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Aging Effect on Hardness of SBR/NR/BR, SBR/NR Composites by using Industrial Scraps as a Filler

[1]Mohammed Al-maamori, [2]Sameer Al-Nesrawy, [3]Abd-ulritha.Hasaani

[1]*University of Babylon, College of Materials Engineering, Iraq.*
[2]*University of Babylon, Department of physics, Education College for Pure Science, Iraq.*
[3]*University of Baghdad, Department of physics, College of Science, Iraq.*

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ABSTRACT

This research project carried out through eight recipes according the type of blends such as, SBR/NR, SBR/NR/BR_{cis} and the type of mixture from carbon black and cement waste or carbon black and reclaim that it used as reinforcement materials in the composites. While the hardness (IRHD) tests carried out according ASTM D 1415-88 specifications in order to using these composites in fender ship application. All composites are composed of carbon black N375 (loading percent 50 pphr) with reclaim (0,10,20)pphr or with cement waste (0,10,20)pphr . The Hardness property was examined before and after aging according ASTM D 573 and aging condition 70° C x 96 hrs. The results appeared that the hardness increase with increasing waste or reclaim loading when the ratio of SBR was greater than NR, so inverse behavior happen when the ratio of NR was greater than SBR for the reclaim and waste loading.

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INTRODUCTION

Perhaps the most widely used test in the rubber industry is the measurement of hardness. Hardness is defined by ASTM as the resistance of material surface to indentation as measured under specified conditions. Rubber technologists use hardness as a convenient means of classifying rubber materials. There are two different hardness tests that claim nearly universal acceptance: the durometer and the International Rubber Hardness tester . Different durometers are designed to cover the wide range of hardness encountered in rubbers. The shore A scale is the most appropriate for rubber compounds commonly used in engineering. The shore D scale is appropriate for harder rubber compounds such as ebonite, plastics. The Rockwell scale is also used for hard urethane (Alan, 2001) (Andrew,1999).

The International Rubber Hardness tester differs from the durometer in several important aspects. It is a small bench top instrument that uses dead weights to apply defined loads to a spherical indenter, while the penetration is measured with a dial gauge. The dial gauge is commonly calibrated directly in International Rubber Hardness degrees (IRHD). The IRHD scale was chosen to have readings numerically equivalent to the popular A scale over the range normally encountered in practical engineering compounds. While the approximate equivalence of the IRHD and the A scales is valid for highly elastic materials, significant differences may be expected for materials that show marked time-dependent behavior (Alan, 2001).

According to the ASTM standard the penetration of the indenter bears a known relation to the Young's modulus of the rubber .This relation is an empirical relation Obtained by (Scott, 1948).

$$\frac{F}{E} = 1.9\, P^{1.35}\, r^{0.6} \qquad (1)$$

Where F is the indenting force (N), E is Young's modulus (MPa) ,p is the depth of Penetration (mm), and r is the radius of the indenter (mm) showed that a theoretical relation may be derived from the classical theory of Elasticity in the form (Alan, 2001).

$$\frac{F}{E} = 1.78\, P^{1.5}\, r^{0.5} \qquad (2)$$

Corresponding Author: Mohammed Al-maamori, University of Babylon, College of Materials Engineering , Iraq.

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If we take Young's modulus to be equal to three times The shear modulus G, we may write:

$$\frac{F}{G} = 5.33\, P^{1.5}\, r^{0.5} \qquad (3)$$

These relations between hardness and Young's or shear modulus , whether empirical or Theoretical ,should be regarded as only approximate .Significant discrepancies may occur Simply from the way Young's modulus is defined and measured hardness. Discrepancies are also expected when the material deviates markedly from perfectly elastic behavior. Although the International Rubber Hardness test is an established ASTM method (Alan, 2001).

This test method covers the effects of elevated temperatures on the properties of a material. Testing is performed in air for a specified period at a specified temperature. Properties are measured prior to and after high temperature exposure. Values represent a percentage change in properties with the exception of the Change in Durometer Hardness and Change in IRHD Hardness. Change in hardness values are reported as the change in hardness points (ASTM D573).

The formula used for calculating the change in a property (except for hardness)is (AL-Masudi, 2007).

$$P=((A-O)/O)*100 \qquad (4)$$

where: P is the percentage change in the property, O is the original value, and A is the value after aging.
The formula used for calculating the change in hardness is:

$$C=A-O \qquad (5)$$

where: C is the change in hardness, O is the original value, and A is the value after aging.

Materials and Experimental part:

The SBR, SBR/NR, NR/SBR/BRcis blends were reinforced by different volume fractions of carbon black (CB) N375, cement waste and reclaimed tire.

- NR used in this study was SMR 20 which has a specific gravity (0.92 gm/cm^3), supplied by the Perlis, Malaysia.
- SBR used in these experiments is SBR 1502 contain 23.5% styrene content and butadiene, it have the specific gravity (o.95 gm/cm^3), supplied by the Petkim, Turkey. Therefore, BR_{cis} (specific gravity 0.90 gm/cm^3)
- Carbon black N375 supplied by Doudah, Iran. It is examined in accordance with the DBP absorption (ASTM D136) and Iodine absorption (ASTM D135).
- Reclaim (specific gravity 1.16 (gm/cm^3) supplied by Babil Tire factory . Cement waste powder supplied by Karbala factory,
- Zinc oxide (97%) and stearic acid (99.4%) were supplied by Durham, U.K. 6PPD N- (1, 3 – Dimethyl butyl) – N – Phenyl – Para – Phenylenediamine (98%) was supplied by Flexsys, Belgium. MBS N-oxydiethylenebenzothiazole 2- sulfonamide (98.2%) supplied by ITT, India. The South Patrol Company supplied Paraphenic wax, processing oil. Sulfur was supplied by the Durham, U.K.

Laboratory mill:

Baby mill was used in this research to prepare the batches, it have two roll mills, having provisions for passing cold water. These rolls are cylindrical in shape and of 150mm diameter and 300mm in length in the other hand the roll speed is 20 r.p.m. The hydraulic press is equipped with thermocouple and maximum temperature is equal to 300°C and vulcanization process was performed at 165º and 20 min.

Mould for Testing hardness:

For preparing samples for hardness and density tests , the mould in the laboratories of Tire Company was used. The mould consists of three parts ,the middle part in a dimension of 200mm*180mm*6.5mm which contains (9) circular equivolume open with 65mm diameter and 5 mm thickness, while one of the other two parts is bottom base and the other is a cover for the purpose of samples thickness regulation. They have a dimension of 150*150*10mm.

Equipment for Hardness (IRHD) measurement:

The International Hardness test is used in the measurement of the penetration of rigid ball (according to Brinall method) into the rubber specimen. The diameter of the ball equal to 2.5 mm; sample for hardness prepared in section (3.6.4), under specified conditions. The measured penetration was converted to the International Rubber Hardness Degrees (IRHD), The scale of degrees is so chosen that zero represents a material having elastic modulus equal to zero and 100 represents a material of infinite elastic modulus. The scale covers all the normal range of hardness. The tests were carried out according to ASTM D 1415-88 specifications (ASTM D 1415).

Preparations of batches:

The batches were preperd by mill labortary, the compounding ingredients are shown in table (1.1).

Table 1.1: Compounding ingredients of recipes**.**

COMPOUNDING INGRADIENTES	RECIPE (1)	RECIPE (2)	RECIPE (3)	RECIPE (4)	RECIPE (5)	RECIPE (6)	RECIPE(7)	RECIPE (8)
SBR 1502	80	60	50	60	30	20	10	30
NR SMR 20	20	40	50	30	70	80	90	60
BRcis	0	0	0	10	0	0	0	10
ZINC OXID	5	5	5	5	5	5	5	5
STEARIC ACID	2	2	2	2	2	2	2	2
PARAPHINIC WAX	2	2	2	2	2	2	2	2
PROCESSING OIL	5	5	5	5	5	5	5	5
CARBON BLACK	50	50	50	50	50	50	50	50
CEMENT WASTE OR RECLAIM	Variable (0,10,20)	Variable (0,10,20)	Variable (0,10,20)	Variable (0,10,20)	Variable (0,10,20)	Variable (0,10,20)	Variable (0,10,20)	Variable (0,10,20)
6PPD	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MBS	1	1	1	1	1	1	1	1
SULFUR	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Results:

The figures (1),(2),(3),(4) indicated that the addition of the mix of C.B(50pphr) and cement waste (0,10,20) or reclaim(0,10,20) showed a marked increase in hardness, this result is expected because as more fillers incorporated in the rubber matrix. It is well known that the addition of the filler in rubber compounding leads to increase in materials hardness; moreover, this attributed to the physical cross-linking that presents between rubber-C.B, rubber- reclaim, rubber-waste interaction lead to increase hardness. This behavior occur when the ratio of SBR rubber was greater than NR rubber, this behavior was agree with (AL-Noumannee, 2010),(,[Hassan , 2011), (Rattanasom, 2005). The inverse behavior occur when the ratio of NR was greater than SBR this attributed to happen over vulcanization results fracture in NR rubber chain that is observed in torque curve for NR composite see Figs. (5), (6),(7),(8).

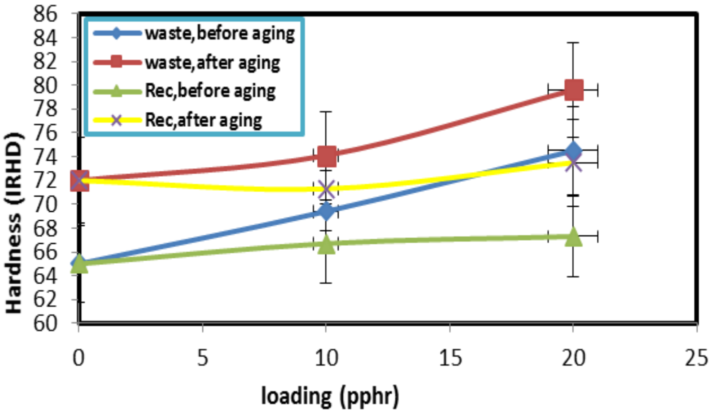

Fig. 1: Relation between hardness against waste and reclaim loading for the composite (SBR 80/NR 20). When C.B=50 pphr.

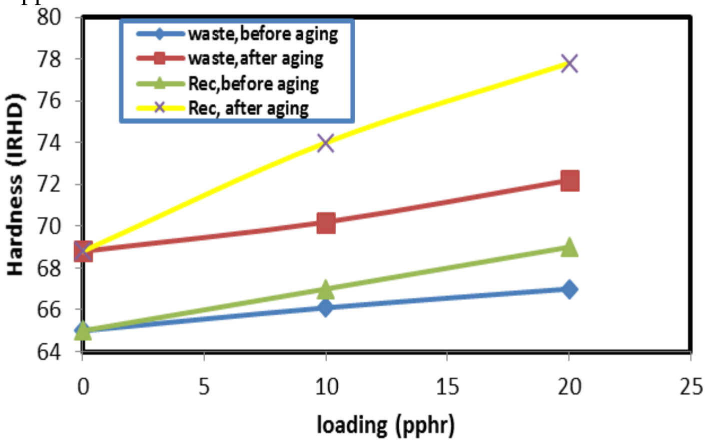

Fig. 2: Relation between hardness against waste and reclaim loading for the composite (SBR 60/NR 40). When C.B=50 pphr.

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After aging the hardness tests were carried out for all the selection recipes before and after ageing when the C.B loading (50 pphr), Cement waste or Reclaim loading is (0,10,20) and the same ratios for another additives.

It can be seen from these figures(1)-(8) that the observed increase in the hardness upon aging at (96 hours) may be attributed to the increase of the crosslinking density inter and at the surface of NR, SBR, BR_{cis} molecular chains with increased of aging time this leads to increase the hardness. So we can indicated that the valuase of hardnesss after aging was increasing less than (8^{o}) from the original value, this increment was gree with the aging condition.

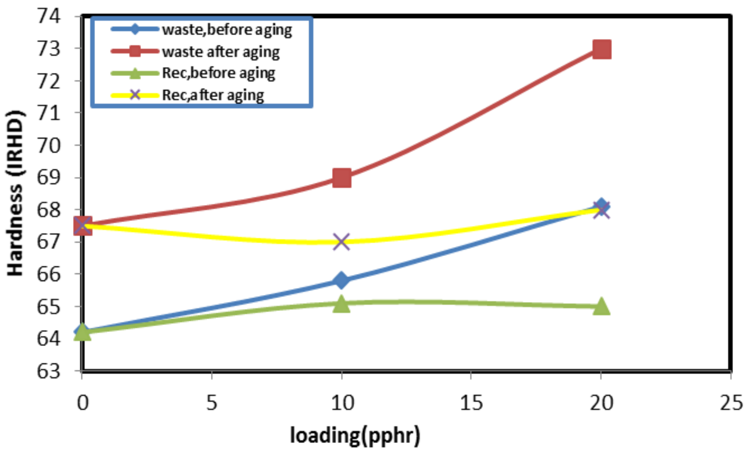

Fig. 3: Relation between hardness against waste and reclaim loading for the composite (SBR 80/NR 30/BR_{cis}10). When C.B=50 pphr.

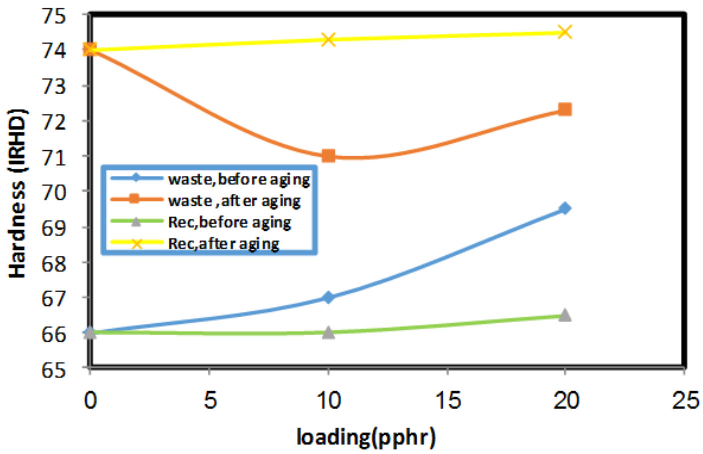

Fig. 4: Relation between hardness against waste and reclaim loading for the composite (SBR 50/NR 50). When C.B=50 pphr.

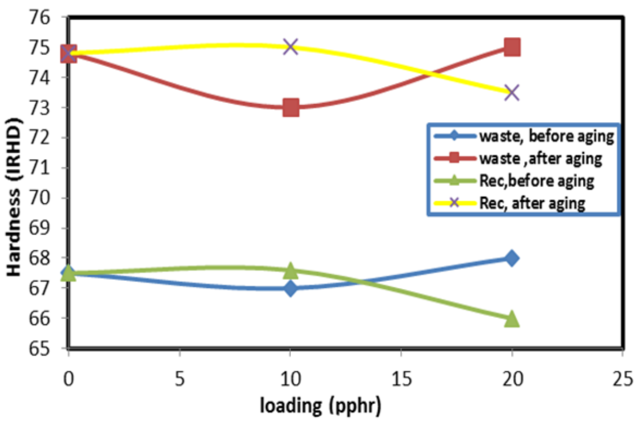

Fig. 5: Relation between hardness against waste and reclaim loading for the composite (SBR 30/NR 60/BR_{cis})10. When C.B=50 pphr.

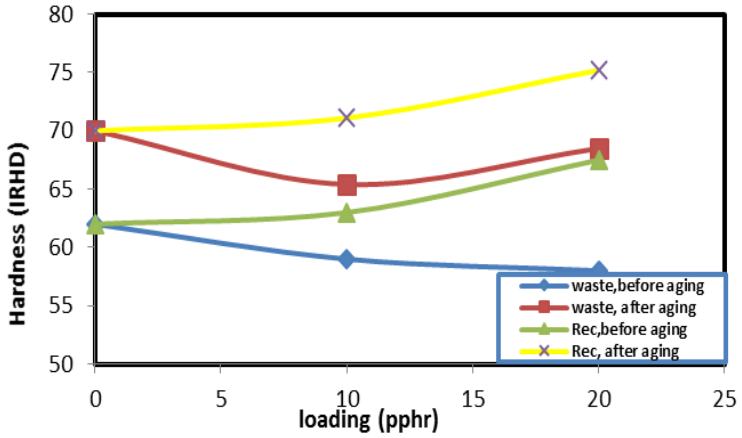

Fig. 6: Relation between hardness against waste and reclaim loading for the composite (SBR 30/NR 70). When C.B=50 pphr.

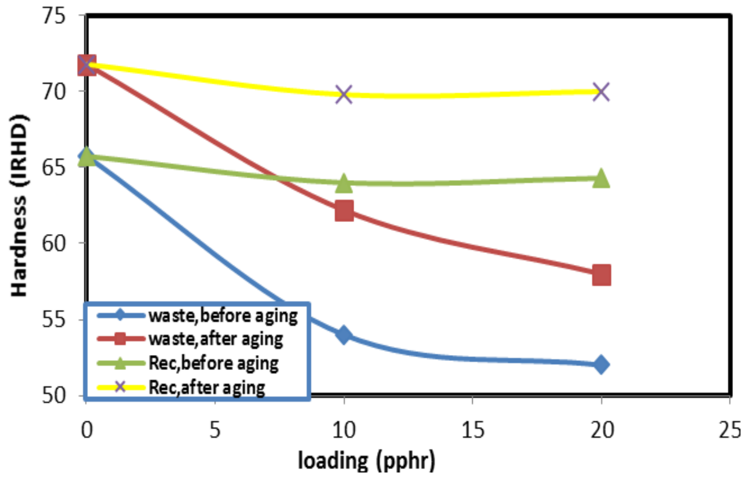

Fig. 7: Relation between hardness against waste and reclaim loading for the composite (SBR 20/NR 80). When C.B=50 pphr.

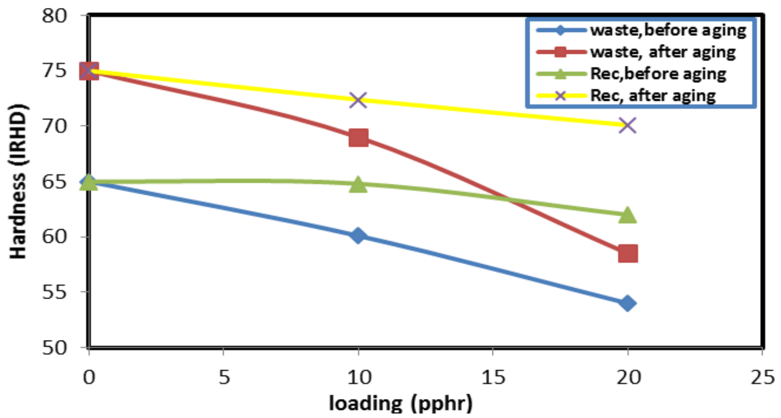

Fig. 8: Relation between hardness against waste and reclaim loading for the composite (SBR 10/NR 90). When C.B=50 pphr.

Conclusion:

1. For the same loading percent the value of hardness is greater when we use reclaim if the ratio of NR greater than SBR . So inverse behaviour happen when we use cement waste if the ratio of SBR greater than NR except (SBR60/NR40).
2. Reclaim and cement waste increasing the hardness when SBR ratio is greater than NR and vice versa.
3. Reclaim and cement waste were satisfying the aging condition.

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