

Physico-Mechanical Studies of Natural Rubber/Carbon Black Vulcanizates Containing Reclaim Rubber

KHALIL AHMED*, NUDRAT ZAHID RAZA, KHAULA SHIRIN AND KHALID MAHMOOD
Applied Chemistry Research Centre PCSIR Laboratories Complex, Karachi. 75280 Pakistan
khalil@yahoo.co.uk, khalilmsrc@gmail.com*

(Received on 12th April 2011, accepted in revised form 27th February 2012)

Summary: Locally available reclaim rubber (RR) was used in this study. It was characterized in terms of its oil soluble parts by acetone extract, rubber identified by pyrolysis and FT-IR, carbon black from TGA and ash content by ignition. The RR was utilized in place of natural rubber (NR) in natural rubber/ carbon black compounding. The physico-mechanical, cure characteristics and swelling properties of the vulcanizates were investigated as a function of RR/NR loading. The minimum and maximum torque, cure time, compression set, hardness, swelling index, swelling coefficient, mol percentage uptake of solvent increases with increasing the amount of reclaim rubber but tensile, strength, elongation at brake, rear strength, resilience, scorch time & volume fraction of rubber vulcanizate decreases. Accelerated aging performance also effected with increasing the loading of reclaim rubber in vulcanizates.

Key words: Reclaim rubber, natural rubber, mechanical properties, cure characteristics, swelling index.

Introduction:

Disposal of rubber wastage is becoming a great problem for industries as it is an emerging environmental health issue. Hence it is a great challenge now a days to recycle or reclaim the waste. The recycling or reclaiming of waste rubber is a difficult process due to the three dimensional structure of cured rubber. This crosslinked structure of rubber product is insoluble and non-melted causing serious problem during re-processing. The major source of waste rubber is used automotive tires. Mainly two processes are involved to utilize these rubber tires. First is to convert the waste into powder form which is used as filler and second is to devulcanize or reclaim the rubber powder.

A comprehensive summary of all the processes involved in reclaiming of rubber waste has given by Adhikaari et, al [1]. The reclamation process involves the friction of higher molecular weight polymer converting into lower one. Both physical and chemical processes are necessary to perform the reclaiming or de-vulcanizing of rubber waste material. The waste rubber powder is either subjected to shearing action in extruder or two-roll mill by a suitable reclaiming agent. The reclaiming agent acts physically as well as chemically to decrosslink the three dimensional structure of cured rubber waste to produce the reclaimed material. Physical process involves the application of mechanical, thermo-mechanical microwave or ultrasound [2-7].

It is reported that the waste rubber powder can be utilized with thermoplastics [8-12], virgin rubber [13-15] and with asphalt [16]. Efforts to improve the physical properties of blends of reclaim

rubber with virgin rubber have attracted many rubber researchers' interest. Different kinds of virgin rubber blending with reclaim rubber have been studied [17-19]. Reclaim rubber is utilized as a substitute of virgin rubber in many rubber compounds, because the addition of reclaim rubber produces cheaper product.

The modification of surface of rubber powder/reclaim rubber by sulphonation [20], monomer grafting [21-23] and oxidation [24-26] was also attempted.

In the present study, we investigate the effects of physico-mechanical properties with cure characteristics and swelling behaviour in different solvents for NR/CB vulcanizates containing reclaim rubber.

Results and Discussion:

The physico-mechanical properties of the Natural Rubber/Carbon Black and Reclaim Rubber (NR/CB/RR) vulcanizates are shown in Fig. 1, NR/CB blend exhibits tensile strength of 235 kgf/cm². The introduction of reclaim rubber with natural rubber effected tensile strength which gradually decreased to 33 kgf/cm² for 20/80 NR/RR vulcanizate. This decrease in the values of NR/CB/RR vulcanizates may be due to the lower molecular weight of reclaim rubber and also due to the immiscibility or incompatibility of Natural rubber/carbon black and reclaim rubber. Additionally, the higher amount of mineral silica in reclaim rubber which is about 36% with 70 meshes, also weaken the matrix in these vulcanizates.

*To whom all correspondence should be addressed.

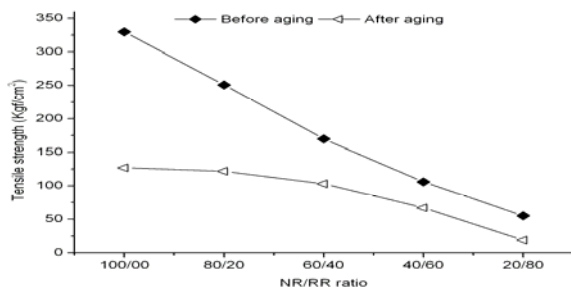


Fig. 1: Tensile strength of NR/CB vulcanizates system before and after aging as a function of NR/RR content ratio.

This fact is further confirmed by the elongation at break value (Fig. 2) of these vulcanizates. Similar pattern was also found for the tear strength (Fig.3) of these vulcanizates. Hardness values (Fig.4)of these vulcanizates also increased by increasing the amount of reclaim rubber due to the higher content of filler found in it. Compression set value (Fig. 6) mainly depends on the elastic recovery done at 70°C for 24 hrs increased with increasing amount of reclaim rubber. This may be due to the weaker interaction between two phases of rubber.

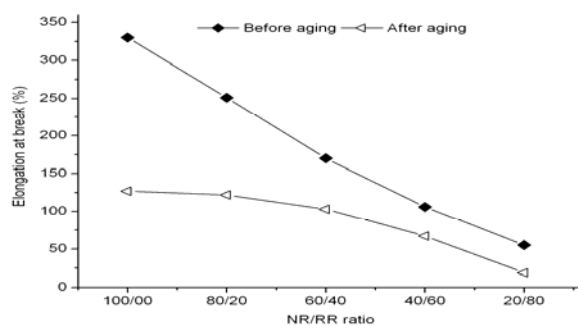


Fig. 2: Elongation at Break of NR/CB vulcanizates system before and after aging as a function of NR/RR content ratio.

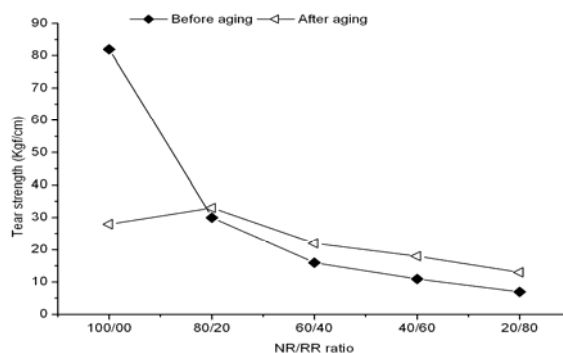


Fig. 3: Tear Strength of NR/CB vulcanizates system before and after aging as a function of NR/RR content ratio.

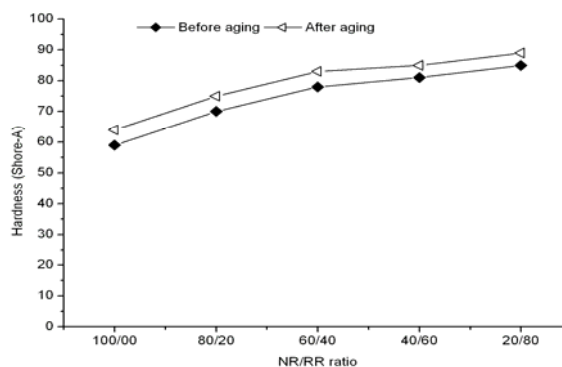


Fig. 4: Hardness of NR/CB vulcanizates system before and after aging as a function of NR/RR content ratio.

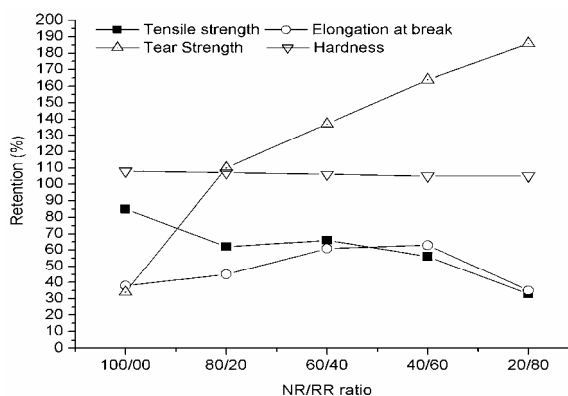


Fig. 5: Effect of NR/RR content ratio on % retention of Tensile Strength, Elongation at Break, Tear Strength and Hardness of NR/CB vulcanizates system.

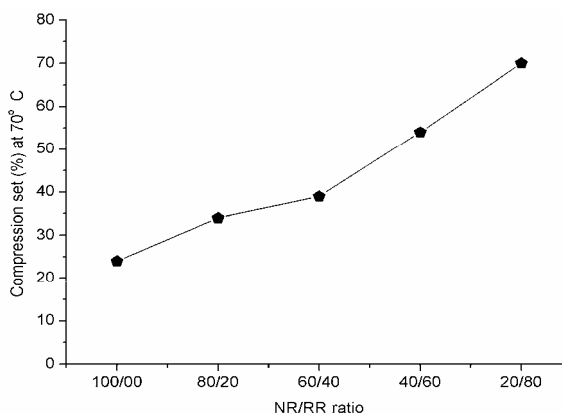


Fig. 6: Compression set of NR/CB vulcanizates system as a function of NR/RR content ratio.

The abrasion and resilience of the NR/ CB/ RR vulcanizates shows (Fig. 7 and 8) the similar trend as shown by the compression set performance. An increase in compression set increases the toughens of the vulcanizates.

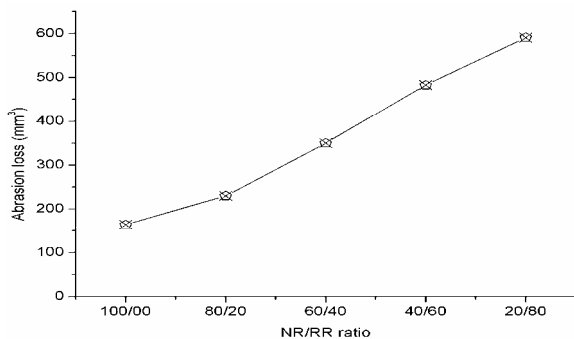


Fig. 7: Abrasion loss of NR/CB vulcanizates system as a function of NR/RR content ratio.

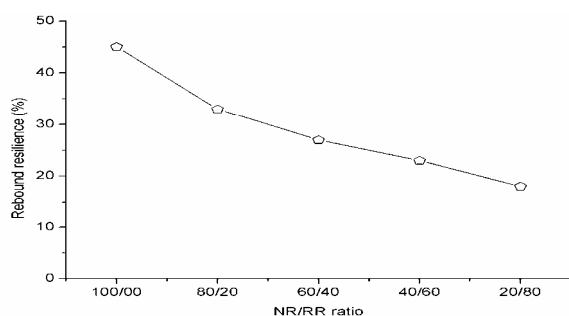


Fig. 8: Rebound resilience of NR/CB vulcanizates system as a function of NR/RR content ratio.

Changes observed in physical properties after accelerated aging of the samples (Fig. 1-4). A decreasing trend is observed in the data of tensile and tear strength, elongation at break and hardness. Gradual increase in the incorporation of reclaim rubber in the blend, which is partially crosslinked, imparts a negative effect on all mechanical parameters (Fig. 5 shows % retention after aging).

Table-1: Compound Formulation

Ingredient	Compound No.				
	A ₁	A ₂	A ₃	A ₄	A ₅
NR	100	80	60	40	20
RR	0	20	40	60	80
Carbon Black	60	60	60	60	60
ZnO	5	5	5	5	5
Stearic Acid	2	2	2	2	2
MBT	1.5	1.5	1.5	1.5	1.5
DPG	0.5	0.5	0.5	0.5	0.5
Sulphur	2.0	2.0	2.0	2.0	2.0

Table-2: Composition of used commercially available reclaim rubber.

Ingredient	Value %
Acetone extract	20
Rubber (NR)	37
Carbon black	7
Ash (Silica)	36

The cure characteristics of the NR/CB/RR vulcanizates are shown in Table-3. It is evident that

with the increase in reclaim rubber at constant cure temperature $155^{\circ}\text{C} \pm 2$, the minimum and maximum torque of the vulcanizates gradually increases. The presence of silica in reclaim rubber restricts the deformation and consequently the vulcanizate becomes hard and stiff as particle size of silica has strong effect on compound viscosity.

Table-3: Rheometric Characteristics of the composition given in Table-4.

Composition #	Min torque dNm	Max torque (dNm)	Scorch time (min)	Cure time (min)	Cure rate index (dNm/min)
A ₁	1.65	5.91	1.88	5.54	27.32
A ₂	2.63	8.95	1.41	6.06	21.5
A ₃	3.30	11.88	1.33	7.49	16.23
A ₄	8.22	19.88	1.01	4.26	30.76
A ₅	12.53	18.03	0.95	3.28	42.9

The scorch time of NR/CB/RR vulcanizate gradually decreases from 100/00 to 20/80 NR/RR ratio. The lower value of scorch time of the vulcanizate can be due to the presence of un-reacted curative, which are present in reclaim rubber. But optimum cure time of reclaim rubber containing compound is slightly superior to those of NR/CB vulcanizate. These parameters differ when the filler (silica) is present in greater amount; however the cure time first increases and then drastically decreases at higher amount of reclaim rubber present. Cure rate index of the vulcanizate decreases due to the increase in optimum cure time and decrease in scorch time. Further increasing in cure rate index is due to the prominent decrease in scorch time.

The effects of various swelling parameters were shown in Table 4-6, where samples were under observation for seven days in toluene, hexane & kerosene. The sorption mechanism in elastomers is essentially connected with the ability of rubber to provide pathways for the solvent. It is observed that the swelling Index, mol% uptake, and Swelling coefficient decreases with addition of reclaim rubber quantity in place of natural rubber, in the NR/RR/ CB vulcanizates but the volume fraction of rubber gradually increases with increasing the content of reclaim rubber in vulcanizate. This observation is due to the presence of crosslinking, causing limitation in penetration of solvent into the vulcanizates particularly in the formulation of A₅. It means that higher content of RR resist the solvent to penetrate into the vulcanizates.

It is also observed that the uptake of aromatic solvent is higher than aliphatic solvent. Maximum uptake was found with toluene followed by hexane and kerosene. The swelling parameters for kerosene, were found to be low. This may be because of the higher molecular weight of the solvent as compare to toluene and hexane.

Table-4: Swelling parameters of NR/RR/CB vulcanization in toluene.

Formulation	Swelling Parameters	1-day	2-day	3-day	4-day	5-day	6-day	7-day
A ₁	Q	1.913	2.11	2.16	2.52	2.52	2.78	2.86
	SI	143.3	168.6	174.64	220	233.4	253.75	263.6
	α	1.653	1.945	2.014	2.536	2.691	2.9	3.04
	V _r	0.357	0.320	0.313	0.281	0.263	0.238	0.231
A ₂	Q	1.51	1.58	1.67	1.75	1.84	1.98	2.00
	SI	101.5	111.7	123.0	133.78	1465	164.95	171.00
	α	1.17	1.28	1.42	1.54	1.69	1.902	1.973
	V _r	0.41	0.387	0.365	0.346	0.326	0.300	0.292
A ₃	Q	1.09	1.10	1.11	1.12	1.14	1.19	1.20
	SI	77.8	83.0	83.2	86.7	90.9	99.1	101.76
	α	0.898	0.958	0.959	1.00	1.05	1.14	1.17
	V _r	0.459	0.441	0.441	0.433	0.420	0.400	0.394
A ₄	Q	0.79	0.83	0.83	0.84	0.842	0.846	0.85
	SI	43.9	50.7	50.9	52.0	52.4	54.6	54.7
	α	0.506	0.585	0.587	0.600	0.604	0.629	0.631
	V _r	0.581	0.543	0.523	0.527	0.526	0.522	0.526
A ₅	Q	0.645	0.676	0.678	0.68	0.68	0.68	0.70
	SI	24.6	30.6	30.6	31.27	31.3	31.55	31.7
	α	0.283	0.353	0.353	0.360	0.361	0.364	0.366
	V _r	0.698	0.649	0.647	0.644	0.641	0.617	0.615

Table-5: Swelling behaviour of NR/RR/CB vulcanizates in hexane.

Formulation	Swelling Parameters	1-day	2-day	3-day	4-day	5-day	6-day	7-day
A ₁	Q	1.35	1.38	1.48	1.52	1.53	1.56	1.57
	SI	49.0	52.66	64.46	68.42	69.58	72.47	74.00
	α	0.743	0.798	0.977	1.036	1.054	1.098	1.11
	V _r	0.551	0.529	0.486	0.470	0.462	0.455	0.449
A ₂	Q	1.15	1.17	1.21	1.22	1.26	1.31	1.31
	SI	39.32	42.17	46.44	48.2	52.3	58.52	58.8
	α	0.596	0.639	0.704	0.730	0.791	0.887	0.891
	V _r	0.623	0.606	0.582	0.573	0.554	0.525	0.524
A ₃	Q	0.91	0.93	0.94	0.95	0.95	0.95	0.99
	SI	27.3	30.2	31.2	32.0	32.15	32.9	32.9
	α	0.413	0.458	0.473	0.486	0.487	0.498	0.498
	V _r	0.688	0.665	0.661	0.654	0.654	0.549	0.609
A ₄	Q	0.74	0.74	0.75	0.762	0.766	0.786	0.788
	SI	16.52	16.85	18.3	19.7	20.2	23.4	23.7
	α	0.25	0.255	0.277	0.299	0.306	0.354	0.359
	V _r	0.771	0.768	0.754	0.739	0.733	0.705	0.702
A ₅	Q	0.65	0.66	0.666	0.67	0.678	0.688	0.693
	SI	7.27	7.37	8.34	8.97	10.25	11.93	12.83
	α	0.11	0.112	0.126	0.136	0.155	0.18	0.194
	V _r	0.878	0.876	0.861	0.853	0.835	0.812	0.803

Table-6: Swelling behaviour of NR/RR/CB Vulcanizates in Kerosene

Formulation	Swelling Parameters	1-day	2-day	3-day	4-day	5-day	6-day	7-day
A ₁	Q	1.06	1.11	1.118	1.12	1.123	1.127	1.128
	SI	90.75	100.0	100.98	101.41	101.75	102.5	102.85
	α	1.21	1.26	1.273	1.28	1.283	1.293	1.297
	V _r	0.444	0.421	0.418	0.416	0.416	0.414	0.415
A ₂	Q	0.803	0.833	0.835	0.838	0.84	0.84	0.842
	SI	66.42	72.46	72.86	73.65	74.27	74.31	74.33
	α	0.838	0.914	0.919	0.928	0.937	0.94	0.43
	V _r	0.492	0.456	0.456	0.468	0.445	0.445	0.445
A ₃	Q	0.59	0.60	0.605	0.605	0.607	0.614	0.616
	SI	46.08	49.0	49.54	49.7	50.2	51.92	52.3
	α	0.581	0.619	0.625	0.627	0.633	0.654	0.659
	V _r	0.568	0.551	0.549	0.549	0.547	0.538	0.535
A ₄	Q	0.39	0.395	0.396	0.398	0.398	0.398	0.399
	SI	26.94	28.9	29.3	29.83	29.86	29.97	30.3
	α	0.34	0.364	0.367	0.376	0.377	0.378	0.382
	V _r	0.661	0.659	0.654	0.651	0.651	0.651	0.644
A ₅	Q	0.333	0.336	0.338	0.338	0.338	0.339	0.339
	SI	13.07	14.94	14.97	15.00	15.11	15.19	15.24
	α	0.165	0.188	0.188	0.188	0.19	0.192	0.192
	V _r	0.798	0.773	0.773	0.776	0.776	0.776	0.776

Conclusion

Following conclusion can be drawn for the use of reclaim rubber in NR/CB vulcanizate in place of natural rubber. The vulcanizate tends to show reduction in tensile strength, elongation at break, tear strength resilience, scorch time, and volume fraction with the increase in reclaim rubber phase but compression set, hardness, abrasion loss, minimum and maximum torque, optimum cure time, swelling index, swelling coefficient, mol percentage uptake of solvent values show the opposite trend. This study shows that the reclaim rubber which is available in local market can be utilized as a compounding additive in non-critical application area where it serves as diluents filler.

Materials and Methods

Materials

The materials used for the preparation of the compounds were;

- 1- Natural Rubber (NR) ribbed smoked sheet (RRS 1)
- 2- Reclaim Rubber (RR)
- 3- Carbon Black (CB)
- 4- Zinc oxide as an activator
- 5- Stearic acid
- 6- Mercapto benzo thiozole (MBT) as accelerator
- 7- Diphenyl guanidine (DPG) as accelerator
- 8- Sulphur as vulcanizing agent
- 9- Toluene as solvent

All materials were commercially obtained from local market. Toluene was purchased from Merck.

Characterization of Reclaim Rubber

Following steps performed for evaluation of reclaim rubber;

1. The oil soluble part of reclaim rubber was extracted with the help of boiling acetone reflux for 18 hours.
2. The percentage of rubber, carbon black and filler were determined by TGA
3. The rubber was identified by pyrolysing the reclaim rubber, the monomer obtained was
4. Analyzed with FT-IR and found to natural rubber.
5. The ash content of reclaim rubber was determined by igniting the sample via

laboratory furnace at 600 °C till constant weight; it was analyzed with FT-IR and found to be silica.

6. The percentage composition of commercially available reclaim rubber is summarized in Table-2.

Methods

Compounding

NR was masticated on the laboratory two roll mill (XK-160) and reclaim rubber was added, then step by step all ingredients were added. The compounds were prepared as per formulation given in Table- 1, according to ASTM method D 3182

Curing

The rheumatic characteristics, minimum torque (M_L) maximum torque (M_H) delta torque (ΔH) Cure rate index (CRI), cure time (t_{90}) and scorch time (t_{52}) were determine using a Monsanto Moving Die Rheometer (MDR 2000) according to ASTM method D 2084. Samples of about 6 gm were tested at a vulcanization temperature of 155°C.

Vulcanization Process

Sheet of 2.5 mm thickness were compressed molded at 155°C with 10 MPa force using a hot laboratory press to respective cure time (t_{90}) determined with the MDR 2000.

Physico-Mechanical Properties

Dumb-bell shaped specimens were punched out from moulded sheets according to ASTM D-15. Tensile strength and percentage of elongation at break were conducted following ASTM D 412 in a tensile testing machine (Instron 4301) at room temperature at uniform speed of 8.33 s⁻¹. Tear strength was determined on Instron 4301 machine as per ASTM D 624. The grip separation speed was 8.33 s⁻¹. Hardness (Shore A) of specimens were measured by hardness tester as per ASTM D 1415. Resilience was measured according to ASTM D 2832. The abrasion loss of vulcanizates were measured using method ASTM D 5963. Compression set values of vucanizates were evaluated base on ASTM method D 395 method B at 70°C for 24 hours in an air aging oven.

For aging resistance, specimens were aged in an air oven for 72 hrs at 70°C as per ASTM

method D 573. The properties of accelerated aging were measured after 24 hours of aging

Swelling Behaviour

Swelling behaviour was determined by change in mass using following method. For cured rubber blends vulcanizates; the test pieces of known weight was immersed in solvent (toluene, hexane, & Kerosene) in diffusion test bottles and kept at room temperature for seven days. Samples were removed from the bottles at every day basis and the wet surfaces were quickly dried using tissue paper and re-weighted. The swelling behaviour of blends were determined at regular intervals, and calculated the following swelling data.

i) Swelling Index SI

Swelling index (SI) was calculated by the equation.

$$SI\% = \frac{W_1 - W_2}{W_2} \times 100$$

ii) Swelling Coefficient

It is an index of the ability with which the test sample swells and is determined by the following equation.

$$\alpha = Sw/W_2 \times 1/ds$$

iii) Calculation of mol % uptake of the Solvent Q_t.

The mol% uptake of the solvent 'Q_t' for the NR/RR/CB vulcanizate was determined by the following equation.

$$Q_t = \frac{(W_1 - W_2) \times 100}{M_s \times W_2} =$$

Where:

W₂= Initial Weight / dry weight.

W₁= Swollen Weight.

S_w= Solvent Sorbed Weight.

M_s= Molar mass of Solvent.

D_s= Density of Solvent.

iv) Volume Fraction (V_r)

Volume fraction V_r of test specimens in swollen mass is calculated from following relation:

$$V_r = \frac{\frac{W_p}{d_p}}{\frac{W_s}{d_s} + \frac{W_p}{d_p}}$$

W_p= Weight fraction of polymer in swollen species.

D_p= Density of polymer

W_s= Weight fraction of solvent

D_s= Density of solvent.

References

1. B. Adhikari, D. De and S. Maiti, *Progress in Polymer Science*, **25**, 909 (2000).
2. D. De, S. Maiti and B. Adlinkari, *Journal of Applied Polymer Science*, **73**, 2951 (1999).
3. B. Diao, A. I. Isayev, V. Y. Levin and S. H. kim, *Journal of Applied Polymer Science*, **69**, 2691 (1998).
4. A. Isayev, J. Chen and A. Tukachinsky, *Rubber Chemistry and Technology*, **68**, 267 (1995).
5. A. Isayev, S. H. Kim and V. Yu. Levin, *Rubber Chemistry and Technology*, **70**, 194 (1997).
6. A. I. Isayev and B. Sujun, *Journal of Elastomer and Plastic*, **38**, 291 (2006).
7. J. K. Kim and S. H. Lie, *Journal of Applied Polymer Science*, **78**, 1573 (2000).
8. H. P. Blom, J. W. Teh and A. Rudin, *Journal of Applied Polymer Science*, **61**, 959 (1996).
9. J. W. Teh, A. Rudin and J. C. Keung, *Advance Polymer Technology*, **13**, 1 (1994).
10. M. Awang, H. Ismail and M. A. Hazizan, *Polymer Testing*, **27**, 93 (2008).
11. M. Awang, H. Ismail and M. A. Hazizan, *Polymer – Plastic Technology and Engineering*, **45**, 463 (2006).
12. M. Awang, H. Ismail and M. A. Hazizan, *Polymer Testing*, **26**, 779 (2007).
13. M. M. Hassan, G. A. Mahmood, H. H. El-Nahas and E. A. Hegazy, *Journal of Applied Polymer Science*, **04**, 2569 (2007).
14. D. S. Ogunniyi and M. Mureyani, *Iranian Polymer Journal*, **10**, 143 (2001).
15. S. W. Kim, K. H. Hong and K. H. Seo, *Journal of Material Research Innovation*, **7**, 149 (2003).
16. M. A. Mull, K. Stuart and A. Yehia, *Journal of Material Science*, **37**, 557 (2002).
17. X. X. Zhang, C. H. Lu and M. Liang, *Journal of Applied Polymer Science*, **103**, 4087 (2007).
18. N. Sombatsompop and C. Kumnuantip, *Journal of Applied Polymer Science*, **100**, 5039 (2006).
19. T. D. Sreeja and S. K. N. Kutty, *Polymer-Plastic Technology and Engineering*, **39**, 501 (2000).

20. A. Yehia, M. N. Ismail, Y. A. Hefny, E. M. Abdel-Bary and M. A. Mull, *Journal of Elastomer and Plastic*, **34**, 305 (2002).
21. E.M. Abdel-Bary, A. M. Dessouki, E. M. El-Nesr and M. M. Hassan, *Polymer-Plastic Technology and Engineering*, **36**, 241 (1997).
22. P. A. Nelson and S. K. N. Kutty, *Polymer-Plastic Technology and Engineering*, **43**, 245 (2004).
23. P. A. Nelson and S. K. N. Kutty, *Progress In Rubber and Plastic Recycling Technology*, **19**, 171 (2003).
24. R. V. A. Rachel, R. M. Gontijo, V. P. Ferraz, M. Rochel, M. Lago, and M. H. Araujo, *Journal of Brazilian Chemical Sciences*, **17**, 603 (2006).
25. F. K. Bangash, S. Alam and M. Iqbal, *Journal of the Chemical Society of Pakistan*, **23**, 215 (2001).
26. S. B. Niazi, R. L. Ali, M. Y. Khokhar and F. Mahmood, *Journal of the Chemical Society of Pakistan*, **23**, 220 (2001).