

## A study of the Hardness and Wear Rate of Elastomer Composites Reinforced by Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> Particles

Jawad K.Olewi\* ,Mohammed S. Hamza\* & Mayyadah Sh. Abed\*\*

Received on:22/9/2008

Accepted on:22/1/2009

### Abstract

This research deals with the study the effect of adding the silica particles and alumina particles separately with different ratio (5, 10, 15, 20, and 25 pphr) on the hardness and wear rate of natural rubber NR and styrene butadiene rubber SBR. The results show that the hardness increases with the increase the loading level of reinforcing particles, while the wear rate decreases with the increase the loading level of the reinforcing particles. The largest value of the hardness and the lowest value of the wear rate were for styrene butadiene reinforced with 25 pphr of silica as compared with natural rubber. Also the reinforcing by SiO<sub>2</sub> increases the hardness and decreases the wear rate more than of Al<sub>2</sub>O<sub>3</sub>.

The results indicated that the hardness and the wear rate for SBR and NR reinforced by SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> at (25 pphr) illustrated in the following table:

Composite	Wear Rate (mm <sup>3</sup> /mm)	Hardness (Shore A)
SBR+25 pphr Al <sub>2</sub> O <sub>3</sub>	2.965	78
SBR+25 pphr SiO <sub>2</sub>	0.91	85
NR+25 pphr Al <sub>2</sub> O <sub>3</sub>	4.3	68
NR+25 pphr SiO <sub>2</sub>	2	76

**Keyword:** Elastomer; Composites; Hardness; Wear Rate

### دراسة الصلادة و معدل البلى لمتراكب مطاطي مقوى بدقائق من Al<sub>2</sub>O<sub>3</sub> و SiO<sub>2</sub>

#### الخلاصة

تناول هذا البحث دراسة تأثير اضافة دقائق السليكا و الالومينا بصورة منفصلة و بنسب مختلفة بيوتاديين. بينت النتائج بان الصلادة تزداد مع زيادة نسب اضافة مادة التقوية, بينما معدل البلى يقل مع زيادة نسب اضافة مادة التقوية. حيث ان اعلى قيم للصلادة و اقل معدل بلى تم الحصول عليه هما للمطاط الستايرين- بيوتاديين المقوى بدقائق السليكا بنسبة (25 pphr) مقارنة بالمطاط الطبيعي. وكذلك عند التقوية بدقائق السليكا يقل معدل البلى اكثر مما عليه عند التقوية بدقائق الالومينا. حيث بلغت قيم الصلادة و معدل البلى للمطاط NR و المطاط SBR المقوى بدقائق السليكا و الالومينا بنسبة (25 pphr) موضحة بالجدول التالي:

الصلادة (Shore A)	معدل البلى (mm <sup>3</sup> /mm)	المتراكب
78	2.965	SBR+25 pphr Al <sub>2</sub> O <sub>3</sub>
85	0.91	SBR+25 pphr SiO <sub>2</sub>
68	4.3	NR+25 pphr Al <sub>2</sub> O <sub>3</sub>
76	2	NR+25 pphr SiO <sub>2</sub>

## Introduction

Elastomer or rubber is amorphous polymer which shows very large strains when subjected to stress and which returned to their original dimensions when stress is removed. There is properly no more complex and widely used class of materials than rubber compounds because of their unusual properties flexibility, extensibility, resiliency and durability, more over their ability to absorb particle filler like carbon black, silica and clay in amounts exceeding their own weight means that the range of properties. The addition of various chemicals to raw rubber, to impart desirable properties is termed rubber compounding of formulation. Typical ingredients include cross linking agent (curatives), reinforcements, antidegradants, process aids, and colorants [1, and 2].

Takguchi 1986 [3], prepared carbon black filled tire tread of blended matrices of butadiene and natural rubber (BR/NR) which blends separately with butyl rubber (IIR), bromo-butyl rubber (BIIR) or chlorinated-butyl rubber (CIIR). Also it had been prepared carbon black filled tire tread of styrene butadiene rubber (SBR) for comparison. It had been study the effect of matrix type on the hardness and wear rate, in order to improve the tire life. The wear resistance for these blended was not significantly improved compared with styrene butadiene rubber (SBR).

Takino *et al.* 1997 [4], reported that tire tread made from styrene butadiene rubber SBR with blend of chlorinated-butyl rubber and bromo butyl rubber (CIIR/BIIR) displayed the highest wet traction than SBR alone, but the laboratory measurement showed that this recipe had the highest volume loss by wear corrosion in tire tread.

Al-Hatimi 1999 [5], studied the effect of loading level and types of carbon black (N330 and N339) on the performance of tire and compared with tire filled with rice husk burned at low

temperature. Improvement in hardness, abrasion resistance, and modulus of elasticity occurred at (70 pphr) of carbon black type (N330), and at (68 pphr) of type (N339).

Parkinson 2000 [6], studied the particle size effect of carbon black on rubber composite. It had been found that the tensile and tear strength, abrasion resistance increase with decreasing particle size of carbon black due to the possibility of occurring the chemical cross linkages in the carbon-rubber interface.

Ismail *et al.* 2003 [7], investigated the effect of recycle rubber powder (RRP) content and various vulcanization systems (conventional (CV), semi-efficient (Semi-EV) and efficient vulcanization (EV)) on curing characteristics and mechanical properties for blends of natural rubber and recycle rubber powder (NR/RRP). They found that the increasing RRP content in NR/RRP blends increases tensile modulus and hardness but decreases the tensile strength, tear strength, resiliency and elongation at break. Although the CV system exhibits the highest tensile modulus and hardness but (NR/RRP) blends cured with EV system show the highest tensile strength, tear strength, resiliency and elongation at break followed by semi-EV and CV systems.

Zanzig *et al.* 2004 [8], used blend of butadiene rubber and styrene isoprene rubber (BR/SIR) as a tire tread recipe, so that BR has the largest loading level (70-90 pphr), and then compared with styrene butadiene rubber SBR performance. It had been found that this blend at loading level (80/20 pphr) of BR/SIR improved the tire tread properties which are abrasion resistance (to enhance tread wear).

Jorge and Kim 2005 [9], studied the mechanical properties and fatigue life of NR with different types of carbon blacks (N330, N650, and N900). It had been noted that logarithmic value of the fatigue life was linearly proportional to

the hysteresis for all types of carbon black. Also the NR reinforced with carbon black type (N330) had the largest value of hardness, abrasion resistance, resilience, and modulus.

Al-Maamory 2006 [10], studied the effect of SiO<sub>2</sub> particle size and its loading level on nitrile butadiene rubber (NBR) properties. He noted that resilience decreases with the decrease particle size of SiO<sub>2</sub> and with increase loading level of it, but the hardness increased. Also he found that ultra violet light UV and aging at high temperatures degraded the rubber properties.

Al-Hatimi 2007 [11], prepared (75) recipes of carbon black filled styrene butadiene rubber SBR blended with (NR, CR, BR and EPDM) separately and at different loading level of SBR (10-60 pphr). It had been studied the effect of carbon black type (N375, N330 and N339), on the properties of tire tread formulation hardness and abrasion resistance, and compared with Babylon tire specifications. The best properties were at loading level for SBR/NR blend was (30/70 and 40/60 pphr) for three types of carbon black. The optimum loading level for SBR/BR blend was (20/80 – 50/50 pphr) and for three type of carbon black, for SBR/CR were (30/70 and 40/60 pphr) for three types of carbon black, and for SBR/LPDM was (10/90 – 50/50 pphr) for carbon black type (N339 and N 330).

The aim of the work is to study the effect of type and loading level for reinforcing particles Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> on the hardness and the wear rate of natural rubber and styrene-butadiene rubber separately.

### Theory

The wear resistance in rubber may be define as the resistance to wearing away by rubbing or sliding surface rubber against abrasives material results in surface material removal. Pin-on-disk was used, which depends on producing relative motion between the rubber and an abradant. The based

standard test in this work is that rubber cylindrical blocks are fixed in vertical holder and pressed against a rotating abrasive paper disc at specific force, time, temperature, and velocity. The test method may be used to estimate the relative abrasion resistance of different rubber compounds for comparison. No correlation between this accelerated test and service performance is given or implied, due in part to the widely varying nature of service conditions [12, and 13].

To estimate abrasion resistance, wear rate could be computed by using the following equation:

$$K_c = \frac{\Delta m}{\rho_c \cdot V_s \cdot T} = \frac{m_1 - m_2}{\rho_c \cdot V_s \cdot T}$$

Where:-

**K<sub>c</sub>** : Wear rate of composite (mm<sup>3</sup>/mm)

**Δm** : Mass loss (g).

**m<sub>1</sub>** : Weight of specimen before test (g).

**m<sub>2</sub>** : Weight of specimen after test (g).

**ρ<sub>c</sub>** : Density of specimen (g/mm<sup>3</sup>).

**V<sub>s</sub>** : Sliding Speed (mm/s).

**T** : Sliding Time (s).

### Experimental work

#### Mixing and vulcanization

The preparation of rubber composite for application of NR and SBR require many mechanical tests which simulate conditions that these parts are subjected to such tension. Rubber composite preparation includes processing technology consists of compounding, mixing by two rod mill (calender), shaping; generally molding, and vulcanization. Rubber is always compounded with additives: vulcanization chemicals (sulphur), and usually reinforcing fillers, antidegradants, oil or plasticizer. It is through compounding that specific rubber vulcanizate obtain its characteristics. This work based on standard practice ASTM D3182 for rubber material, equipment and procedures for mixing [14].

The basic ingredients of recipe formulation which used in this work are shown in table (1). Table (2 and 3) [15, and 16] show some characteristics of rubbers and reinforcing particles respectively.

#### Hardness Test

This test is done by using measurement Shore A according to ASTM D 2240. It should be make five measurements of hardness at different positions on the specimens at least (6mm) apart and determine the average value. Also hardness value is very sensitive to specimen thickness and the distance of any edge, the preferred thickness is (6-10 mm) and at least (12 mm) from any edge [17].

The test specimens are shown in figure (1). Test equipment is shown in figure (2).

#### Wear Rate Test

Two-body abrasive wear tests were conducted on a pin-on-disk abrasive wear tester, designed for standard wear tests described in ASTM (D 5963). In this method, the test specimen translates over the surface of an abrasive paper (SiC) with particle size (200 μm) which mounted on a revolving disk. The test done under conditions: period of testing 4 min, applied load (5 N). Test specimens are shown in figure (3), and abrasion wear machine is shown in figure (4).

#### Results and Discussion

Figures (5) and (6) show the shore hardness is plotted against the loading level of reinforcing fillers Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> for SBR and NR respectively. From these figures it can be seen that rubber hardness shows significant increment with the increasing loading level of reinforcing fillers in a non-linear behavior but at different rate. Also, it can be seen that SiO<sub>2</sub> reinforcing fillers increases the hardness at a rate higher than Al<sub>2</sub>O<sub>3</sub> fillers in both rubber SBR and NR. The SBR hardness reaches values 78 and 85 shore (A). The NR hardness reaches values 68 and 76 shore (A). This is due to *firstly*: SiO<sub>2</sub> material

is harder than Al<sub>2</sub>O<sub>3</sub>, and this will contribute to increase the composite hardness more than Al<sub>2</sub>O<sub>3</sub> material at equal loading level in volume unit, and *secondly*: SiO<sub>2</sub> reinforcing fillers have grain size finer than Al<sub>2</sub>O<sub>3</sub>. This means that SiO<sub>2</sub> has larger surface area than Al<sub>2</sub>O<sub>3</sub> fillers, which in contact with rubber mostly by physical bonds than Al<sub>2</sub>O<sub>3</sub>. Composite with strong bonds made it harder by impeding the matrix motion along the stress direction. Figure (7) shows the effect of the matrix type (NR and SBR) and particles type (Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>) on the hardness.

Figures (8) and (9) show the wear rate of SBR and NR (as indicator of reciprocal of abrasion wear resistance) versus the loading level of reinforcing fillers respectively. These figures show that the wear rate of SBR and NR are inversely proportional with the loading level of reinforcing fillers and the relationship is non-linear.

Wear resistance of unfilled rubber can generally be enhanced by introducing reinforcing filler into the matrix material. The explanation is that the sliding of abrasives on a solid surface results in volume removal, and wear mechanism depends on the hardness of the composite component which is a key parameter in governing the amount of material removal, so that the presence of the hard reinforcing filler increases the effective hardness of the composite which acts to reduce the amount of material removal [18].

It is noted from these figures that the wear rate of SBR at 0 pphr equal to 6.689 mm<sup>3</sup>/mm, and it reaches to 2.96 mm<sup>3</sup>/mm and 0.91 mm<sup>3</sup>/mm at 25 pphr of reinforcing fillers Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> respectively. Thus the percentages of decrease of SBR wear rate are 64% and 89% when reinforced with 25 pphr of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> respectively compared with 0 pphr loading level. Also, the wear rate of NR at 0 pphr loading level is equal to 8.276 mm<sup>3</sup>/mm, and it reaches to 4.3 mm<sup>3</sup>/mm and 2.1 mm<sup>3</sup>/mm at 25

pphr of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> respectively. Thus the percentages of decrease of NR wear rate are (38%) and (71%) when reinforced with 25 pphr of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> respectively compared with 0 pphr loading level.

This means that the rubber reinforced with SiO<sub>2</sub> fillers has decreased the wear rate (increase abrasion wear resistance) higher than Al<sub>2</sub>O<sub>3</sub> fillers. This is because the reinforcement is decreased due to failure at the matrix-reinforcement interface or in the reinforcement itself. The abrasions wear resistance influenced by the following factors *firstly*: interfacial properties where the SiO<sub>2</sub> fillers has tougher interfacial bond with rubber by silane coupling agent than Al<sub>2</sub>O<sub>3</sub> bonding. This made the wear by interfacial debonding more difficult, *secondly*: geometrical properties where the particle size of SiO<sub>2</sub> fillers is finer than Al<sub>2</sub>O<sub>3</sub> fillers; therefore it has larger surface area than Al<sub>2</sub>O<sub>3</sub> fillers. Fillers contribution to the abrasion wear resistance is inversely proportional to its particle size i.e. the finer particle size enhances the abrasion wear resistance by lowering wear rate. *Thirdly*: mechanical properties of the reinforcement i.e. SiO<sub>2</sub> ceramic is harder than Al<sub>2</sub>O<sub>3</sub> in nature. Figure (10) shows the effect the matrix type and particle type on the wear rate [19].

### Conclusions

- Hardness of rubber composites increases with the loading level of reinforcing fillers and reaches a maximum value (85 Shore A) for SBR reinforced with 25 pphr SiO<sub>2</sub>. The hardness of Styrene butadiene rubber is a higher than of natural rubber at the same reinforcing fillers and loading level.
- The wear rate decreased with the increase loading level of reinforcing particles Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> and for the both rubbers SBR and NR. The minimum value of this characteristic

was (0.91 mm<sup>3</sup>/m) for SBR reinforced with 25 pphr of silica.

- SiO<sub>2</sub> reinforcing particles increase the hardness and decrease the wear rate more than Al<sub>2</sub>O<sub>3</sub> particles at the same loading level.
- The both reinforcing particles affect the hardness and the wear rate for styrene butadiene rubber significantly more than NR.

### References

- [1] W. Bolten, "Engineering Materials Technology", 3<sup>rd</sup> edition, Butter Worth Heinemann BH, Inc., Great Britain (1998).
- [2] C. A. Harper, "Handbook of Plastics", the McGraw Hill company, Inc., New York (2006).
- [3] E. Takiguchi, "Carbon Black Filled Tire Tread", Britain patent 2140447, U.S. patent 4567928, (1986).
- [4] H. Takino, R. Nakayama, Y. Yamada and S. Kojiya, "Preparation blends of rubber for Tire Tread", Journal of Rubber Chemistry and Technology, Vol. 70, No.384, Japan, (1997), P.45
- [5] M. Al-Hatimi, "Improvement of Tread Properties of Babylon Tire" M. Sc. Thesis, Eng. College, Babylon University, Babylon, Iraq, (1999).
- [6] D. Parkinson, "The Reinforcement of Rubber by Carbon Black" Institute of Physics and IOP Publishing Limited, Research Center, Dunlop Rubber Co. Ltd., Birmingham, (2000).
- [7] H. Ismail, R. Nordin and A. M. Noor, "The Effects of Recycle Rubber Powder (RRP) Content and Various Vulcanization Systems on Curing Characteristics and Mechanical Properties of Natural Rubber/RRP" Iranian Polymer Journal Vol. 5, No.12, (2003), P. 373-380, Iran.
- [8] D. J. Zanzig and J. C. Aaron, U. S. patent, 6812277, [www.freepatentonline.com](http://www.freepatentonline.com) (2004).
- [9] H. R. Jorge and J. H. Kim, "Study the Mechanical Properties and Fatigue Life of NR Composites", International

- Journal of Fatigue, Vol. 2, No.7, (2005), P. 263.
- [10] M.H. Al-Maamory, "**Mechanical and Physical Properties of Rubber Composite**", Ph.D. Thesis, Applied Science, University of Technology, Baghdad, Iraq, (2006).
- [11] M.H. Al-Hatimi, "**Optimization Study of Rubber Blends and Their Effects on Passenger Tire Tread properties**", Ph.D. Thesis, Material Eng., University of Babylon, Babylon, Iraq, (2007).
- [12] L. R. G. Treloar, "**The Physics of Rubber Elasticity**", 3<sup>rd</sup> ed., Clarendon Press, Inc., Oxford, (1975).
- [13] Standard Test Method for Rubber Property-Abrasion Resistance **D 2228**, Annual Book of ASTM Standard, Vol 09.01, USA, (1988).
- [14] C.A. Harper, "**Handbook of Plastics**", the McGraw Hill Co., Inc., New York, (2006).
- [15] M. Chanda, S.K Roy, "**Plastic Technology Handbook**", 4<sup>th</sup> edition, Taylor and Francis Group, LLC, USA, (2006).
- [16] [www.negevsilica.com/company/partnership](http://www.negevsilica.com/company/partnership). "**Specialty Silica**", Diamond Silica Co. Ltd., (2008).
- [17] Standard Test Method for Rubber Properties-Durometer Hardness **D 2240**, Annual Book of ASTM Standard, Vol. 09.01, USA, (1988).
- [18] D.Hols, K. Janssen, and K. Fredrick, "**Abrasive Wear of Ceramic-Matrix Composites**", Journal of the European Ceramic Society, (1989).
- [19] G.Y. Lee, C.K. Dharan, and R.O. Ritchie, "**A Physically-Based Abrasive Wear Model for Composite Materials**", Depart. Of Materials Science and Engineering, University of California, (2007).

Table (1) The Used Recipe Formulation.

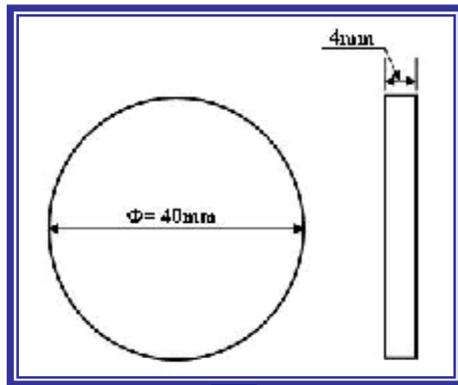
Item	Material	Loading level (pphr)	Loading level (pphr)
1	SBR	100	0
2	NR	0	100
3	Zinc oxide (activator)	5	5
4	Stearic acid (activator)	2	2
5	Antioxidant	1.5	1.5
6	Antiozonant	1.5	1.5
7	Process oil	5	5
8	Carbon black (N339)	25	25
9	Precipitated silica	(0, 5, 10, 15, 20, 25)	(0, 5, 10, 15, 20, 25)
10	Alumina	(0, 5, 10, 15, 20, 25)	(0, 5, 10, 15, 20, 25)
11	Silane Coupling agent	----	----
12	Sulphur	5	5
13	Accelerator (TMTD)	1.7	1.7
14	Retarder (MBTS)	0.1	0.1
15	Reclaim	5	5

Table (2) shows some characteristics of *SBR* and *NR* [15].

Property	$Al_2O_3$	$SiO_2$
appearance	Fine white powder	Fine agglomerate white powder
Sp.gr.	3.88	1.95
Surface area ( $m^2/g$ )	.....	60
Particle size	30 $\mu m$	(20 – 25) nm

Table (3) shows some characteristics of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> [15, and 16].

Property	SBR	NR
Color	Yellow	Brown
Sp.gr.	0.92	0.934
T <sub>g</sub> (°C)	- 55	- 70
Tensile strength at break (MPa)	12.4 - 20.7	17.23 - 25
Modulus of elasticity at 100% elongation (MPa)	2 - 10	4 - 15
Elongation% at break	500 – 1000	300 – 700



-a-



-b-

Figure (1): Hardness Test Specimens;

a: Schematic specimen, b: Specimens.



Figure (2): Shore A Durometer

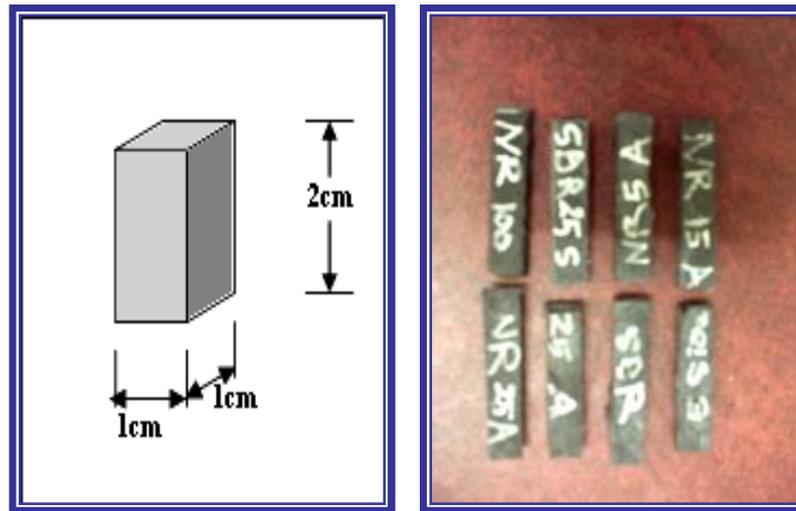


Figure (3): Wear Test Specimen;  
a- Schematic Representation; b- Specimens.

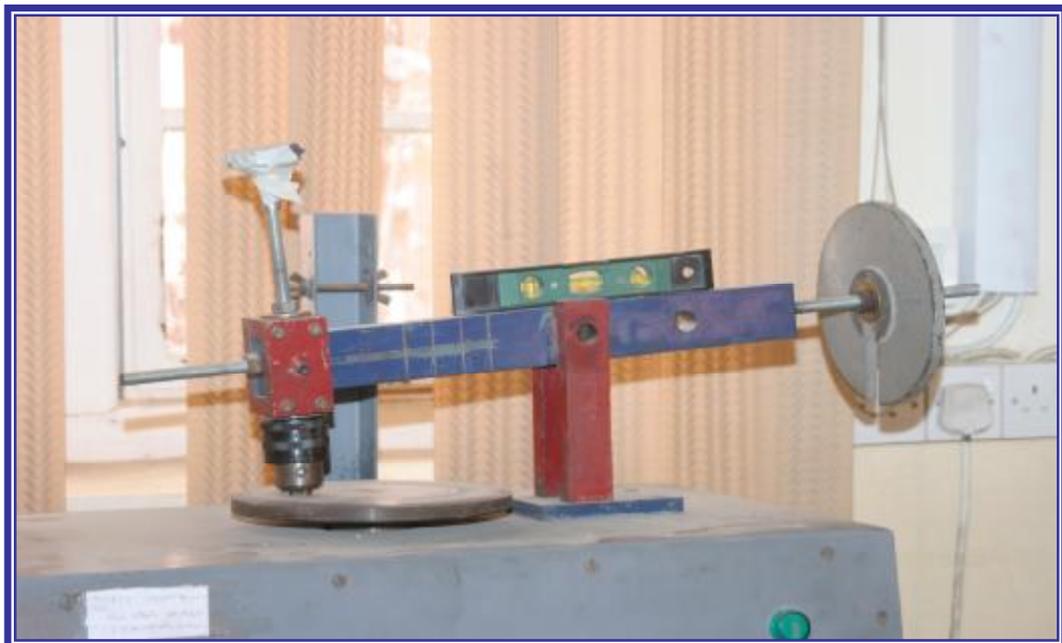


Figure (4): Wear Test Machine.

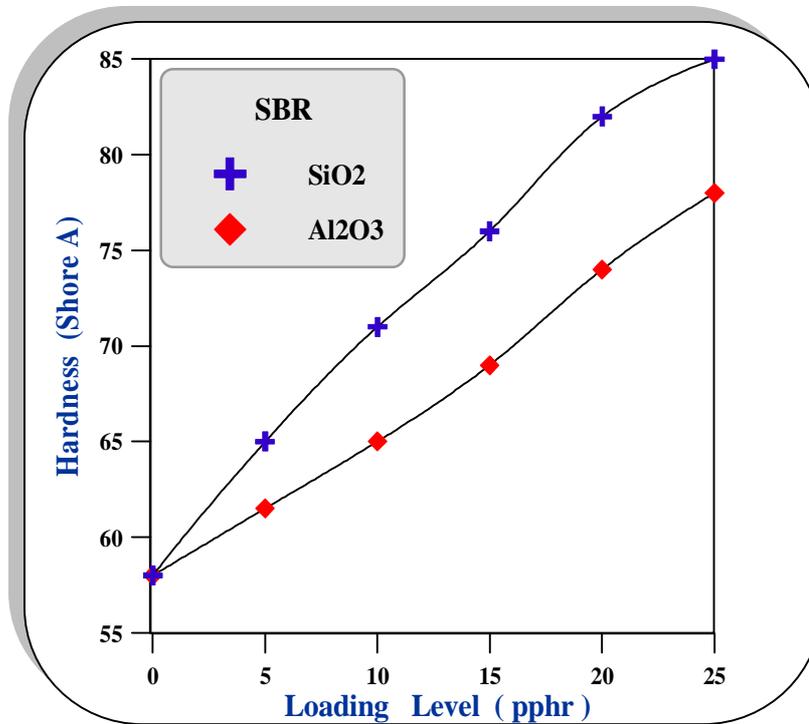


Figure (5) Hardness (shore A) vs. Loading Level of Reinforcing Particles Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> for SBR Composites.

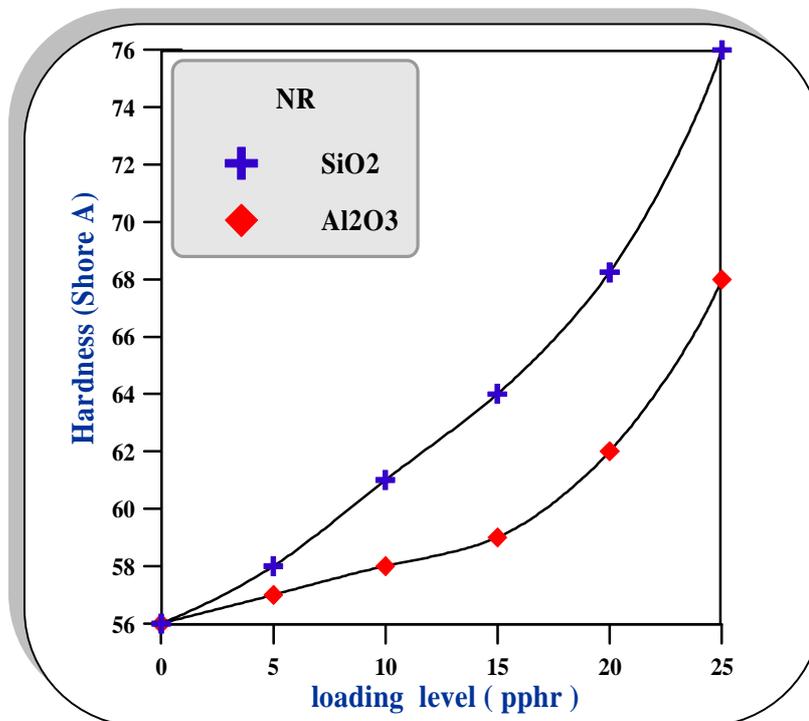


Figure (6) Hardness (shore A) vs. Loading Level of Reinforcing Particles Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> for NR Composites.

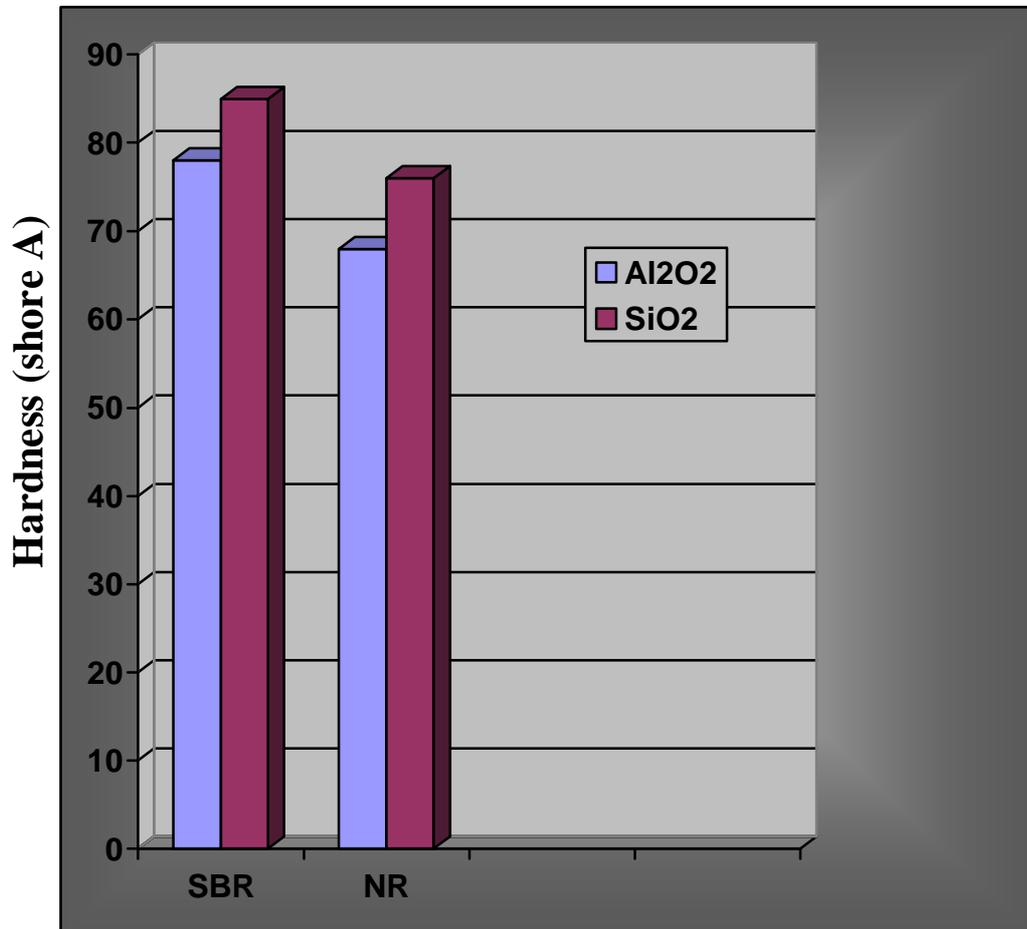


Figure (7) Hardness (shore A) vs. Matrix Type (NR and SBR) and Reinforcing Particles type (Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>) at loading level 25 pphr.

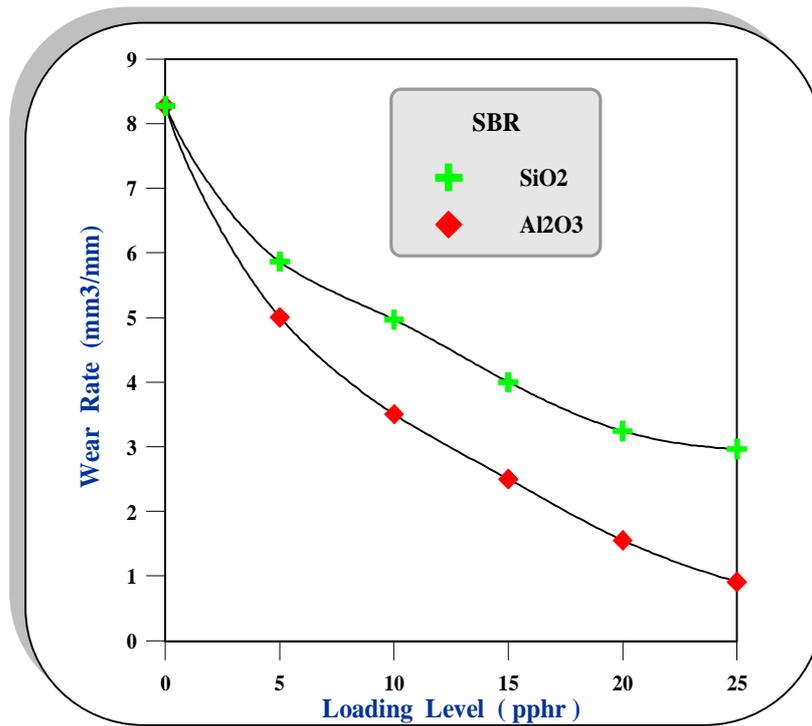


Figure (8) Wear Rate vs. Loading Level of Reinforcing Particles Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> for SBR Composite

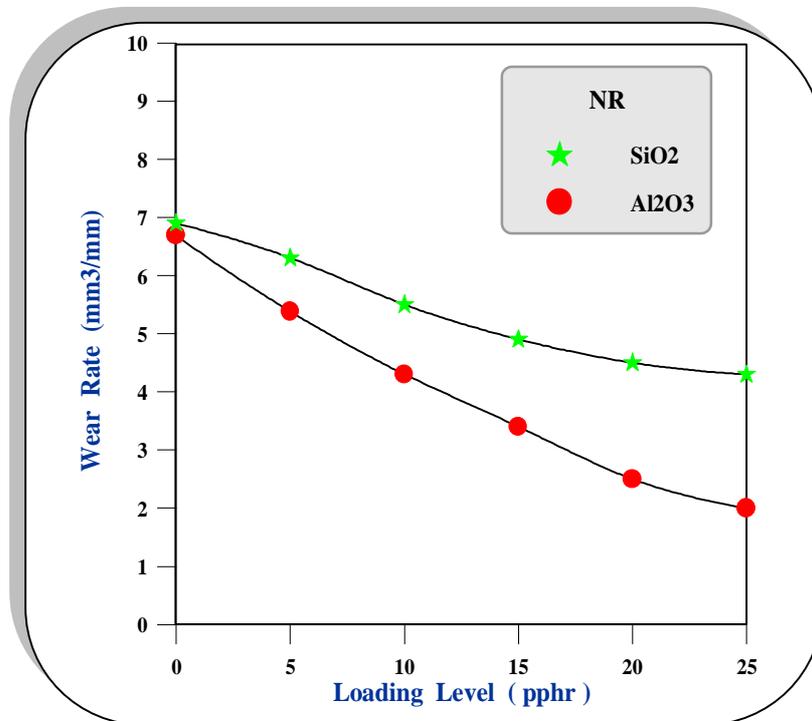


Figure (9) Wear Rate vs. Loading Level of Reinforcing Particles Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> for NR Composites.

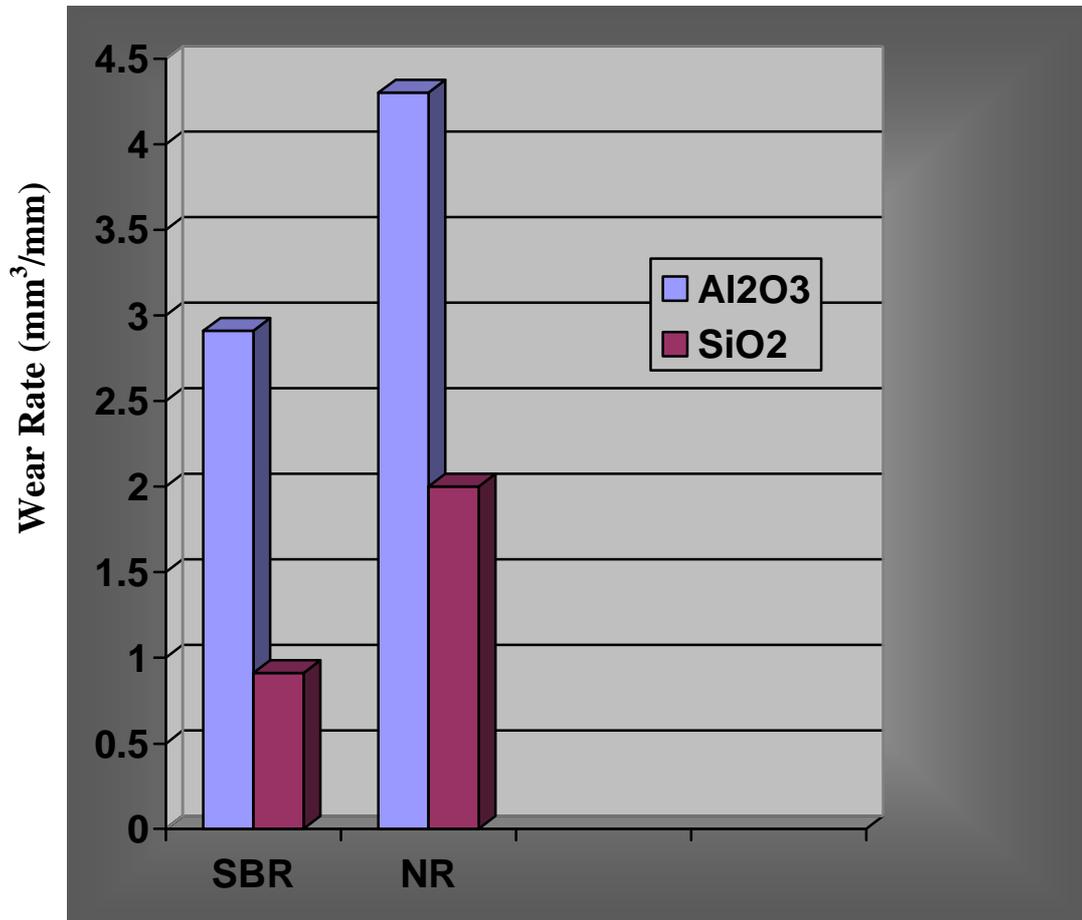


Figure (10) Wear Rate vs. Matrix Type (NR and SBR) and Reinforcing Particles type (Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>) at loading level 25 pphr.