Polymer Bulletin

Mechanical and Viscoelastic Properties of Natural Rubber/ Reclaimed Rubber Blends

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Abstract

Addition of reclaimed rubber affected mechanical properties, processing and rheological behavior of rubber compounds. Sulfur left in reclaimed rubber affected curing process of NR/reclaimed rubber blends. The most suitable curing was achieved with ratio 1:1 of natural rubber and reclaimed rubber which was used in this study. Presence of fillers in reclaimed rubber, non-homogeneity of phases, non-uniform filler dispersion and lower molecular weight of reclaimed rubber due to chain scission in reclaiming process caused diminishing of mechanical properties of NR/reclaimed blends, particularly dynamic-based properties. Reclaimed rubber also affected rheological behavior of natural rubber. In a strain sweep viscoelastic test, it could be observed that NR/reclaimed blend show more non-linear viscoelastic and viscous behavior than predicted one which was due to non-homogenized phases. This non-homogenized morphology was detected using scanning electron microscopy (SEM) and the blend with ratio 1:1 had the most homogenized morphology.

Introduction

The ever-increasing volume of polymer waste is a severe problem deserving serious attention. Of this polymer waste, only 8-12% is plastic while the rest lion share is elastomer [1]. The difficulty in recycling of the waste tires is that the scraped tire is a crosslinked polymer that is hard to melt and to process [2]. Different types of physical reclaiming processes reported so far are mechanical [3], thermomechanical, microwave [4] and ultrasound methods [5-6]. Reclaimed rubber, prepared from scrap rubber, has been used as a substitute for virgin rubber in many rubber compounds [7].Thus, while this opens up a route for utilizing scrap rubber, it makes the products cheaper. Whole tire reclaimed (WTR), a popular form of reclaimed rubber prepared from used and scrap tires, is inherently non-polar and has been used to prepare blends with non polar rubber such as NR [7-10], SBR [11-12] and BR [13] also polar rubber such as NBR [14-16] as well as thermoplastics [17-19]. The addition of reclaimed rubber affects processing and rheological behavior of compounds, but there are some reports on effect of the reclaimed rubber on rheological behavior of rubber compounds. [9-10].

The purpose of this study is to investigate the rheological behavior and cure characteristics of NR/Reclaimed rubber blends compounds and mechanical properties of these vulcanizates.

Experimental

Materials: Natural rubber (SMR-20) is supplied by Malaysia and reclaimed rubber prepared from scrap tire was supplied by Yazd Reclaim Co. (Yazd, Iran). Zinc oxide (ZnO), stearic acid, IPPD (N-isopropyle-N′-phenyl-p-phenylene diamine), MBTS (dibenzothiazoledisulfide), TMTD (tetramethylthiuram disulfide), and sulfur used were all commercial grade.

Characterization of reclaimed rubber: Oil, Rubber, carbon black and ash content were calculated using thermal gravimetery analysis (TGA). The oil of reclaimed was extracted using acetone at 25°C in 5 days and analyzed with FTIR. In addition, the reclaimed rubber was pyrolized and monomers were analyzed with FTIR which showed that the reclaimed rubber is a blend of NR, SBR and BR. From TGA thermograph the percentages of these rubbers calculated as 39 % for NR and 20 % for SBR and BR. The ash of reclaimed rubber was also extracted using a laboratory furnace at 600°C in 8 hours and analyzed with FTIR. The characteristics peaks of silica type fillers (1020 and 669cm^{-1}) were seen in this FTIR graph. The characteristics of used reclaimed rubber are summarized in table1.

Preparation of compounds: Natural rubber was masticated on a laboratory two-roll mill (Polymix 200L) and reclaimed rubber was added at different percentages. The blends were prepared as per the formulation given in Table 2 according to ASTM D3182-1982.

Table 1. Characteristics of used reclaimed rubber

Parameter	Value	Standard	Type
Mooney viscosity (ML 1+4)@ 100°C	39.8	ASTM D-1646	-
Acetone extract	7.5	ASTM D-297	-
Composition of reclaimed rubber			
Oil (wt %)	5	ASTM D-1131	Paraffinic and aromatic mineral oils
Rubber (wt %)	59	ASTM D-1131	SBR, BR and NR
Carbon Black (wt %)	25.4	ASTM D-1131	-
Ash (wt %)	10.6	ASTM D-1131	Silica

Table 2. Formulations

Material	A	B	C	D	E
NR	100	75	50	25	0
reclaimed	0	50	100	150	200
ZnO	4	4	4	4	4
stearic acid	2	2	2	2	2
IPPD	1	1	1	1	1
MBTS	0.5	0.5	0.5	0.5	0.5
TMTD	1.8	1.8	1.8	1.8	1.8
S	0.3	0.3	0.3	0.3	0.3

Analysis: Thermal gravimetery analyzer (TGA), (PERKIN_ELMER Pyris1, Germany) at 10°C/min heating rate and N2 atmosphere up to 550°C then O2 atmosphere was used for analyzing the composition of reclaimed rubber.Fourier transform infrared (FTIR), (BRUKER IFS 484, Germany) and elementary analysis (ELEMENTAR, VARIO III EL, Germany) were also used for analyzing and characterization of the component of reclaimed rubber.

Rheology: Rheology of compounds was analyzed using rubber processing analyzer (RPA-2000) (Monsanto, USA) with strain sweep test at 100°C and 10cpm (cycle per minute) frequency. In addition, mooney viscosity (ML 1+4) of compounds was measured using shear money viscometer (Zwick, Germany) at 100°C according to ASTM D-1646.

Curing: Cure rate, scorch time (t5) and cure time (t95) of the rubber compounds were detected using an oscillating disk curemeter, 4308 Zwick (Germany) at a test temperature of 150°C ,then the compounds were compression molded using a 25 tone press (Davenport, England) at 150°C based on their respective t95 value.

Mechanical properties: Tensile properties were measured following ASTM D412 using a MTS tensometer at 500mm/min cross head speed. Hardness (shore A) was done using Zwick (Germany) hardness tester according to ASTM D2240. Resilience and abrasion loss tests were also done using Frank (Germany) resilience and abrasion testers according to ASTM D1054 and D5963, respectively. Fatigue life of vulcanizates was measured using a fatigue to failure tester (Monsanto, Germany) according to ASTM D430 and compression set test was done at 25°C for 72 hours according to ASTM D395.

Morphology: The failure mechanisms of rubber vulcanizates were investigated using an Oxford scanning electron microscope (SEM), (model S360 Cambridge, England) at 25kv accelerating voltage, examining fractured surfaces of rubber vulcanizates obtained after immersion in liquid nitrogen.

Results and Discussion

Rheology

Figure 1 shows the Mooney viscosity of the NR blends with different reclaimed rubber content. It can be seen that Mooney viscosity of reclaimed rubber is lower than virgin natural rubber due to chain scission which occurs during reclaiming process. Higher Mooney viscosity was predicted for reclaimed rubber, if polymer chains scission was not considered, due to the filler left in reclaimed rubber, but it seems that base polymer viscosity has the major role in Mooney viscosity. It can be seen that Mooney viscosity of NR/reclaimed rubber blends is lower than virgin NR and pure reclaimed rubber. This negative deviation from direct line (i.e. ideal mixtures law) can be described with non-homogeneity of morphology and non compatibility between the phases, that can be seen also in SEM photographs (Figures 2-B to 2-D). It is likely that two phases, NR and filler containing NR/SBR/BR blend (i.e. reclaimed rubber) are not completely compatible and homogenized.
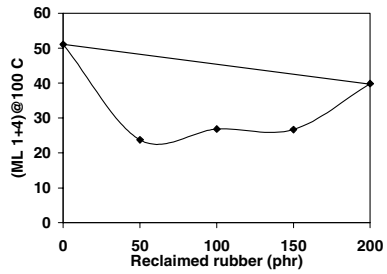
Figure1. Mooney viscosity of compounds

SEM studies

Figure 2 shows the SEM photographs of fractured surface of NR/reclaimed rubber vulcanizates with 1000 times magnification. In Figure 2-A it can be seen that pure NR vulcanizate is homogenized but NR/reclaimed rubber blend (75/50, 50/100 and
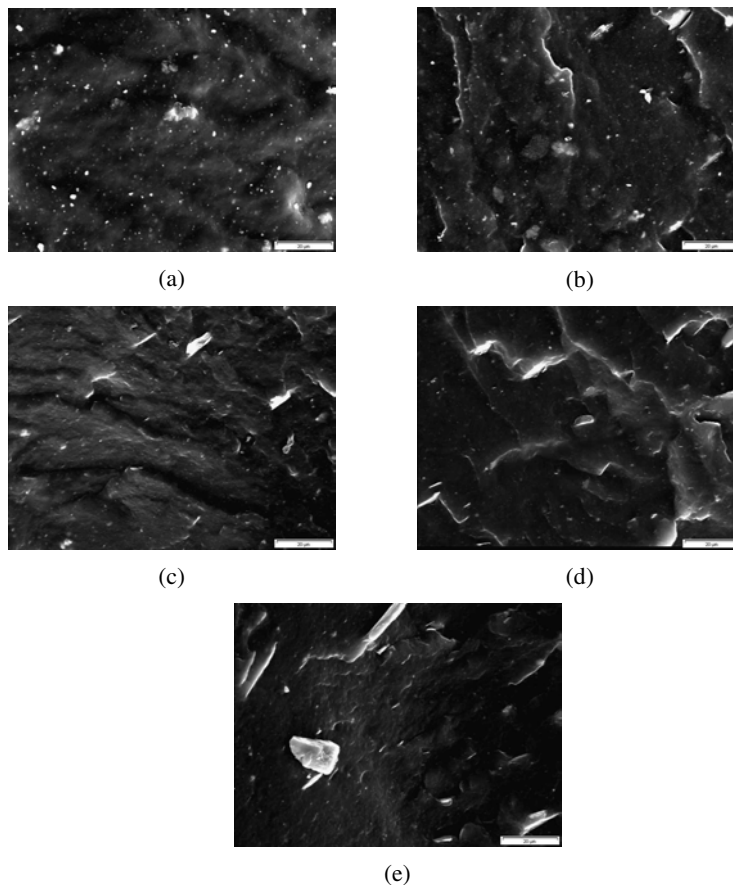

(a)

(b)

(c)

(d)

(e)

Figure2. SEM photograph of NR/reclaimed rubber blends: (a) 100/0, (b) 75/ 50, (c) 50/100, (d) 25/ 50 and (e) 0/ 200. Values are expressed in phr and magnification is 1000

25/150 phr) have not homogenized phase and two rubber phases (dark and light) can be seen in Figures 2-B to 2-D. Lighter phase, probably reclaimed rubber, is circular in NR/reclaimed rubber 75/50 blend but by increasing reclaimed rubber, phases shape becomes layered and cylindrical. Fiber present in reclaimed rubber also can be detected in NR/reclaimed rubber blends (Figures 2-B to 2-D) and pure reclaimed rubber vulcanizates (Figure 2-E). Cracks due to the filler detachment and pits (sign of detached fillers) can be detected also in Figures 2-B to 2-D (i.e. NR/reclaimed rubber blend vulcanizates) and Figure 2-E (i.e. pure reclaimed rubber vulcanizate). Low wettability of fillers with rubber phase is the reason for the above observations. Due the layered morphology less fillers, detachment, less pits and cracks that is evidenced in Figure 2-C, the most suitable and homogenized phases can be achieved with blending 100phr reclaimed and 50 phr virgin NR (i.e. 1:1 ratio).

Viscoelastic properties

RPA is used for studying viscoelastic parameters of rubber compounds [20-24]. Viscoelastic behavior of compounds is studied in strain sweep mode at 100°C, strain range 1-1200% and frequency 10 cpm(cycle per minute).

Figure 3 shows torque (S) and shear modulus (G) versus strain. It can be seen that torque (S) increases in higher shear strains, because bigger deformations need more torque but polymer chains flow more easily thus shear modulus decreases in higher strains. Torque (S) of NR/reclaimed rubber blends is lower than two polymers (i.e. natural rubber and reclaimed rubber), while authors predicted that the torque of blends is between the torque of two polymers. This behavior can be attributed to non-homogeneity of phases in blends. It seems that friction of polymer chains in a completely homogenized and compatible blend is more than non homogenized one. Figure 4 shows elastic torque (S′) and loss torque (S″) and Figure 5 shows elastic modulus (G′) and loss modulus (G″) of compounds.
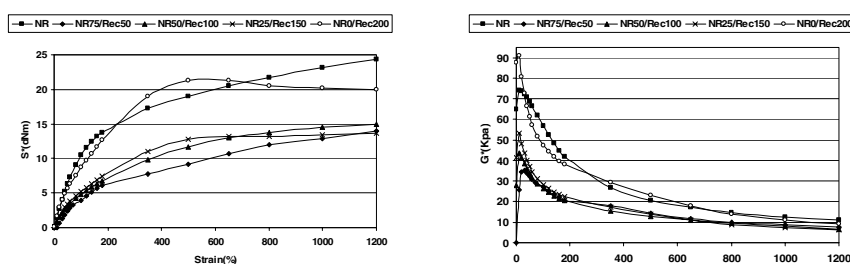

Figure3. Torque (S) and shear modulus (G) of compounds versus strain

In Figure 4, elastic torque (S′) changes with strain can be divided into three different zones: low strains, medium strains and high strains, respectively. In the first zone (low strains) S′ increases, in the second zone (medium strains) S′ decreases and in the third zone (high strains) S′ has no significant change with strain. In the first zone, it seems that shear strain causes breakdown of filler-filler and rubber-filler networks as well as chain entanglements. It can be seen that maximum S′ increases with increasing reclaimed rubber amount because of fillers (i.e. carbon black and silica) left in reclaimed rubber. Since there is no filler in NR and shear torque is applied just for

chain disentanglement, the maximum elastic torque and strain of maximum elastic torque in NR compounds are lower than reclaimed rubber. In the second zone (i.e. medium strains), S′ drops more rapidly in reclaimed rubber in comparison with virgin NR and in high strains (i.e. third zone) torque of NR is higher than reclaimed rubber. This can be attributed to longer chains and higher molecular weight of NR. It seems that in high strains, polymer chains are oriented.

The elastic torque (S′) of blends has similar trend to their major phase (i.e. NR or reclaimed rubber). For example the rate of S′ decreases and maximum S′ is higher and final S′ in high strains is lower in NR/reclaimed rubber 25/150 blend compared with the NR/reclaimed rubber 50/100 and 75/50 blends, because this blend contains more reclaimed rubber and as a result more filler, also its molecular weight is lower due to more reclaimed rubber content. Loss torque (S″) of all compounds increased with strain and shows a plateau in high strains. It can be seen that loss torque of NR in low strains is more than reclaimed rubber. It can be attributed to the fillers left in reclaimed rubber. In medium strains (400-600%) loss torque (S″) of reclaimed rubber is more than natural rubber. It seems in this zone, energy is dissipated for breakdown of filler-filler and filler-rubber networks. In high strains the loss torque (S″) of NR is more than reclaimed rubber which is due to its higher molecular weight and higher friction of long NR chains. NR/reclaimed blends have lower loss torque (S″) than virgin NR and reclaimed rubber due to non-homogenized morphology and lower inter-molecular friction. The S″ change with strain in each NR/reclaimed rubber blend is similar to their major phase (i.e. NR or reclaimed rubber).
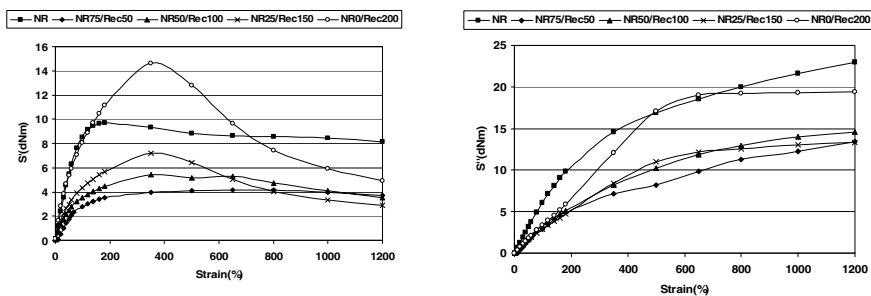

Figure4. Elastic torque (S′) and loss torque (S″)

Figure 5 shows the elastic modulus (G′) and loss modulus (G″) of compounds. It can be seen that the G′ changes with strain can be divided to three different zones: linear viscoelastic in low strains, non-linear viscoelastic in medium strains and linear viscoelastic in high strains. In low strains, elastic modulus (G′) of reclaimed rubber is higher than natural rubber due to the fillers left in reclaimed rubber. But non-linear viscoelastic behavior of reclaimed rubber begins in lower strains than NR. This can be attributed to the beginning of the filler-filler and rubber-filler networks breakdown in these strains. In medium strains, elastic modulus (G′) decreases due to rubber-filler and filler-filler networks breakdown and disentanglement of polymer chains. The rate of G′ drop in this non-linear viscoelastic zone in reclaimed rubber is less than NR due to filler presence in reclaimed rubber and its elastic nature. In high strains, G′ of compounds is the same but linear viscoelastic behavior (i.e. the plateau) of reclaimed rubber begins in higher strains than NR. In other words, non-linear viscoelastic zone

in reclaimed rubber is longer than NR, begins in lower strains and finishes in higher strains.

The elastic modulus of NR/reclaimed rubber blends is lower than NR and reclaimed rubber which is due to non-homogeneity and non-uniform dispersion of filler in these blends. The G′ of blends has similar trend to their major phase (i.e. NR or reclaimed rubber).

Three zones indicated in G′, can also be detected in the graph of loss modulus (G″) versus strain. In low strain, the first linear viscoelastic zone, loss modulus (G″) of reclaimed is lower than NR due to its filler content. In higher strains, loss modulus of NR compounds decreases due to disentanglement of polymer chains whereas, reclaimed rubber has different behavior. In medium strains, loss modulus of reclaimed rubber increases due to energy dissipation for rubber-filler and filler-filler networks breakdown and then decreases due to rubber chains disentanglement.
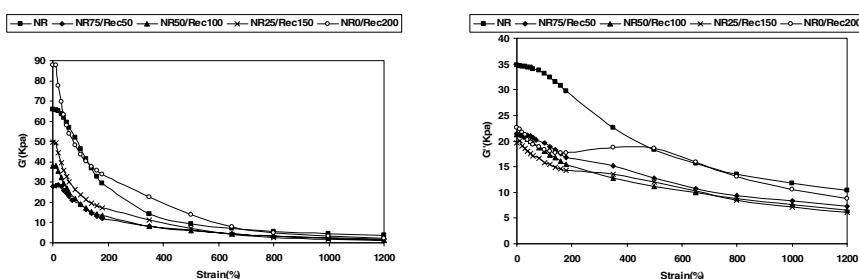
Figure5. Elastic modulus (G′) and loss modulus (G″) of compounds

In high strains, moving of polymer chains is completely laminar and all compounds have linear viscoelastic behavior, thus loss modulus (G″) has no significant change. Final G″ of reclaimed rubber is lower than NR which is due the fillers left in reclaimed rubber. Loss modulus (G″) of NR/reclaimed rubber blends has similar trend to the major phase of blend (i.e. NR or reclaimed rubber). It is indicated that the increase of loss modulus in non-linear viscoelastic zone can be detected in NR/reclaimed rubber 25/150 blend while this behavior can not be observed in NR/reclaimed rubber 75/50 blend. In high strains linear viscoelastic zone, non-homogeneity of phases and non-uniform dispersion of filler cause lower loss modulus of NR/reclaimed rubber blends than NR and reclaimed rubber. In addition, in the first low strain linear viscoelastic zone, loss modulus (G″) of NR/reclaimed rubber blends has no significant difference with reclaimed rubber. It seems filler amount, homogeneity of phases and filler dispersion have no significant effect on the loss modulus in low strains and effect of these parameters can be detected in medium and high strains.

Figure 6 shows loss factor (tanδ) of compounds versus strain. It can be seen that tanδ of all compounds increases with increasing in strain. The trend of tanδ can be divided in two zones i.e. elastic zone (tanδ < 1) and viscose zone (tanδ > 1). It is indicated that the elastic zone of reclaimed is longer than NR, and in NR/reclaimed rubber blends with increasing reclaimed rubber content elastic zone becomes longer. This is due to the fillers left in reclaimed rubber. Non-homogeneity of phases and non-uniformed dispersion of fillers in NR/reclaimed rubber 50/100 and 75/50 cause shorter elastic

zones in these blends than virgin natural rubber. The rate of $\tan\delta$ increasing in compounds is compared in Figure 7. According to this figure it is shown that the increasing rate of $\tan\delta$ and viscose behavior in reclaimed rubber and blends are more than virgin NR. Positive deviation from direct line (i.e. ideal mixtures law) is the sign of non-homogeneity of phases and non-uniform dispersion of fillers, since elastic nature of blends is less than what can be predicted theoretically. Increasing reclaimed rubber in blends intensifies this phenomenon because as the deviation from straight line increases with increasing reclaimed rubber content in blends.
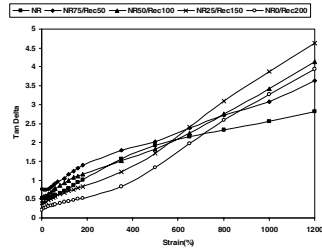
Figure6. Loss factor ($\tan\delta$) of compounds
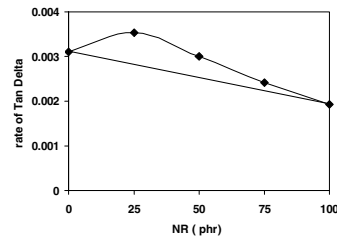
Figure7. The rate of $\tan\delta$ increase
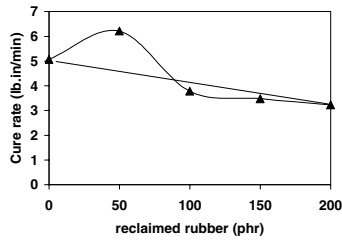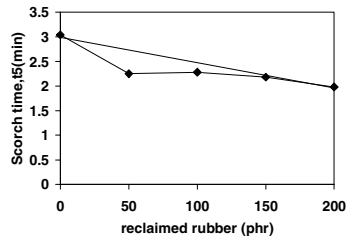

Figure8. Cure rate of compounds
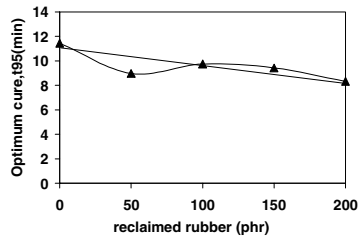

Figure9. Scorch time of compounds

Figure10. Optimum cure time of compounds

Cure characteristics

Figures 8, 9 and 10 show the cure rate, scorch time (t_5) and optimum cure time (t_{95}) of compounds, respectively. This demonstrates that, scorch time and cure time decrease and cure rate increases up to 50phr reclaimed rubber content. This can be attributed to free sulfur left in reclaimed rubber. Results of elementary analysis of reclaimed rubber and acetone extracted part of reclaimed rubber showed that 80.75% of sulfur is in acetone extracted part of reclaimed rubber. This result supported the above idea. In the

case of compounds containing more than 50 phr reclaimed rubber up to 100 phr, cure rate decreases, scorch time increases but cure time has no significant change. Cure characteristics of compounds containing 100 to 200 phr reclaimed rubber is same. These results are not agree with previous observations and predicted behavior. Accelerator/sulfur ratio is the reason of this phenomenon. The accelerator/sulfur ratio was calculated according to reclaimed rubber characterization (Table 1), formulations (Table 2) and elementary analysis data of reclaimed rubber. The results showed that in formula B (i.e. containing 50phr reclaimed rubber) accelerator/sulfur ratio is 1.02 and curing system is semi-efficient but in formulas C,D and E (i.e. containing 100,150 and 200 phr reclaimed rubber) this ratio is less than 1. Therefore in compounds containing more than 50phr reclaimed rubber, accelerator concentration is less than essential one and as a result the rate of curing reaction decreases.
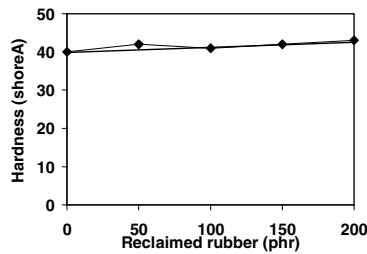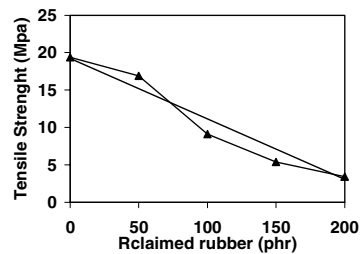

Figure11. Hardness of vulcanizates

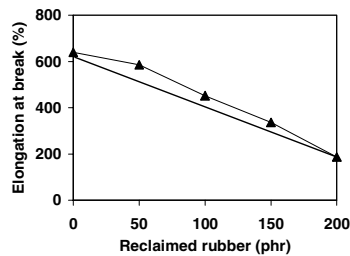**Figure12.** Tensile strength of vulcanizates

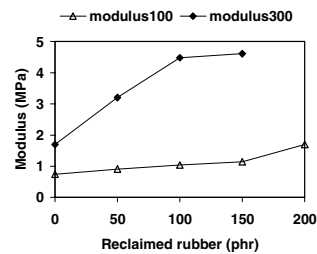**Figure13.** Elongation at break of vulcanizates

Figure14. Modulus of vulcanizates

Mechanical properties

Figures 11 to 17 show the mechanical properties of NR/reclaimed rubber blend vulcanizates. It can be seen that hardness, modulus and compression set of vulcanizates increase and tensile strength, elongation at break, fatigue life and resilience decrease when reclaimed rubber content increases. This can be attributed to filler presence in reclaimed rubber, lower molecular weight of reclaimed rubber and non homogeneity of phases. Fatigue life is the most affected mechanical properties. The deviation of properties curves of direct line (i.e. between pure NR and pure reclaimed rubber vulcanizates properties) is a suitable guide for the determination of the share of above parameters on mechanical properties changes. It seems that non homogeneity of phases has the most effect on tensile strength, elongation at break,

modulus, fatigue life and compression set while increasing the filler content in compound is the major parameter in hardness and resilience changes. Because hardness and resilience of NR/reclaimed rubber blends variations with reclaimed rubber content are more linear than other properties. In the case of NR/reclaimed rubber 75/50 blends due to specific cure behavior described above, mechanical properties such as hardness, tensile strength and resilience show positive deviation from the direct line while other blends do not show positive deviation in these properties. It seems that crosslinked rubber network of this blend is stronger than other blends.
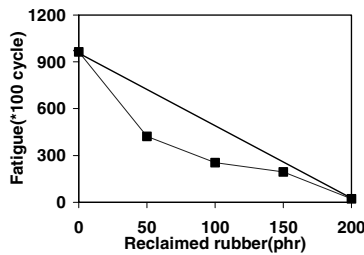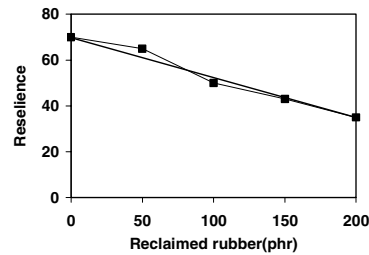

Figure15. Fatigue life of vulcanizates

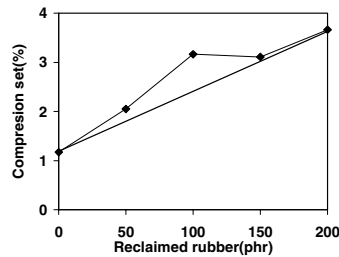**Figure16.** Resilience of vulcanizates

Figure17. Compression set of NR/reclaimed rubber vulcanizates

Conclusion

From the results of this study can be conclude that: reclaimed rubber affects curing of NR due to sulfur left in reclaimed rubber. Reclaimed rubber should be analyzed and cure system should be optimized. Effect of reclaimed rubber on curing, fillers (carbon black and silica) left in reclaimed rubber, lower molecular weight of reclaimed rubber due to chain scission during reclaiming process and non-homogeneity of phases in natural rubber/reclaimed rubber blends cause diminishing of mechanical properties of NR with the addition of reclaimed rubber. The dynamic-based mechanical properties, such as fatigue life, resilience and compression set, show the most reduction while some properties such as modulus and hardness increase due to the fillers left in reclaimed rubber. Mooney viscosity of reclaimed rubber is lower than NR due to its lower molecular weight. Due to Non-homogeneity of phases viscosity of NR/reclaimed rubber blends is lower than predictable values according to the ideal mixture law. Rheological studies show that in low strains, the fillers left in reclaimed rubber cause higher elastic modulus (G′) and elastic torque(S′), lower loss modulus

(G˝) and loss torque(S˝) than NR. But in medium to high strains, reclaimed rubber has non-linear viscoelastic behavior which is in wider strains zone in comparison with NR. Viscoelastic behavior of NR/reclaimed rubber blends is similar to their major phase but the torque and the modulus of these blends is lower than pure reclaimed rubber and virgin NR due to non-homogeneity of phases. Non-homogenized phases can be detected also in SEM photographs.

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