agent. Physical properties of compounds with either TCR powder or untreated crumb do not differ greatly up to 20%. At higher concentrations, the TCR powder performs better. At higher levels of untreated crumb, processing becomes difficult due to the increased Mooney viscosity; with TCR the viscosity is not increased. The advantage of these two processes is that they are very energy-efficient.

Isayev and coworkers^{3–5} studied the devulcanization of different rubbers using an ultrasonic reactor at various temperatures. Gel fraction, crosslink density, mechanical properties, and dynamic properties were also determined for the virgin vulcanizate, the ultrasonically devulcanized rubber, and the revulcanized rubber. Kohler⁶ reported a technology for the devulcanization of sulfur cured scrap elastomers using a material developed by Sekhar.⁷ They did a comparative study of a fully virgin NR compound and the same compound containing 30% of devulcanized rubber. The Mooney viscosity and 300% modulus was higher, whereas tensile strength, elongation at break, and tear strength was lower for the reclaim blend. However, the influence of reclaim on the mechanical properties was not very strong.

Correspondence to: J. W. M. Noordermeer (J.W.M.Noordermeer@utwente.nl).

TABLE I
Materials Used for the Study

Component	Source	
	CUSAT	UT
NR	Rubber Research Institute of India (ISNR 3)	Standard Indonesian Rubber (SIR 20)
BR	Indian Petrochemicals Corporation Ltd.	Korea Kumho Petrochemical Co. Ltd.
ZnO	Meta Zinc Ltd.	Merck
Stearic acid	Godrej Soaps Pvt. Ltd.	Merck
Carbon black (N330)	Carbon and Chemicals	Degussa AG
Aromatic oil	Hindustan Petroleum Corporation Ltd.	BP Oil Europe
2-(4-Morpholinyl-mercapto) benzothiazole (MBS)	Flexsys B.V.	Flexsys B.V.
Sulphur	Standard Chemical Company	J.T. Baker
Poly-2,2,4-trimethyl-1,2-dihydroquinoline (TMQ)	Flexsys B.V.	Flexsys B.V.
N-(1,3-Dimethyl butyl)-N'-phenyl-p-phenylenediamine (6PPD)	Flexsys B.V.	Flexsys B.V.
Examination gloves (WLR1)	Primus Gloves Pvt. Ltd.	Primus Gloves Pvt. Ltd.
2,2'-dibenzamido-diphenyldisulphide (DBADPDS)	Lancaster, 97%	Lancaster, 97%
Diphenyldisulphide (DPDS)	Acros, 99%	Acros, 99%

In this study, the reclamation of natural rubber based waste latex rubber is carried out by using a novel reclaiming agent, 2,2'-dibenzamidodiphenyldisulphide as reclaiming agent. The sulfur content in a reclaiming agent is an important characteristic because it influences the ratio of mono-, di- and polysulphidic crosslinks in the reclaimed rubber: The higher the sulfur content in the reclaiming agent, the higher the probability of formation of mono- and disulphides.⁸ The sulfur content of diphenyldisulphide (DPDS), a common reclaiming agent used for natural rubber vulcanizates, is 29%; and the sulfur content of 2,2'-dibenzamido-diphenyldisulphide (DBADPDS) is 14% of its mass.

After the reclamation of WLR1 with DBADPDS, the WLR1 reclaim is mixed with a virgin rubber compound using two different compounding principles. In the first case, the curing system of the compound is adjusted to compensate for the extra input of sulfur and accelerator by the reclaim. In the second case, the cure system is kept constant: fixed curing system. The cure behavior, final crosslink density and distribution, mechanical properties and dynamic

viscoelastic properties of the blends with reclaimed WLR1 are measured and compared to the properties of the virgin compound without reclaim. The morphology of the blends and sulfur migration is also investigated.

EXPERIMENTAL

The research performed in this study was partly done at the Cochin University of Science and Technology (CUSAT), India and the University of Twente (UT), The Netherlands.

Materials

The latex rubber used in this investigation was examination gloves (WLR1) from factory as waste. In the following, WLR1 used at CUSAT and UT will be designated as WLR1C and WLR1T respectively, to differentiate between these two feedstocks. The materials used in the experiment and the source are listed in Table I and the instruments used are given in Table II.

TABLE II
Different Instruments Used at CUSAT and UT

Instruments	CUSAT	UT
Tensile tester	Schimadzu	Zwick Z1.0
Rubber process analyzer (RPA 2000)	Alpha Technologies	Alpha Technologies
Hardness TESTER	Zwick 3114	Zwick 2585
Two-roll mill	Santhosh	Schwabenthan
Press	Santhosh	Wickert
Internal mixer	Haake Rheomix	Brabender PL2000

TABLE III
Reclamation Recipe

Ingredients	Amount (phr)
WLR1	100
2,2'-dibenzamidodiphenyldisulphide	1
Reclaiming oil, treated distillate aromatic extract (TDAE)	5

Reclamation experiments

The reclaim was prepared according to the recipe shown in Table III by a batch process in an internal mixer. The reclaiming conditions and the properties of the reclaim are shown in Table IV. The reclaiming conditions at CUSAT and UT are different because different mixers were used in each occasion.

Rubber mixing and compounding

Mixing and homogenization of rubbers and compounding ingredients were done on a laboratory size two roll mill ($15 \times 33 \text{ cm}^2$) at a friction ratio of 1 : 1.25 at 50°C . The compounds were sheeted off at a thickness of approximately 2 mm, which was convenient for the subsequent preparation of test specimens. All experiments were carried out using a truck tire tread composition as shown in Tables V and VI. In the compositions shown in Table V, NR was progressively replaced by WLR reclaim. The amount of accelerator was decreased by 0.05 phr for each 10 phr of WLR reclaim. In the other test series (Table VI), the amount of accelerators was kept constant.

Curing

The cure characteristics of the different compounds were determined with a Rubber Process Analyzer (RPA 2000), a moving die rheometer from Alpha Technologies. The measurement was done at 150°C , 0.833 Hz, and 2.79% strain over a time period of 30 min. The optimum vulcanization time (t_{90}), initial torque, and final torque of the compound were determined. The compounds were cured in a Santhosh laboratory press (CUSAT) having $46 \times 46 \text{ cm}$ platens at 150°C and 150 bar or a Wickert laboratory press (UT) $1600/5 \times 4/3$ at 150°C and 100 bar. The curing time was chosen as t_{90} of the respective compounds.

The cured samples were $90 \times 90 \text{ mm}^2$ in area and 2 mm in thickness.

Testing procedures

Tensile tests were carried out on dumb-bell shaped specimens (Type 2) according to ISO 37. Tear strength was measured with angle test pieces according to ISO 34. Compression set tests were done at 70°C for 22 h, according to ISO 815. Hardness of the samples was measured with a Zwick hardness-tester Shore A, according to ASTM D 2240. Accelerated ageing tests were carried out according to ISO 188 on dumb-bell shaped specimens after putting them at 100°C for 24 and 48 h in an air-ageing oven without forced aeration.

Swelling measurements were done to obtain information on the crosslink density. Before swelling, the cured samples were extracted in a Soxhlet apparatus, first with acetone for 48 h and then with tetrahydrofuran for 72 h. The elastically active network chain density was measured by equilibrium swelling in toluene for 72 h at room temperature. The crosslink density was calculated according to the Flory-Rehner equation⁹ with the Kraus correction¹⁰ for carbon black. The crosslink distribution of the compounds was studied using thiol/amine chemical probes.^{11,12}

Dynamic measurements of the uncured and cured compounds were performed with the RPA 2000. Frequency sweeps of cured compounds were done to measure the $\tan \delta$ at 60°C as a measure of the rolling resistance, an important property for tire tread applications. For this measurement, an uncured sample was vulcanized for a time period corresponding to the optimum vulcanization time, t_{90} . After vulcanization, the sample was cooled down to 60°C and the loss tangent ($\tan \delta$) was measured at different frequencies. The frequency was varied from 0.1 to 209 rad/s at 0.56% strain.

A frequency sweep was also conducted on uncured compounds to measure the storage modulus. The measurement was done at a temperature of 100°C and a strain of 14%. The frequency was varied from 0.1 to 209 rad/s.

Sulfur distribution was investigated by means of scanning electron microscopy in combination with an energy dispersive X-ray spectrometer (SEM-EDX,

TABLE IV
Reclaiming Conditions and Properties of the Reclaim

Material	Temp. ($^\circ\text{C}$)	Time (min)	Mooney viscosity, ML(1 + 4) 100°C	Sol fraction (wt %)	Crosslink density (10^{-4} mol/cm^3)	Relative decrease in crosslink density
WLRR1C	150	10	48	31	0.22	0.85
WLRR1T	160	7.5	55	29	0.24	0.84

TABLE V
Composition of NR-BR-WLRR Compounds with Adjusted Cure System

Compound	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
NR (ISNR3)	70	65	60	55	50	45	40	30	20	0
WLRR	0	5	10	15	20	25	30	40	50	70
BR (Cisamer1220)	-	-	-	-	30	-	-	-	-	-
ZnO	-	-	-	-	4.5	-	-	-	-	-
Stearic acid	-	-	-	-	2	-	-	-	-	-
HAF black (N330)	-	-	-	-	52	-	-	-	-	-
Aromatic oil	-	-	-	-	8.5	-	-	-	-	-
Accelerator (MBS)	1	0.975	0.95	0.925	0.90	0.875	0.85	0.80	0.75	0.70
Sulfur	-	-	-	-	2.2	-	-	-	-	-
Antioxidant (TMQ)	-	-	-	-	1	-	-	-	-	-
Antioxidant (6PPD)	-	-	-	-	0.5	-	-	-	-	-

LEO 1550 FEG, Thermo NORAN Instruments model Vantage). The samples were prepared by cutting a cross section of the vulcanized material with a microtome (Leica EM FCS) at a temperature of -130°C; then an elemental analysis was performed with a resolution of 2 μm². Before the analysis, the sample was coated with carbon. The accelerating voltage was 15 kV and the sample distance was 9 mm. On every composite, a line scan was performed in threefold.

RESULTS

The effect of WLR1C and WLR1T reclaim, reclaimed with DBADPDS on the properties of a virgin compound is studied. The blends were compounded either with an adjusted curing system or with a fixed curing system. The results obtained with these two curing systems are compared. The adjusted cure system study was carried out at CUSAT, whereas the fixed cure system study was done at UT.

Cure behavior of the compounds mixed with WLR1C and WLR1T reclaim

Figures 1 and 2 show the rheogram of the virgin rubber compound and compounds containing vari-

ous amounts of reclaim with an adjusted cure system and a fixed cure system at 150°C. The maximum torque as well as the difference between final and initial torque are decreasing for both curing systems with an increase in the amount of reclaim in the compound. Another interesting point is that with a fixed curing system the reversion of the compound is higher than that for adjusted curing system.

The optimum cure times, *t*₉₀, for the fixed cure system compounds and adjusted cure system compounds at 150°C are given in Figure 3. For the fixed cure system compounds, the cure time significantly decreases with increase in reclaim content. Only a very slight decrease in cure time is observed for the adjusted cure system compounds. The decrease in cure time as well as scorch time for the fixed curing system is also obvious from Figure 3.

Mechanical Properties of the compounds mixed with WLR1C and WLR1T reclaim

In Figures 4-7, the tensile strength of the unaged as well as aged samples and elongation at break of the adjusted cure system compounds and fixed cure sys-

TABLE VI
Composition of NR-BR-WLRR Compounds with Fixed Cure System

Compound	T1	T2	T3	T4	T5
NR (SIR20)	70	60	45	30	0
WLRR	0	10	25	40	70
BR (Kosyn KBR 01)	-	-	30	-	-
ZnO	-	-	4.5	-	-
Stearic acid	-	-	2	-	-
Carbon black (N330 HAF)	-	-	52	-	-
Aromatic oil (Enerflex 75)	-	-	8.5	-	-
Accelerator (MBS)	-	-	1	-	-
Sulfur	-	-	2.2	-	-
Antioxidant (TMQ)	-	-	1	-	-
Antioxidant (6PPD)	-	-	0.5	-	-

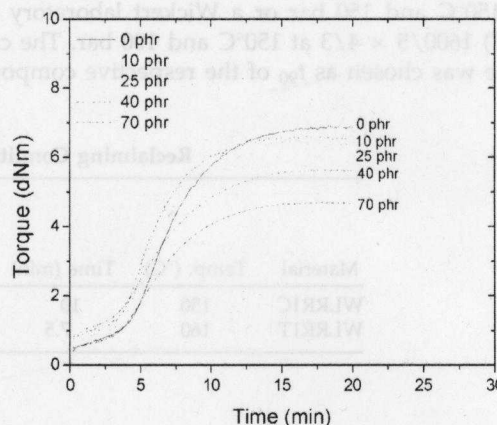


Figure 1 Rheogram of the compounds containing various amounts of WLR1 reclaim for the adjusted cure system.

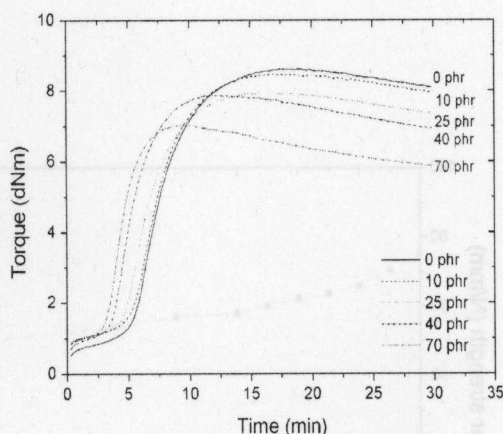


Figure 2 Rheogram of the compounds containing various amounts of WLR1 reclaim for the fixed cure system.

tem compounds as a function of the reclaim content are given. The tensile strength decreases with increase of the reclaim content. An increase of ageing time results in a further decrease of the tensile strength. A sharp decrease in tensile strength is found for the adjusted curing system compounds with increasing reclaim contents. The tensile strength of aged samples decreases strongly with the first 10 phr of reclaim, but then levels off. Fixed curing system compounds behave differently: a linear decrease in tensile strength is observed with increase in the amount of reclaim for unaged and aged compounds. Since the adjusted cure system and fixed cure system were compounded with different feedstock, the absolute values cannot be compared, but the relative changes with increase of the reclaim can be compared. For the fixed curing system, the decrease in tensile strength with the increase in the reclaim content is less compared to the adjusted

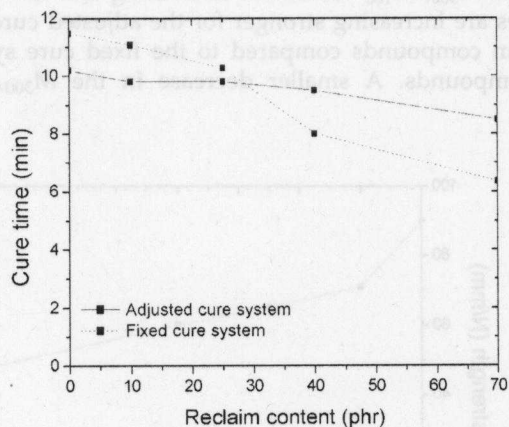


Figure 3 Optimum cure time of adjusted cure system and fixed cure system compounds as a function of WLR1 reclaim content at 150°C.

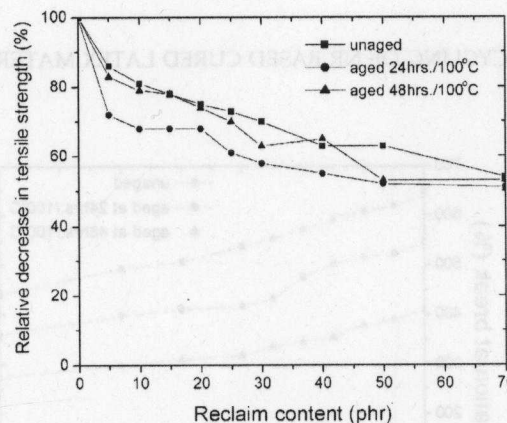


Figure 4 Tensile strength as a function of WLR1 reclaim content for the adjusted cure system compounds.

cure system. Elongation at break values are also decreased for both the cure system compounds with the increase in the amount of reclaim. A linear decrease is observed for both cases.

The tear strength values for both cure systems against reclaim content are given in Figures 8 and 9. Tear strength decreases with an increasing amount of reclaim in the compound. A strong decrease of tear strength is observed in the initial period and afterwards a linear decrease is observed with fixed curing system compounds, whereas a less strong decrease in tear strength is observed with adjusted curing system compounds.

Figures 10 and 11 show the modulus at 100% as well as at 300% elongation and hardness against the reclaim content for both compounds. A small increase in 100% modulus and hardness with increasing amount of reclaim is found for both cure systems. The modulus at 300% elongation is decreasing for the adjusted cure system, whereas it is

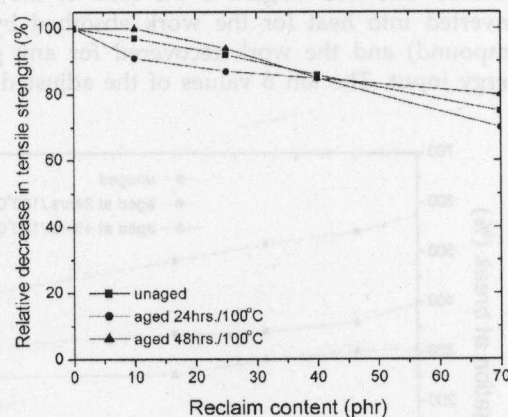


Figure 5 Tensile strength as a function of WLR1 reclaim content for the fixed cure system compounds.

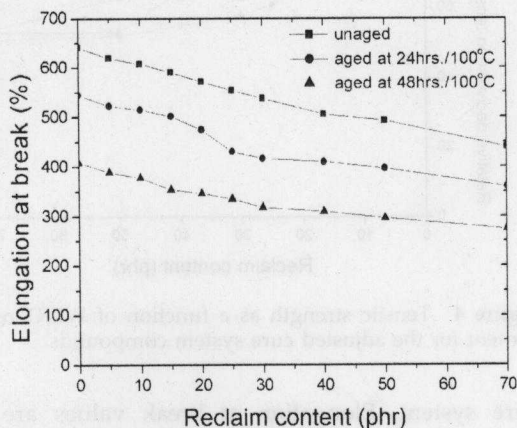


Figure 6 Elongation at break as a function of WLR1 reclaim content for adjusted cure system compounds.

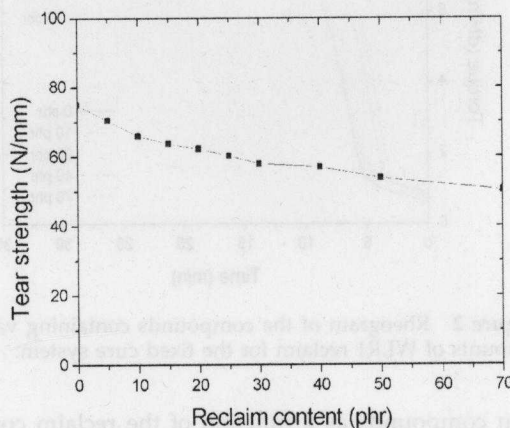


Figure 8 Tear strength as a function of WLR1 reclaim content for adjusted cure system compounds.

increasing in the fixed cure system compounds with increasing amounts of reclaim.

The compression set of the adjusted cure system compounds as well as the fixed cure system compounds as a function of the reclaim content is given in Figures 12 and 13. The compression set increases with an increase of the reclaim content.

Dynamic viscoelastic properties of the compounds mixed with WLR1C and WLR1T reclaim

The loss tangent $\tan \delta^{13}$ of this material is important, because $\tan \delta$ values in the temperature range of 50–80°C are a measure of tire rolling resistance. As the compound used in this investigation is a typical truck tire tread compound, this is a prominent characteristic. The loss tangent is the ratio of the work converted into heat (or the work absorbed by the compound) and the work recovered for any given energy input. The $\tan \delta$ values of the adjusted cure

system and fixed cure system compounds against the frequency at 60°C for various cured compounds are depicted in Figures 14 and 15. The $\tan \delta$ is increasing with an increase in reclaim content for a wide frequency range for the adjusted curing system compounds. When the cure system is fixed, the $\tan \delta$ values remain all in the same range over a wide frequency range. A significant increase in $\tan \delta$ is observed for the adjusted cure system compounds when the amount of reclaim is increased from 0 to 70 phr; in contrast to this, the increase is marginal in the case of the fixed cure system compounds.

The M_{300}/M_{100} as well as $\tan \delta$ values at 15 Hz and 60°C as a function of the reclaim content for cured compounds are given in Figures 16 and 17. The M_{300}/M_{100} values are decreasing and $\tan \delta$ values are increasing stronger for the adjusted cure system compounds compared to the fixed cure system compounds. A smaller decrease in the M_{300}/M_{100}

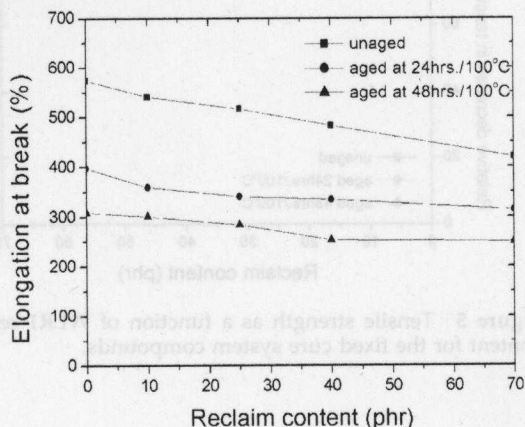


Figure 7 Elongation at break as a function of WLR1 reclaim content for fixed cure system compounds.

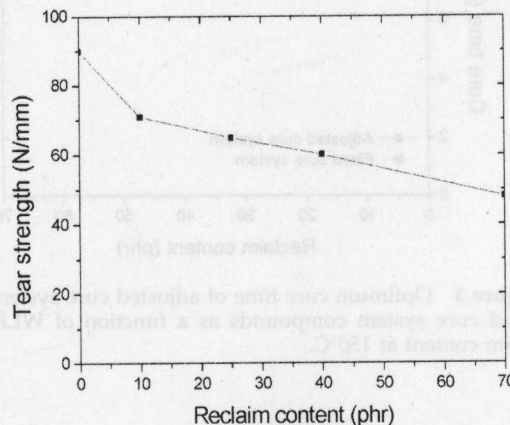


Figure 9 Tear strength as a function of WLR1 reclaim content for fixed cure system compounds.

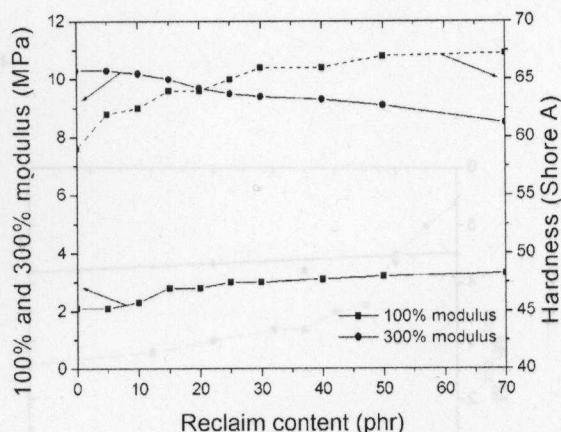


Figure 10 Modulus and hardness as a function of WLR1 reclaim content for adjusted cure system compounds.

values and almost constant $\tan \delta$ values are found for the fixed cure system compounds.

The storage modulus of the vulcanized compounds for both cure systems as a function of frequency at 60°C and 0.56% strain for various cured compounds is plotted in Figures 18 and 19. The storage modulus is found to decrease with increasing amount of reclaim for both cure systems. This indicates that the revulcanizates are not able to achieve the modulus values of the virgin vulcanizates: The elasticity of the revulcanized rubbers is lower than that of virgin vulcanizates.

The storage moduli of the unvulcanized compounds for the two cure system compounds against the frequency at 100°C and 14% strain for different uncured compounds are given in Figures 20 and 21. Both compounds show an increase in storage modulus with increase of reclaim concentration. This trend is very distinct at lower frequencies; at higher frequencies, the trend is not very clear. No significant

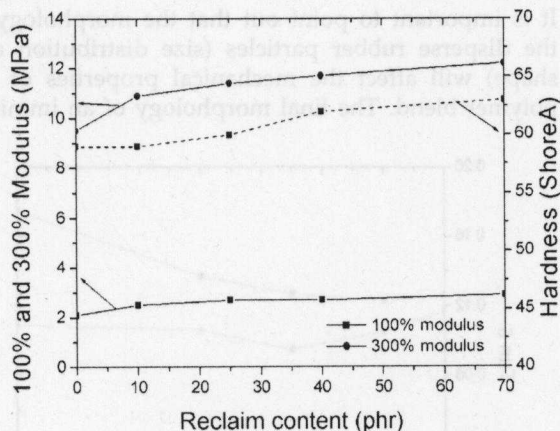


Figure 11 Modulus and hardness as a function of WLR1 reclaim content for fixed cure system compounds.

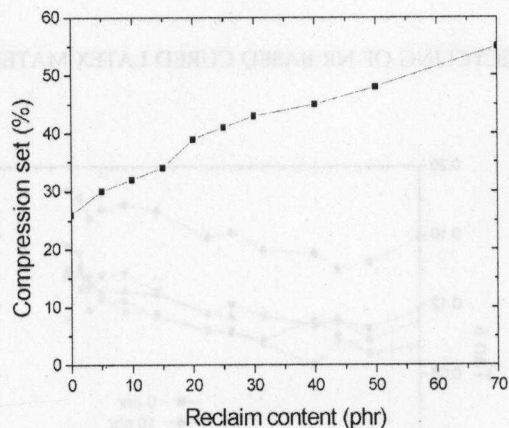


Figure 12 Compression set as a function of WLR1 reclaim content for adjusted cure system compounds.

difference is found between adjusted and fixed curing system compounds.

Crosslink density and distribution of the compounds mixed with WLR1C and WLR1T reclaim

In Figures 22 and 23, the overall crosslink density and crosslink distribution of the adjusted cure system and fixed cure system compounds as a function of reclaim content are depicted. For the adjusted cure system compounds, the overall crosslink density and the amount of polysulphidic crosslinks decrease, while the number of mono- and disulphidic crosslinks increases with increase of reclaim content. For the fixed cure system compounds, the overall crosslink density, polysulphidic crosslinks as well as the mono- and disulphidic crosslinks increase with increase in reclaim content.

The amount of mono- and disulphidic crosslinks could not separately be calculated because of the phase

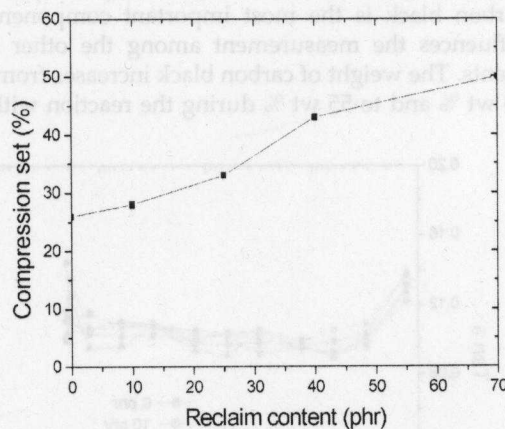


Figure 13 Compression set as a function of WLR1 reclaim content for fixed cure system compounds.

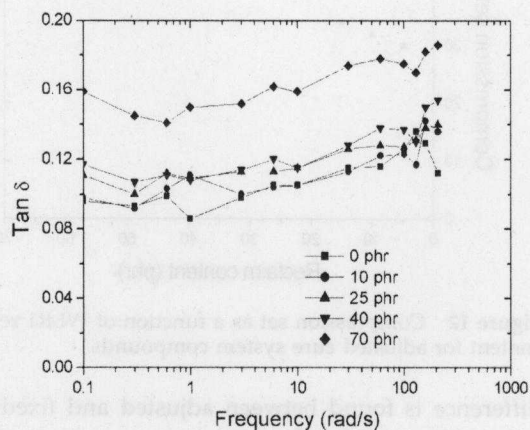


Figure 14 Tan δ of the adjusted cure system compounds with WLR1 reclaim as a function of frequency.

inversion which occurred during the reaction with hexane-1-thiol and piperidine, where all the poly- and disulfidic crosslinks are broken. An extraction with acetone and tetrahydrofuran is preceding the crosslink density measurements. During the extraction, all debound rubber polymer that is released during the thiol-amine reaction is removed from the network.

Considering the fact that out of the total weight of the sample 63 wt % is rubber hydrocarbon, a weight loss calculation on the basis of the original rubber hydrocarbon was done. During the reaction with propane-2-thiol, the rubber hydrocarbon content decreased from 63 to 60% and with hexane-1-thiol it decreased to 35 wt %. As the weight of the rubber hydrocarbon decreased, the weight of other ingredients in the sample increased relative to the rubber hydrocarbon. In regard to the crosslink density measurement, carbon black is the most important component that influences the measurement among the other ingredients. The weight of carbon black increases from 33 to 35 wt % and to 55 wt % during the reaction with pro-

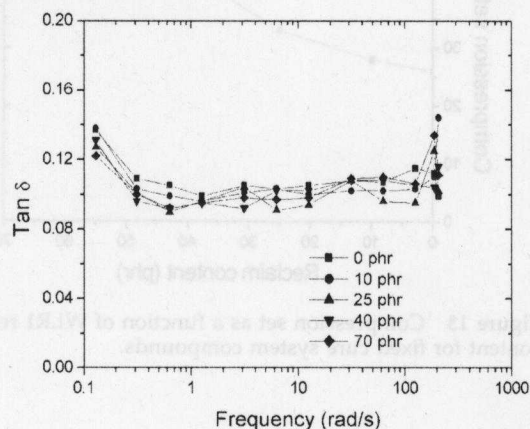


Figure 15 Tan δ of the fixed cure system compounds with WLR1 reclaim as a function of frequency.

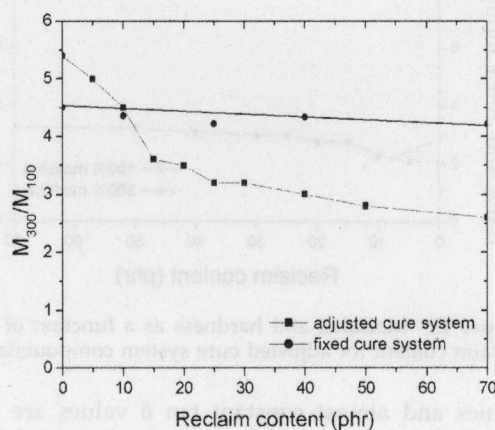


Figure 16 M_{300}/M_{100} for adjusted cure system and fixed cure system compounds as a function of WLR1 reclaim content.

pane-2-thiol and with hexane-1-thiol. The relative increase of carbon black concentration with propane-2-thiol is limited, but during the reaction with hexane-1-thiol, it increases significantly. The sample that is treated with hexane-1-thiol contains more carbon black than rubber hydrocarbon. In the original sample, the ratio of polymer content to carbon black content is approximately 2. After hexane-1-thiol treatment, the ratio decreases to 0.63, indicating that a phase inversion occurs during this process. This high amount of carbon black inhibits the rubber chain to swell properly and results in an improper calculation of monosulfidic crosslink density values with these samples.

Morphology study: SEM-EDX

It is important to point out that the morphology of the disperse rubber particles (size distribution and shape) will affect the mechanical properties of the polymer blend. The final morphology of an immisci-

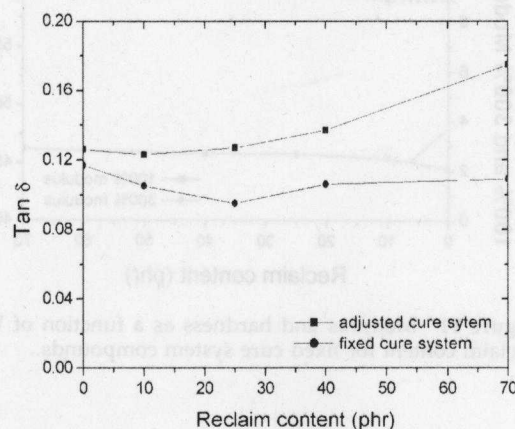


Figure 17 Tan δ for adjusted cure system and fixed cure system compounds as a function of WLR1 reclaim content.

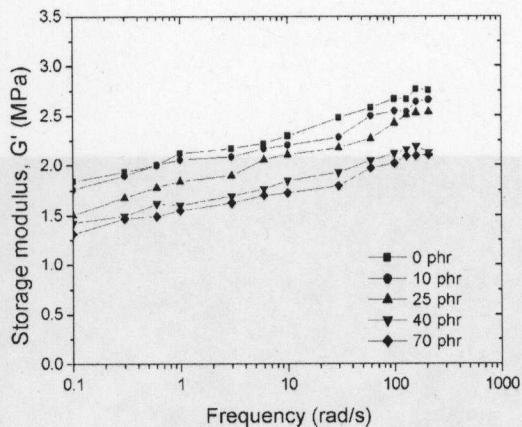


Figure 18 Storage modulus of adjusted cure system compounds after curing with WLR1 as a function of frequency.

ble polymer blend is known to depend on several factors: the rheological properties of the components (viscosity, elasticity), the composition, the processing conditions (deformation rates, stresses, and temperature), and the interfacial properties.¹⁴

An EDX study was performed to determine the sulfur concentration in the virgin matrix and the reclaimed particle. A concentration difference between these two phases can create a curing mismatch between the phases making the material susceptible to early failure.

Figure 24 shows the SEM photomicrographs of a cured compound loaded with 40 phr reclaim. The dark areas are the reclaim particles, which are dispersed in the NR/BR phase. These particles are generally circular, but irregular shapes are also observed.

The SEM-EDX measurements of samples containing 0 and 70 phr are shown in Figures 25–28.

A SEM picture is coupled with the EDX analysis of the sulfur content in the reclaim particle and in

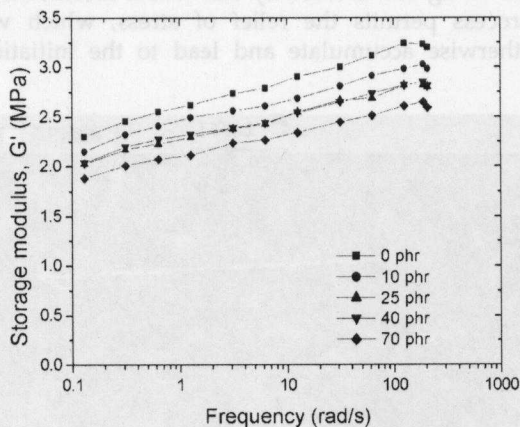


Figure 19 Storage modulus of fixed cure system compounds after curing with WLR1 as a function of frequency.

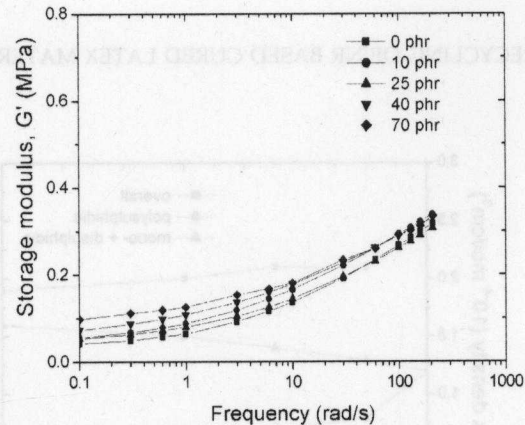


Figure 20 Storage modulus of adjusted cure system compounds before curing with WLR1 reclaim as a function of frequency.

the matrix. A line scan is carried out to measure the difference in the amount of sulfur in the matrix and in the reclaim particle. In the virgin compound, Figure 27, a constant sulfur count is observed showing that the sulfur is uniformly distributed within the matrix. In Figure 28, where the sample contains 70 phr of reclaim, a difference in the amount of sulfur is observed between the matrix and reclaim particle: a higher amount of sulfur is observed in the reclaim particle; the matrix and reclaim particle: a higher amount of sulfur is observed in the reclaim particle.

DISCUSSION

In this study, the influence of different amounts of reclaim on the properties of a virgin compound is discussed in terms of mechanical and dynamic viscoelastic properties, crosslink density and distribution and sulfur distribution between the matrix and the

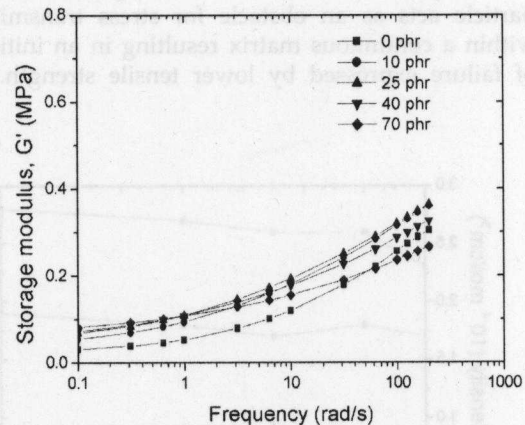


Figure 21 Storage modulus of fixed cure system compounds before curing with WLR1 reclaim as a function of frequency.

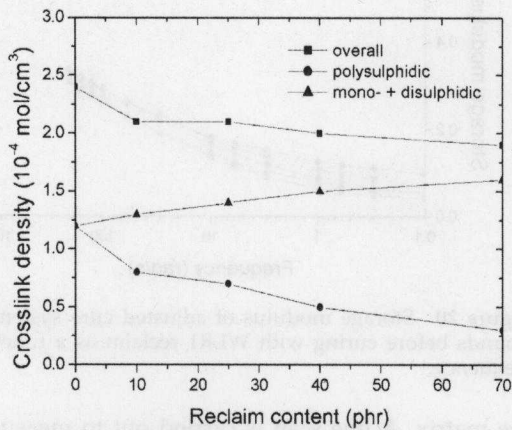


Figure 22 Crosslink distributions for adjusted cure system compounds as a function of WLR1 reclaim content.

reclaim. The mechanical and viscoelastic properties are affected by the following factors^{15,16}:

- Presence of gel in the reclaim;
- Adhesion of the reclaim to the matrix;
- Particle size of the reclaim;
- Sulfur distribution between the matrix and reclaim;
- Crosslink density and distribution.

The decrease in tensile strength with increasing concentrations of reclaim is reported by many researchers¹⁵⁻¹⁸ with respect to the decrease in the molecular weight of the sol fraction in the reclaim and the presence of the crosslinked gel. The reclaim particle acts as an obstacle for stress transmission within a continuous matrix resulting in an initiation of failure expressed by lower tensile strength. The

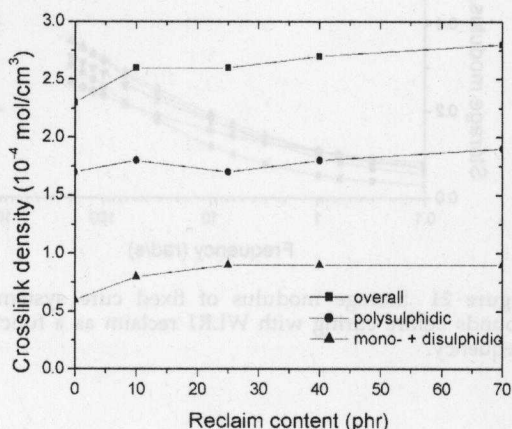


Figure 23 Crosslink distribution for fixed cure system compounds as a function of WLR1 reclaim content.

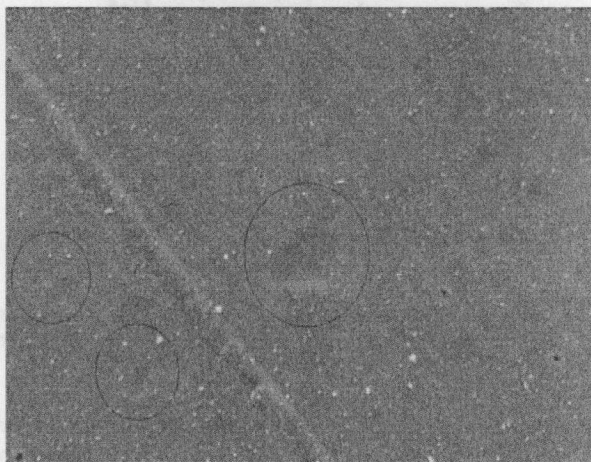


Figure 24 SEM picture of a compound mixed with 40 phr WLR1T reclaim.

stress accumulates on the interface between the reclaimed particle and the matrix and fracture starts from this point. With increasing concentrations of reclaim, the concentration of weak spots increases and the tensile strength of the system decreases.

It is known that the tensile strength increases with increasing crosslink density, reaches a maximum value, and then decreases again. It is also known that tensile strength increases with an increasing number of polysulfidic crosslinks and decreases with an increasing amount of mono- and disulfidic crosslinks. The improvement in tensile strength with an increasing number of polysulfidic crosslinks can be related to the greater flexibility and lability of the polysulfidic crosslinks. Under stress, these crosslinks can straighten and finally cleave and recombine. This process permits the relief of stress, which would otherwise accumulate and lead to the initiation of

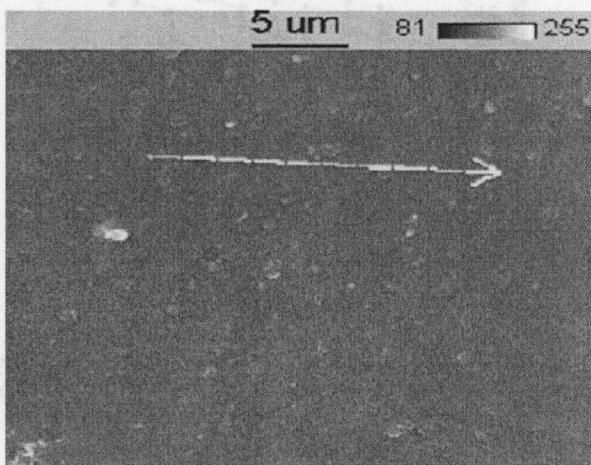


Figure 25 SEM picture of compounds containing 0 phr WLR1T reclaim.

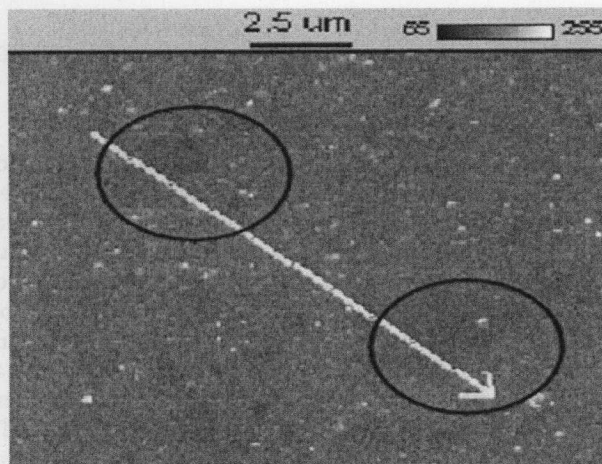


Figure 26 SEM picture of compounds containing 70 phr WLR1T reclaim.

failure.¹⁹ Viscoelastic dynamic properties are improved by polysulfidic crosslinks.

The initial decrease in tensile stress is higher for adjusted cure system compounds than for fixed cure system compounds (Figs. 4 and 5). The crosslink density measurements for both systems show that the crosslink density decreases for the adjusted cure system and increases for the fixed cure system (Figs. 22 and 23). The crosslink distribution studies show that the amount of polysulfidic crosslinks decreases and that the cumulative number of mono- and disulfidic linkages is increased for the adjusted cure system. For the fixed cure system, the number of polysulfidic crosslinks remains basically constant, and the number of mono- and disulfidic crosslinks increases (Figs. 22 and 23). The sulfur contents in the matrix and in the reclaim particle show a difference: Figures 25, 26, 27 and 28. Owing to the higher sulfur concentration of the reclaim particle compared to the

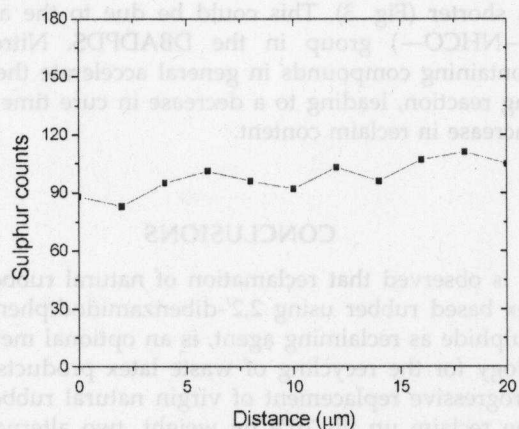


Figure 27 Sulfur content of compounds mixed with 0 phr WLR1T reclaim as a function of line scan distance.

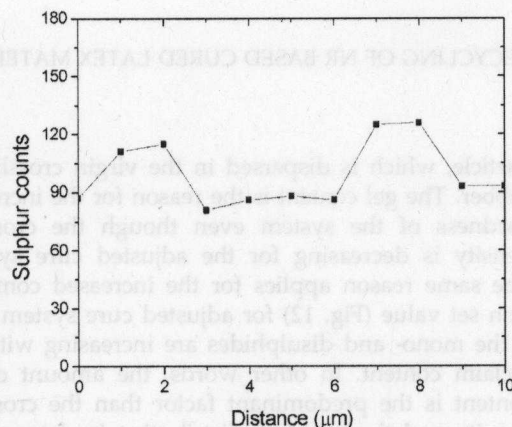


Figure 28 Sulfur content of compounds mixed with 70 phr WLR1T reclaim as a function of line scan distance.

matrix, these spots become highly crosslinked during vulcanization and over-cured. The tensile strength of these areas decreases and the tensile failure starts from these spots. The excess crosslinks in the reclaim particles and the increasing amount of mono- and disulfidic crosslinks explain the decrease in tensile strength for the fixed cure system compounds even though the overall crosslink density is increased with increasing reclaim content.

These are not the only factors which affect the mechanical properties of the compound. Factors like a decrease in chain length of the polymer during reclamation and the presence of crosslinked gel in the reclaim also influence the mechanical strength.²⁰

Elongation at break is another property which depends mainly on the crosslink density and its distribution. The decrease in elongation at break for a fixed cure system and adjusted cure system can be explained similar to the reduction of the tensile strength (Figs. 6 and 7).

The tear strength is influenced by the change in strain crystallization of NR. This property might be disturbed by the addition of the reclaim which is still partly vulcanized and has a different structure (Figs. 8 and 9).

The 300% modulus increases for the fixed cure system compounds but decreases for adjusted cure system compounds. This is a consequence of the increase and decrease of the polysulfidic crosslinks in both cure systems respectively. The increase in the 100% modulus in both cases (Figs. 10 and 11) could be due to the increase of mono- and disulfidic crosslinks with increase in the amount of reclaim.

Modulus at 300% elongation (Fig. 10) and overall crosslink density (Fig. 22) decreases but the hardness increases for adjusted cure system. Because of the presence of gel in the reclaim, the compound is two-phase in nature, the crosslinked rubber and the gel

particle, which is dispersed in the virgin crosslinked rubber. The gel content is the reason for the increased hardness of the system even though the crosslink density is decreasing for the adjusted cure system. The same reason applies for the increased compression set value (Fig. 12) for adjusted cure system even if the mono- and disulphides are increasing with the reclaim content. In other words, the amount of gel content is the predominant factor than the crosslink density and the crosslink distribution in determining the hardness and compression set in this system.²⁰

A comparison of the mechanical and dynamic properties of adjusted and fixed cure system compounds shows that fixed cure system compounds have better properties compared to adjusted cure system compounds for the same amount of reclaim concentration (Figs. 4-21). This is due to the difference in the sulfur crosslink distribution and crosslink density between adjusted cure system and fixed cure system (Figs. 22 and 23). For adjusted cure system, the overall crosslink level as well as polysulphidic level decreases and the mono- plus disulphidic crosslinks increases with increasing reclaim content in the compound. In the case of fixed cure system, a different trend is observed. The overall as well as the polysulphidic crosslinks increases, also the mono- plus disulphides. But, most important is the amount of overall and polysulphide level, which have an opposite behavior for adjusted and fixed cure system: Both increases for fixed cure system, whereas both decreases for adjusted cure system. This explains the better mechanical and dynamical performance of fixed cure system compounds over adjusted cure system compounds.

The elasticity of the material decreases mainly due to the increase in the amount of mono- and disulfidic crosslinks with increasing reclaim content in the compound and due to the presence of gel in the reclaim. Both factors reduce the elastic nature of the compound, which is also the reason for the increased heat build-up, which is reflected in the $\tan \delta$ values (Figs. 14 and 15). The increased compression set values and hardness is also due to the presence of gel in the reclaim.²¹

The storage modulus of the unvulcanized samples increases with the increase of reclaim concentration (Fig. 20 and 21) again due to the presence of an increased amount of gel in the compound. The three-dimensional gel imparts a certain elastic contribution to the unvulcanized sample causing the storage modulus to increase. However, in the vulcanized sample, the storage modulus shows an inverse effect (Figs. 18 and 19). As the sample is vulcanized, the gel particles also get attached to the matrix and crosslinked, hence the mobility and flexibility of the gel particle is lost. Therefore, these particles act as harder spheres with reduced elastic properties.

It is important to understand whether the difference in the sulfur level between the matrix and reclaimed particle is due to the migration of sulfur from the matrix to the reclaim particle or due to the initial distribution of sulfur between the two phases during mixing of the compound (Figs. 25 and 26). A calculation based on the vulcanization recipe of WLR1 and the amount sulfur in DBADPDS, which is added during the devulcanization of WLR1, shows that WLR1 reclaim contains 1.2 wt % of sulfur and that the virgin compound, T1 (Table VI), contains 1.43 wt % of sulfur. The concentration of sulfur was also calculated from the sulfur counts during the EDX measurement and shows that the virgin compound (0 phr of WLR1 reclaim) contains 1.4 wt % of sulfur and that the matrix of the 70 phr reclaim containing compound also has a sulfur level of 1.4 wt %. The reclaim particle in the same sample contains 2.9 wt % of sulfur. Considering the fact that 1.4 wt % of sulfur was added during mixing of all compounds given in the Table VI, an additional 1.2 wt % of sulfur is added to the original sulfur content in the reclaim particle. Together with the initial sulfur level of 1.2 wt % this adds up to approximately 2.6 wt %: This is the sulfur concentration found back during the EDX measurement (Figs. 27 and 28). These calculations show that the difference in sulfur concentration between the matrix and the reclaim particle is not due to migration of sulfur between the matrix and the reclaim but due to a homogeneous distribution of sulfur throughout the matrix and reclaim during mixing of the compound. The sulfur stays in the matrix and in the reclaim and no major migration during and after vulcanization occurs.

At higher concentrations of reclaim the cure time of the compounds with DBADPDS reclaimed WLR1 is shorter (Fig. 3). This could be due to the amido ($-\text{NHCO}-$) group in the DBADPDS. Nitrogen-containing compounds in general accelerate the curing reaction, leading to a decrease in cure time with increase in reclaim content.

CONCLUSIONS

It is observed that reclamation of natural rubber latex based rubber using 2,2'-dibenzamido-diphenyldisulphide as reclaiming agent, is an optional methodology for the recycling of waste latex products. For progressive replacement of virgin natural rubber by the reclaim up till 70% by weight, two alternatives were investigated for the curing system: adjustment or reduction of the curing system with increasing reclaim content, to compensate for the extra sulfur-amount brought along by the reclaim, to keep the total sulfur in the compound constant. For fixed curing system, as if the reclaim were equivalent to virgin natural rubber. With the use of the adjusted cure

package, a significant decrease in properties is generally observed with increasing reclaim content. But, for obtaining better properties, fixed curing system, as if the reclaim were equivalent to virgin natural rubber should be preferred. With the fixed cure system, many properties like tensile strength and compression set do still deteriorate, but to a lesser extent. Most conspicuous are the values obtained for $\tan \delta$ and M_{300}/M_{100} , representative for the rolling resistance of tires. With the fixed cure system, both quantities indicate an improved rolling resistance with increasing amounts of reclaim versus the virgin compound. With the adjusted cure system both quantities deteriorate. This is the consequence of the predominantly polysulphidic crosslink network obtained with the fixed cure system, well known to favor dynamic properties of rubber compounds, versus the mainly mono- and disulphidic crosslink network obtained with the adjusted cure system.

References

1. Myhre, M. J.; MacKillop, D. A.; Rubber World 1996, 214, 42.
2. Anonymous (Trelleborg, A. B.) Eur Rubber J 1980, 162, 36.
3. Isayev, A. I.; Chen, J.; Tukachinsky, A. Rubber Chem Technol 1995, 68, 267.
4. Tukachinsky, A.; Schworm, D.; Isayev, A. I. Rubber Chem Technol 1996, 69, 92.
5. Tapale, M.; Isayev, A. I. J Appl Polym Sci 1998, 70, 2007.
6. Kohler, R.; O'Neill, J. Rubber World 1997, 216, 32.
7. Sekhar, B. C.; Subramaniam, A. (to STI-K Polymers SDN BDH). EP 0748837, 1996.
8. Rajan, V. V.; Dierkes, W. K.; Joseph, R.; Noordermeer, J. W. M. Rubber Chem Technol 2005, 78, 572.
9. Flory, P. J.; Rehner, J., Jr. J Chem Phys 1950, 18, 108.
10. Kraus, G. J Appl Polym Sci 1963, 7, 861.
11. Campbell, D. S. J Appl Polym Sci 1969, 13, 1201.
12. Campbell, D. S.; Saville, B. In Proceedings of the International Rubber Conference, Brighton, UK, 1967; pp. 1.
13. Wang, M. J. Rubber Chem Technol 1998, 71, 520.
14. Scuracchio, C. H.; Bretas R. E. S.; Isayev, A. I. J Elastomer Plast 2004, 36, 45.
15. Fujimoto, K.; Nishi, T.; Okamoto, T. Int Polym Sci Technol 1981, 8, T/30.
16. Burgoyne, M.; Leaker, G.; Krekic, Z. Rubber Chem Technol 1976, 49, 375.
17. Fesus, E. M.; Eggleton, R. W.; Rubber World 1991, 203, 23.
18. Knorr, K. Kautsch Gummi Kunstst 1994, 47, 54.
19. Coran, A. Y. In Science and Technology of Rubber; Eirich, F. R., Ed.; Academic Press: New York, 1978.
20. Isayev, A. I.; Jun, J. Rubber Chem Technol 2003, 76, 253.
21. Sombatsompop, N.; Kumnuantip, C. J Appl Polym Sci 2003, 87, 1723.