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Effect of Carbon Black Particle Size on the Damping Properties of Butadiene Composites

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ABSTRACT

The effect of the molecular size of the black carbon (N326, N375, N660) on the damping properties such as (Rebound Resilience, damping time) and Mechanical properties (hardness, specific gravity) had been studied in this research. Synthetic rubber BR_{cis} known as Bona given extensive applications, especially in the tire making because of its high resistance to friction. The research includes the preparation of 13 batches where the synthetic rubber BR_{cis} in each batches was (pphr 100). The ratios of black carbon (N326, N375, N660) follows are (0, 10, 20, 30, 40) pphr for each type of black carbon. All the mechanical tests and damping properties measured according ASTM such as hardness by Shore A according to standard ASTM D2240 as well as the specific gravity was measured by a device Densitron instrument, in addition to the properties of damping such regressive or reactionary as well as the damping time was measured by Tripsometer equipment according to standard ASTM D1054. The results revealed that the values of hardness and specific gravity for carbon black (N326) composites are larger than the values of these properties of N375 and N660 composites, so the inverse relation for rebound resilience and damping time property.

KEY WORDS: Rebound Resilience, Damping properties, Butadiene Composites.

1. INTRODUCTION

Viscoelastic behavior is a time-dependent mechanical response and is usually characterized with creep compliance, stress-relaxation, or dynamic mechanical measurements. Since time is an additional variable to deformation and force, to obtain unique characterizing functions in these measurements one of the usual variables is held constant. In a shear creep experiment a shearing stress so is created in a previously relaxed material and held constant while the resulting shear strain increases monotonically with time (James and Erick, 2005).

The ease of deformation called plasticity characterizes of the un vulcanized rubber compound, and causes the highly plastic rubber to flow easily. Viscosity is the resistance to plastic deformation or flow and, hence, the inverse of plasticity. Un vulcanized rubbers are not totally viscous but exhibit some elastic behavior. Rubber does not exhibit Newtonian flow as the shear rate is not proportional to the shear stress. Moreover ,measurements of flow properties should be made at the shear rate of interest (Ronald, 2010; Jean and Losif, 2009).

Although this is a significant elastomer, it is most commonly used as a blend with other rubbers. BR is traditionally difficult to process on rubber machinery; this difficulty is not apparent when BR is blended with other nonpolar elastomers such as NR (Andrew, 1999).

BR vulcanizes confer high resilience and T_g is about -100°C. Therefore low heat buildup, and good abrasion resistance to blends with other rubbers. In view of the above properties, its major application area is in tires. Other applications are golf ball centers, modification of polystyrene to make high impact polystyrene and miscellaneous products needing improvements in abrasion, low temperature and resilience.

Chemical Structure of BR: The chemical structure of polybutadiene rubber BR is existing at three configurations (Fig.1).

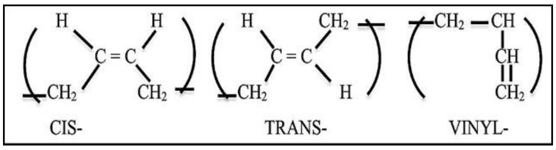

Figure.1. Polybutadiene rubber configuration (AL-Husainey, 2012)

Fillers are classified into reinforcing (active) and inert fillers, and can be either black or nonblack fillers. Those which have a pronounced effect on the mechanical properties of rubbers, such as tensile strength, abrasion resistance, tear resistance, and fatigue resistance, are called reinforcing fillers. Examples are carbon black, zinc oxide, magnesium carbonate, china clay, etc. Fillers do not have an influence on these properties are called inert fillers (e.g., ebonite dust, graphite powder) (Chandrasecaran, 1994).

Carbon black is the most widely used material for reinforcement. The mechanism of the reinforcement is believed to be both chemical and physical in nature. Its primary properties are surface area and structure. Smaller particle-size blacks having a higher surface area give a greater reinforcing effect. Increased surface area gives increased tensile, modulus, hardness, abrasion resistance, tear strength, and electrical conductivity and decreased resilience and flex-fatigue life. The same effects are also found with increased levels (parts per hundred rubber) of carbon black, but peak values occur at different levels. Structure refers to the high temperature fusing together of particles into grape-like aggregates during manufacture. Increased structure will increase modulus, hardness, and electrical conductivity but will have little effect on tensile, abrasion resistance, or tear strength (Ronald, 1994; Al-Nesrawy, 2016).

Different carbon black grades were produced by chemical decomposition of hydrocarbons at elevated temperatures. It is still the most desirable reinforcing filler where resistance to abrasion, cutting, and ageing must be at a maximum. The four main processes of the formation of four type carbon blacks are (Al-Noumannee, 2010; Fauvarque, 1996);

- Lampblack:
- Channel black:
- Furnace black (e.g N110 to N762)
- Thermal black (e.g N990, N991): Table 1 gives the various properties associated with the four types of processes.

Table.1. Properties of different carbon black (Indian, 2000)

Characteristic	**Channel**	**Furnace**	**Lampblack**	**Thermal**
Average particle size (nm)	1 – 3	14 – 80	100 – 150	240 – 320
Surface area (N_2) (m^2/g)	100–1125	27 – 145	20 – 95	7 – 11
Oil absorption (ml/g)	1.0 – 6.0	0.67 – 1.55	1.05 – 1.65	0.32 – 0.47
Volatile matter (%)	3.5 – 16.0	0.3 – 2.8	0.4 – 0.9	0.1 – 1.0
Ash %	0 – 0.1	0.1 – 1.0	0 – 0.16	0.2 – 0.5
Sulfur	0 – 0.1	0.5 – 1.5	—	10 ppm
pH	5.0 – 9.5	5.0 – 9.5	3 - 7	7 - 9

High structure blacks exhibit a high number of primary particles per aggregate, which is called strong aggregation, whereas low structure blacks show only weak aggregation. These aggregates may form loose agglomerates linked by Van der Waals interactions (Al-Enesie, 2013). The empty space within the aggregates and agglomerates, expressed as the volume of Di-Butyl Phathalate (DBP) in cubic centimeters absorbed by a given amount (100gm) of carbon black, is described by the term(structure) of carbon black, the larger is the DBP value , the higher is the carbon black structure (Fig.2) (Al-Nesrawy, 2014).

The important damping properties is rebound resilience. This property is one of the outstanding features of rubber. It shows the ability of a rubber vulcanized to return the energy used to deform it. Resilience is important mainly because it affects the operating temperature of a rubber product, thus influencing its strength and ageing behavior. Rebound resilience increases with temperature (Al-Maamory, 2005).

Resilience is the ratio of the energy returned upon recovery from deformation to the energy required to produce the deformation. The study of impact strength of material is considered as the first key to study the properties of the material, and it is defined for un notched sample as the absorbed energy during the impact to the cross section area of the sample at the fracture of polymer of high toughness has high crack energy, and it is possible to calculate the impact strength from the following relation.

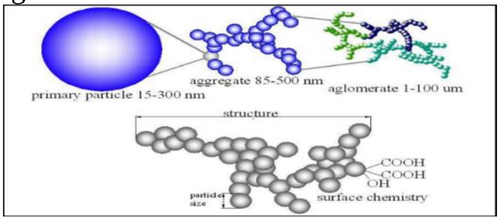

Fig. 2: Carbon Black structures (Mattham, 1998**)**

Impact strength =Energy required for crack/sample cross sectional area. It depends on various variables including type of the materials, temperature, stress system, strain rate, manufacture, and geometry of article, fabrication and environment conditions. In case of rubber the case is different, when rubber is deformed, the energy, which is not returned as mechanical energy, is dissipated as heat in the rubber. The ratio of the energy returned to the energy applied is termed the resilience.

Resilience is related to rebound angle and angle of drop (Al-Masudi, 2007)

Rebound resilience (R %) uncorrected = $(1-\cos i)/(1-\cos j) \times 100$ (1)

Where i = rebound angle, j =angle of drop (45^o)

Then from equation (1) get:

$R\% = 341.421\,(1-\cos i)$ (2)

(R %) corrected = $(1-\cos\{i+i.x/2\})/(1-\cos\{j+j.x/2\}) \times 100$ (3)

Where $x = 1/2n \times \log_e j/i$, and n= number of swings

2. MATERIALS

- BR_{cis}, (specific gravity 0.90 gm/cm^3)
- Carbon black N_{326}, N_{375}, N_{660}. It was examined in accordance with DBP absorption (ASTM D136) and Iodine absorption (ASTM D135).
- Zinc oxide (97%) and stearic acid (99.4%).
- 6PPD N- (1, 3 – Dimethyl butyl) – N – Phenyl – Para – Phenylene diamine (98%) was supplied by Shenyang Sunny Joint Chemicals CO. China.
- MBS N- oxy diethylene benzothiazole 2- sulfonamide (98.2%) supplied by ITT, India. The South Patrol Company supplied Paraphenic wax, processing oil. Sulfur was supplied by Al-Meshrak CO. Iraq.

Preparation of BR_{cis} composites: The batches recipe were prepared by using mill laboratory, the compounding ingredients are shown in Tables.2-4.

Table.2. Compounding ingredient of BR_{cis} composites (group 1)

BR_{cis}	N_{326} (pphr)	Zinc oxide (pphr)	stearic acid (pphr)	Sulfur (pphr)	MBS (pphr)
100	0	2	1.5	1.5	1
100	10	2	1.5	1.5	1
100	20	2	1.5	1.5	1
100	30	2	1.5	1.5	1
100	40	2	1.5	1.5	1

Table.3. Compounding ingredient of BR_{cis} composites (group 2)

BR_{cis})	N_{375} (pphr)	Zinc oxide (pphr)	Strearic acid (pphr)	Sulfur (pphr)	MBS (pphr)
100	0	2	1.5	1.5	1
100	10	2	1.5	1.5	1
100	20	2	1.5	1.5	1
100	30	2	1.5	1.5	1
100	40	2	1.5	1.5	1

Table.4. Compounding ingredient of BR_{cis} composites (group 3)

BR_{cis})	N_{660} (pphr)	Zinc oxide (pphr)	Strearic acid (pphr)	Sulfur (pphr)	MBS(pphr)
100	0	2	1.5	1.5	1
100	10	2	1.5	1.5	1
100	20	2	1.5	1.5	1
100	30	2	1.5	1.5	1
100	40	2	1.5	1.5	1

Equipment and Instruments:

Laboratory mill: A two -roll mill was used, it consists of two hollow cast iron rolls of cylindrical shape of 150mm in diameter and 300mm in length, having provision for passing cold water or steam through the rolls. The mixing of powder takes place at the compressive zone of the roll nip, where the mixing take place along the circumferential direction of the rubber bank on the mill. In mill mixing, temperature control is very important so, chilled water is passed through the rolls at a regulated flow rate to remove excessive heat developed during mixing, and prevents scorching of compound, and heat is also necessary in some processes to warm up the rolls instead of cooling them.

Hydraulic press: The vulcanization processes are function of pressure, heat, and time according to the specification test. The preparation processes of samples were carried out by the hydraulic press has maximum pressure equal to 700bar, the hydraulic press is equipped with thermocouple and maximum temperature is equal to 300°C.

Equipment for Specific gravity measurement: Mansanto–Densitron equipment used to measure the specific gravity. The operating of equipment according to Archimedes principle, the sample was weighed in air then in water the results data were given to the compile which was linked to the equipment.

Equipment for Rebound Resilience Measurement: The Dunlop tripsometer takes the form of an out of balance metal disc revolving on virtually frictionless bearing and which acts as a slow moving pendulum. The test piece was placed against a rigid support so that it receives a blow at its centre. A circular scale was provided for measuring the angle of displacement. The measured quantity is the angle to which the disk rebounds after the hammer strikes the specimen. Tests are carried out according to ASTM D1054.

Equipment for Hardness (ShoreA) measurement: The tests were carried out by Shore A equipment according ASTM D2240 shore.

3. RESULTS AND DISCUSSION

Hardness of BR_{cis} composites: The hardness was examined by Shore A hardness, and the results are shown in Fig.3. These figure indicate that the addition of the C.B filler showed a marked increase in hardness, this result is expected because of more fillers incorporated in the rubber matrix.

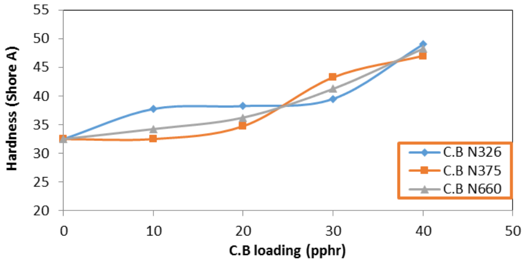

Figure.3. Graphical relation between C.B loading and hardness

It is well known that the addition of the filler in rubber compounding leads to a linear increase in materials hardness; moreover, this attributed to due to the presence of carbon black which resulted an increasing the number of high adsorption active sites

Leads to active correlated sites between the rubber chains and rubber-C.B, all these reasons leads to increase in hardness. This behavior is agreeing with the results of (Rattanasom, 2005; Hassan, 2011) but with other fillers. Fig. 3 demonstrate that the values hardness of the composite BR_{cis} (group 1) with C.B (10, 20, 30 and 40) pphr gives the range values (32.5-48.25) shore A, these values was more than the hardness values of group 2 and group 3 at the same loading ratios of C.B. This result is attributed to that C.B N_{326} have small particle size which leads to high surface area to cross-linked with rubber (Al-Nesrawy, 2016; Alan, 2001; Ahmed, 2016).

Specific Gravity of BR_{CIS} composites: The specific gravity was measured by Mansanto – Densitron equipment it is operating according to Archimedes principle, the results shown in the Fig.4.

The relationship between specific gravity and the loading level of carbon black shown in Fig. 4 from these figure it can be seen that the specific gravity is linearly increasing with increasing the loading level of carbon black. This attributed to the interfere between rubber chains and the of C.B and these fillers have high specific gravity than rubber, this makes that the rubber composite denser per unit volume (Ahmed, 2016), so the specific gravity values of carbon black N_{326} is higher than the other two types.

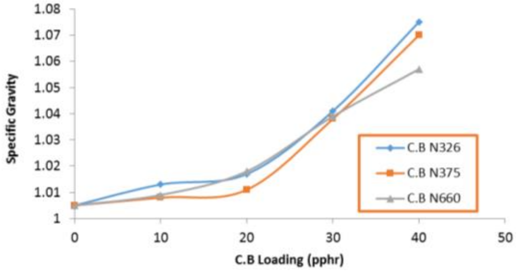

Figure.4. Graphical relation between C.B loading and specific gravity

Rebound Resilience of BR_{CIS} composite: The rebound resilience investigated by Dunlop tripsometer equipment, the results are shown in the Fig.5. This figure indicated that the relation between the rebound resilience and the loading percent of C.B percent, while the rebound resilience decreasing with increase C.B. N_{326}, N_{375} $N_{660.}$ The decrement in the rebound resilience is due to the excess of the loading level of C.B in composites leads to increasing physical cross-linking between rubber and C.B particle and filling the vacancies between the rubber chains, so it is inversely proportional with increase damping (hysteresis) and hardness. This property is very important for the dampers due to the ability of absorbent to the sudden shocks. This absorption caused by high strain elastic deformation, which results in dissipation of the impact energy without fracture or fatigue failure. Fig. 5 shows that the rebound resilience values for C.B N_{326} composites (group 1) was less than the other types group 2 and group 3, this attributed to that the surface area of C.B. N_{375} N_{660} was less than C.B. N_{326}

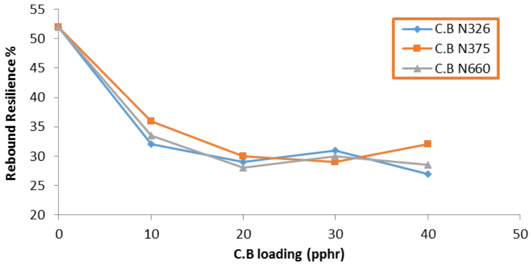

Figure.5. Graphical relation between C.B loading and rebound resilience

Damping Time of BR_{CIS} composite: The damping time were examined by Dunlop tripsometer equipment, and the results are shown in the figures.6, 7, 8, 9. These figures indicate that damping time decreased with increasing the loading level of C.B. This decrement attributed to the same causes of resilience decrement. In addition, increased loading level of C.B to increase the hysteresis and the molecular interaction between rubber chains and carbon black grain surfaces since it has higher polarity and interactive site.

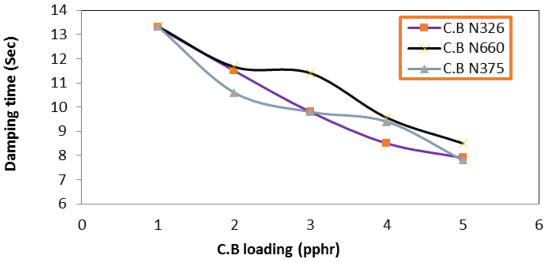

Figure.6. Graphical relation between C.B loading and Damping time

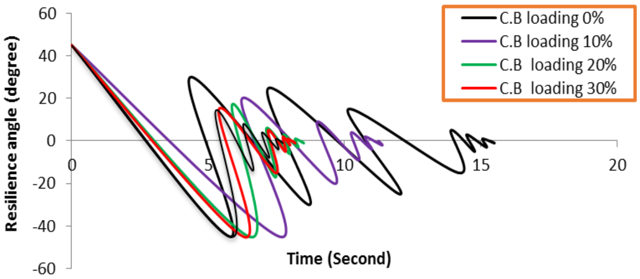

Figure.7. Variation of resilience angle with damping time for carbon black N326

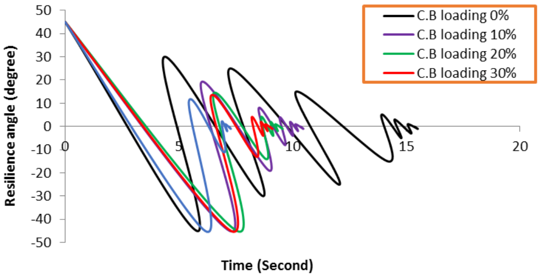

Figure.8. Variation of resilience angle with damping time for carbon black N375

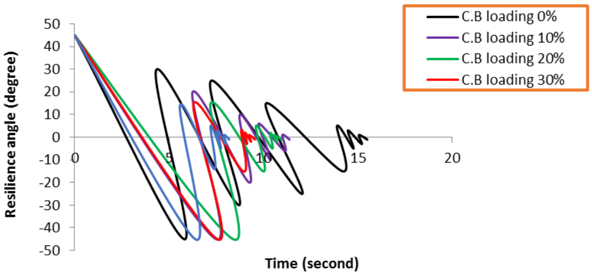

Figure.9. Variation of Resilience angle with damping time for carbon black N660

4. CONCLUSIONS

Having realized the scope of the present thesis and carried out all result analyses, one can figure out the following concluding remarks:

- Specific gravity increased with increasing loading level of carbon black (N_{326} , N_{375}, N_{660}) and it was higher values for black carbon type N_{326} the types N_{660}, N_{375}.
- Increasing of hardness with increase loading ratio of carbon black, as the hardness be higher with respect carbon black type N_{326} and less for carbon black N_{660} and least hardness carbon black N_{375}.
- Rebound Resilience and damping time decrease with increasing loading ratio for all type of carbon black and less values for carbon black type N_{326} because of the higher hardness values.

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