

# Influence of Carbon Allotropes on Some Physical Properties of Natural Rubber (NR)

**Ammar E. Khadom**  
Assistant Lecturer  
Collage of Materials Eng.  
Babylon University

**Kutaiba H. Mohammed**  
Assistant Lecturer  
Collage of Materials Eng.  
Babylon University

## الخلاصة

ثلاثة أشكال مختلفة من الكربون هي (اسود الكربون N330، كرافايت Gr والكربون المنشط AC) وبنسب وزنيه مختلفة هي (10، 20، 30، 40، 50%) لكل نوع تم استخدامها مع المطاط الطبيعي (cis 1-4 -isoprene) في هذا البحث كدقائق تقوية ودراسة تأثيرها على خواص (الرجوعية، الصلادة، اللزوجة، مقاومة الشد والاستطالة) للمطاط الطبيعي. وقد وجد انه عند استخدام الكربون المنشط فان العجنة المطاطية تتفتت أثناء عملية المضع الأولي وتفشل عملية الفلكنة وسبب ذلك يعود إلى القابلية القوية لسطح الكربون المنشط على امتزاز السلاسل المطاطية وتكورها حول حبيبات الكربون بالإضافة إلى امتزاز الكبريت (عامل الفلكنة) ولم تنجح عملية الفلكنة إلا عند النسبة الوزنيه % (10 و 20) حيث حصلت فلكنة وكانت خواص المطاط الناتج رديئة. أما عند تقوية المطاط بالكربون (N330) فقد لوحظ أن خواص (الصلادة، اللزوجة ومقاومة الشد) تكون أعلى من المطاط المقوى بالكرافايت، في حين أن خواص الرجوعية والاستطالة للمطاط المقوى بالكرافايت تكون أعلى من المطاط المقوى بالكربون N330.

## Abstract

Three different carbon allotropes (Black carbon (N330), Graphite(Gr) and Active carbon (AC)) with different weight percent (10, 20, 30, 40 &50)% for each type had been used with natural rubber (cis 1-4 –isoprene) in this research as reinforcing particles and studying its Influence on rubber properties (Resilience, hardness, moony viscosity, tensile strength and elongation). The results show that using (AC) with rubber the recipe of rubber separate to small spheres during primary mastication process and the vulcanization process fails, the reason behind this behavior backs to the strong ability for active carbon surface to adsorb the chains of rubber and spheroid around carbon particles so as adsorbing sulfur (vulcanization agent), only at the ratios (10,20)% vulcanization process take place and the properties of produced rubber was bad. While when using (N330) the properties (hardness, viscosity and tensile strength) was higher than rubber reinforced by graphite, while rebound resilience and elongation for rubber reinforced by graphite was higher than rubber reinforced by (N330).

## 1- Introduction:

The reinforcement of elastomers by particulate fillers has been extensively studied in the past, particularly in the 1960s and 1970s. The first reason is naturally the drastic changes in mechanical properties that induces fillers reinforcement, many of the usual applications of elastomers could not be envisaged without the use of particulate fillers.[J. E. Mark et al, 2005]

For plastics, reinforcement results are an increase in modulus and hardness. The effect of particulate fillers is quite clear, they replace a part of the matrix: so modulus becomes higher, but deformation at break decreases in the same time.

The situation is very different for elastomers: the use of reinforcing fillers induces a simultaneous increase modulus and deformation at break. Curiously, the replacement of a part of the deformable matrix by solid objects doesn't reduce its deformability. The increase of these two antagonistic properties characterizes elastomer reinforcement. [J. B. Donnet, 1999]

There are several allotropes of carbon of which the best known are graphite, diamond, and amorphous carbon. The physical properties of carbon vary widely with the allotropic form.[world of carbon, 2008]

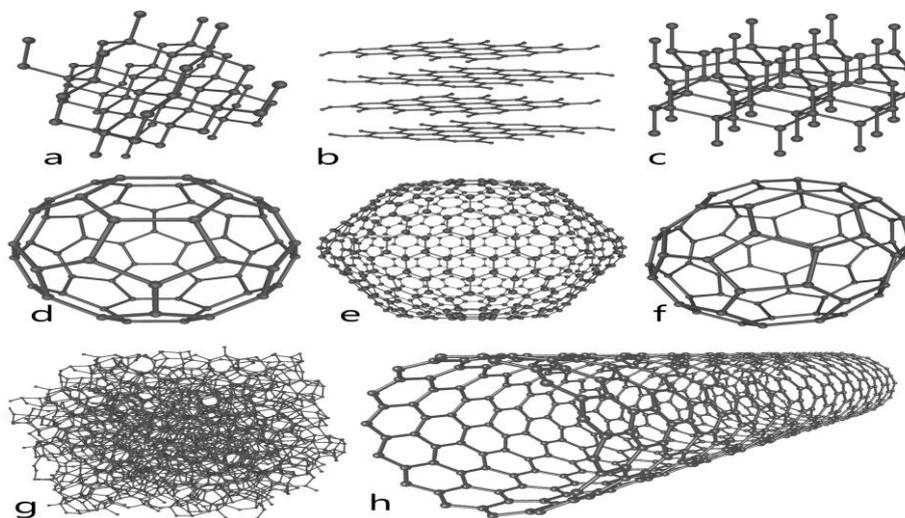
The amorphous form (carbon black and active carbon), is an assortment of carbon atoms in a non-crystalline, irregular, glassy state, which is essentially graphite but not held in a crystalline macrostructure. It is present as a powder, and is the main constituent of substances such as charcoal, lampblack (soot) and activated carbon. [T. D. Burchell, 1999]

At normal pressures carbon takes the form of graphite, in which each atom is bonded trigonally to three others in a plane composed of fused hexagonal rings, just like those in aromatic hydrocarbons. The resulting network is 2-dimensional, and the resulting flat sheets are stacked and loosely bonded through weak van der Waals forces. This gives graphite its softness and its cleaving properties (the sheets slip easily past one another).[P. Delhaes, 2001]

Because carbon black has high surface energy, elastomeric chains are strongly adsorbed onto its surface. This adsorption, even if it is limited to a small part of the elastomeric chains, called "trains," drastically slows down their mobility.[A.P. Legrand et al, 1992]

Very recently, many studies have been conducted to identify new reinforcing systems. These systems are similar to silica compounds and characterized by the use of a coupling agent to chemically bond elastomer chains to filler surface. Many reinforcing systems have been patented: alumina oxyhydroxide and oxide, titanium oxides, and silicon nitride/carbide.[L. Simonot et al, 2002]

Figure (1) shows different allotropes structure of carbon. [H. O. Pierson, 1993]



**Fig.(1):** Some allotropes of carbon: a) diamond; b) graphite; c) lonsdaleite; d–f) fullerenes (C60, C540, C70); g) amorphous carbon; h) carbon nanotube.[H.O. Pierson, 1993]

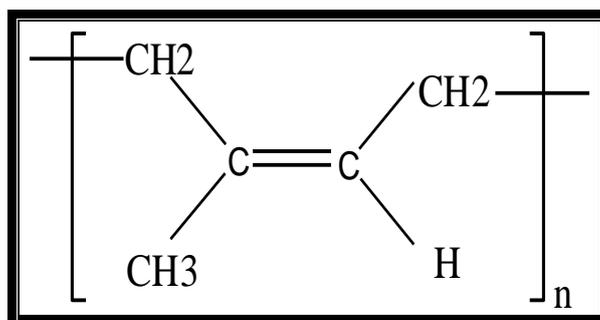
## 2-Experimental Work

This part divided into tow sections, first section include the materials used in this research and the second one describe the preparation of the samples to the testing.

### 2-1-Materials:

#### 1- Natural rubber:

Cis 1-4- isoprene class: Diene elastomer structure, high degree of stereogravity in structure presence of the reactive double bonds (unsaturated) as shown in figure(2). [ J. E. mark, 1999]



**Fig. (2):** Chemical structure of natural rubber

## **2- Active carbon(AC):**

Also called activated charcoal or "Activated coal" is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions.[**CPL Caron Link, 2008**]

A gram of activated carbon can have a surface area in excess of 500 m<sup>2</sup>, with 1500 m<sup>2</sup> being readily achievable, Under an electron microscope, the high surface-area structures of activated carbon are revealed. Individual particles are intensely convoluted and display various kinds of porosity; there may be many areas where flat surfaces of graphite-like material run parallel to each other, separated by only a few nanometers or so. These micropores provide superb conditions for adsorption to occur, since adsorbing material can interact with many surfaces simultaneously. [**E. J. Bottani et al, 2008**]

Activated carbon used in this research has the following properties listed in table (1).

**Table 1:- Properties of Activated carbon used.**

<i>Test</i>	<i>Specification</i>
<i>Dimension (granular)</i>	<i>12x40 mesh (0.4-1.6)mm</i>
<i>Bulk density (kg/m<sup>3</sup>)</i>	<i>460-480</i>
<i>Void fraction</i>	<i>0.45</i>
<i>Specific surface area (m<sup>2</sup>/g)</i>	<i>1100-1130</i>
<i>Ash (%)</i>	<i>5 (max.)</i>
<i>Microporos</i>	<i>high</i>

## **3- Graphite (Gr):**

The mineral graphite is one of the allotropes of carbon, Graphite is a layered compound. In each layer, the carbon atoms are arranged in a hexagonal lattice with separation of 0.142 nm, and the distance between planes is 0.335 nm.[**P. Delhaes, 2001**]

The two known forms of graphite, alpha (hexagonal) and beta (rhombohedral), have very similar physical properties (except that the graphene layers stack slightly differently).

graphite is an electrical conductor, a semimetal, and can be used, for instance, in the electrodes of an arc lamp. Graphite holds the distinction of being the most stable form of carbon under standard conditions.

Graphite and graphite powder are valued in industrial applications for its self-lubricating and dry lubricating properties. There is a common belief that graphite's lubricating properties are solely due to the loose inter- lamellar coupling between sheets in the structure. However, it has been shown

that in a vacuum environment (such as in technologies for use in space), graphite is a very poor lubricant. This observation led to the discovery that the lubrication is due to the presence of fluids between the layers, such as air and water, which are naturally adsorbed from the environment. This molecular property is unlike other layered, dry lubricants such as molybdenum disulfide. Recent studies suggest that an effect called superlubricity can also account for graphite's lubricating properties.[**H. O. Pierson, 1993**]

#### **4- Carbon Black (N330):**

Carbon black is a material produced by the incomplete combustion of heavy petroleum products such as FCC tar, coal tar, ethylene cracking tar, and a small amount from vegetable oil. Carbon black is a form of amorphous carbon that has a high surface area to volume ratio, although its surface area to volume ratio is low compared to activated carbon. It is dissimilar to soot because of its much higher surface area to volume ratio and significantly less (negligible and non-bioavailable) PAH content. Carbon black is used as a pigment and reinforcement in rubber and plastic products. The most common use [70%] of carbon black is as a pigment and reinforcing phase in automobile tires. Practically all rubber products where tensile and abrasion wear properties are crucial use carbon black, so they are black in color.[ **International Carbon Black Association, 2009**]

Fillers and other ingredients were added to rubber on twin-roller according to the formulation shown in Table (2).

**TABLE 2**  
**Formulation for Rubber Compounding**

MATERIALS	AMOUNTS(pphr)
NR	<b>100</b>
Stearic acid (SA)	<b>2</b>
ZnO	<b>5</b>
<b>(N330) or (AC) or (GR)</b>	<b>(10,20,30,40 &amp;50)%</b>
Sulfur	<b>2.25</b>
MBS	<b>0.8</b>
<b>Medoplast oil</b>	<b>12</b>

#### **2-2-Samples preparation**

First we prepared the rubber recipe by mixing and homogeneity of all the constituents used during mastication process by using laboratory mill and following the sequence below:

passing rubber between mill rollers at 70°C then adding the reinforcing particles (N330 or Gr or AC with the weight percentage mentioned before) with the processing oil, after that we add stearic acid, zinc oxide, anti oxidation and antiozone. then cooling the rubber recipe to the room temperature and adding the sulfur and the accelerator MBS.

samples of viscosity were prepared from the rubber recipe before vulcanization process with diameter of (2 mm) and thickness of (6 mm) then but them in the rheometer and studying their properties during vulcanization process.

samples for mechanical tests (hardness and resilience) prepared by preheating of the dies up to 100°C, die dimensions are (180X200X6.5)mm, after that we fill the die with the rubber recipe then but the die under hydraulic compaction and press the recipe under 500psi and 160°C for 15 min to complete the vulcanization process after that we let the samples to cool for (10-15)hr and then they were ready to be tested according to the ASTM-D 2240 (shore A hardness).

Tensile strength and elongation samples prepared according to ASTM-D 3182 and D-13192 respectively standards, first heating the die then filled with the rubber recipe and pressed under 500psi and 145°C for 45 min and after the vulcanization process is complete we extracted the slices and let them to cool for 12hrs then they were ready to be tested. [S. Blow, 1998]

### **3-Results and Discussion**

Rubber composite chains had been adsorbed into the surface of carbon particles in all kinds of carbon allotropes, but we notice that there is clear different between each type. From the information we have about each type of carbon used we found that the surface energy variants from type to another one. [L. L. Ban et al, 1974]

The surface energy for (AC) will be largest than (N330) which in his part be larger than (Gr) which have the lowest surface energy, and because the mechanical reinforcement in rubber depending on the behavior of the surface in adsorbing the spices , so the ability of (AC) in adsorbing the chains of rubber very high (higher than the required level) which made the rubber chains accumulated as a separate spherical besides that it adsorbed the sulfur which is represent the vulcanization agent and consequently causes the failure of the vulcanization process.

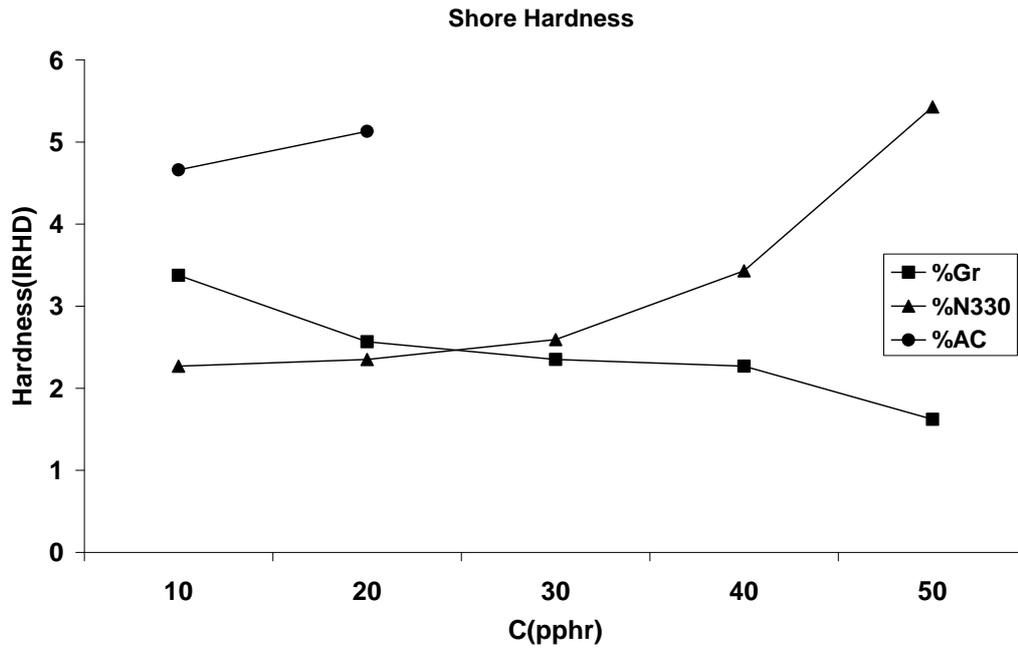
for rubber composite reinforced by (N330) its ability for adsorbing rubber chains is greater than (Gr) which make it more hardness and strength at break than (Gr) the reason behind that is that the (N330) make the rubber chains mobility more difficult as shown in figures (3&4).

from figure (5) we clearly observed that the viscosity of rubber reinforced by (Gr) is decreased with increasing the (Gr) weight percentage, in opposed to that we observed that the viscosity of rubber reinforced with (N330) increased with increasing the weight percent of (N330), that because the nature of graphite layers which sliding one over the other under the effect of stresses, while in cause of used (N330) which have amorphous structure makes the viscosity increasing with increasing its weight percent in rubber.

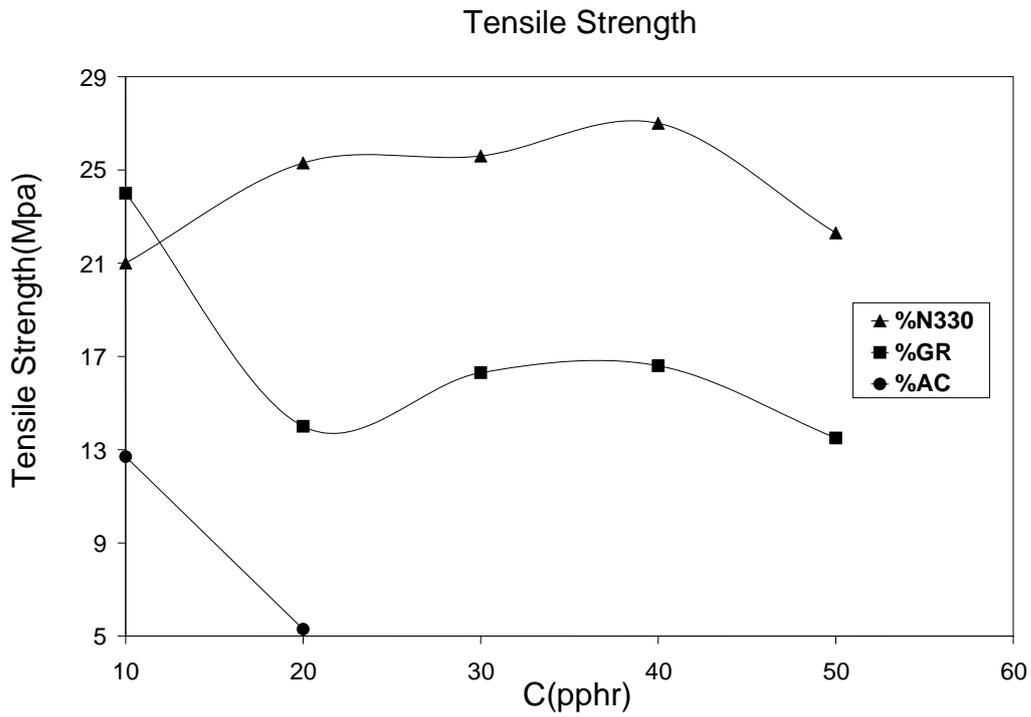
from figure(6) we find that the resilience behavior for all kinds of carbon allotropes are similar and its inversely proportional to the weight percent of carbon, the resilience curve for composite rubber reinforced by (Gr) is higher than that for (N330) and that goes to the lubricant nature of graphite himself which gave the composite rubber a bigger ability in gave back the most energy of fallen pendulum, so as the behavior in elongation we notice that the curve for(Gr) is higher than that for (N330) as shown in figure (7).

### **4-CONCLUSIONS**

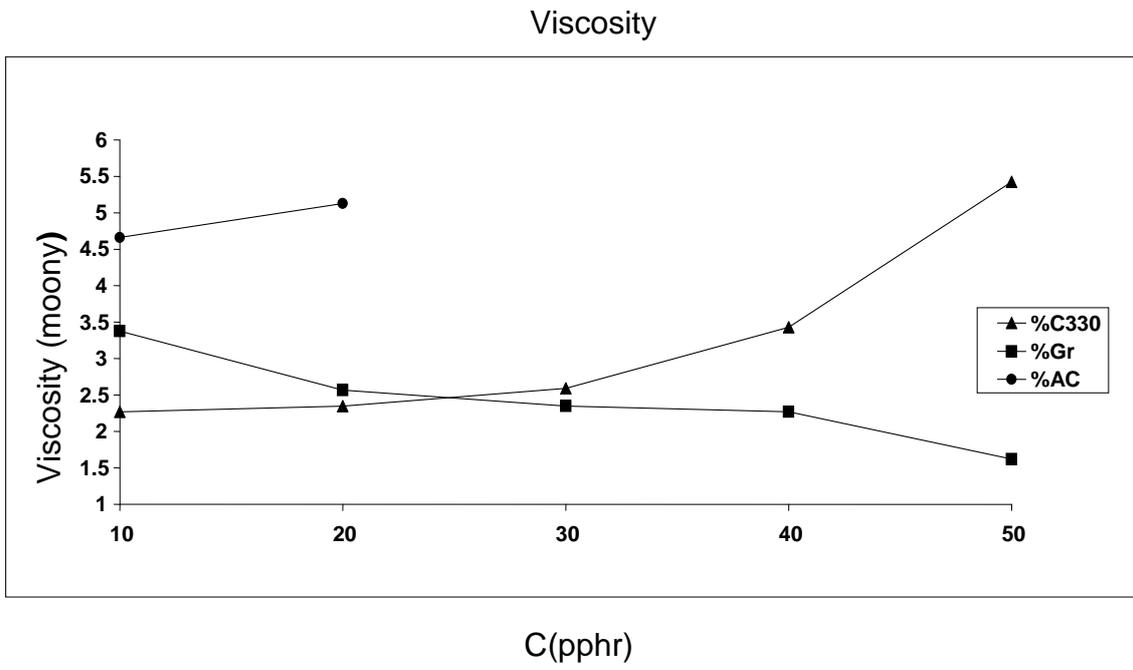
In this study, Three different allotropes of carbon used as reinforcing particle which are (carbon black N330, Graphite and Activated carbon) with different weight percentage were mixed with (NR) and studying their effect on mechanical properties of rubber. It was found that when we used (AC) with rubber the recipe of rubber separate to small spheres during primary mastication process and the vulcanization process fails, while the properties of the rubber recipe (Hardness, Viscosity and Tensile strength) reinforced with (N330) were better than rubber reinforcing with graphite, and all these properties increased with increasing weight percentage of carbon, while when reinforcing with graphite the properties of (rebound resilience and elongation) were better than (N330), in general elongation and resilience decreased with increasing carbon percentage.



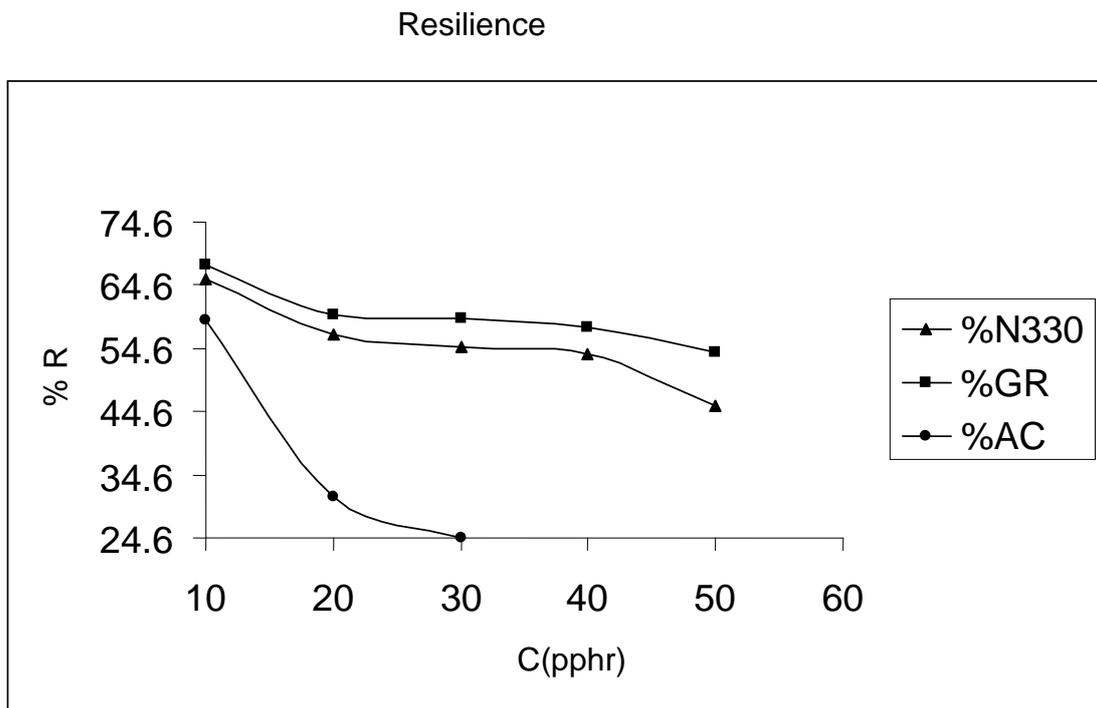
**Fig. (3): Effect of carbon percentage on hardness of rubber**



**Fig. (4): Effect of carbon percentage on tensile strength of rubber**

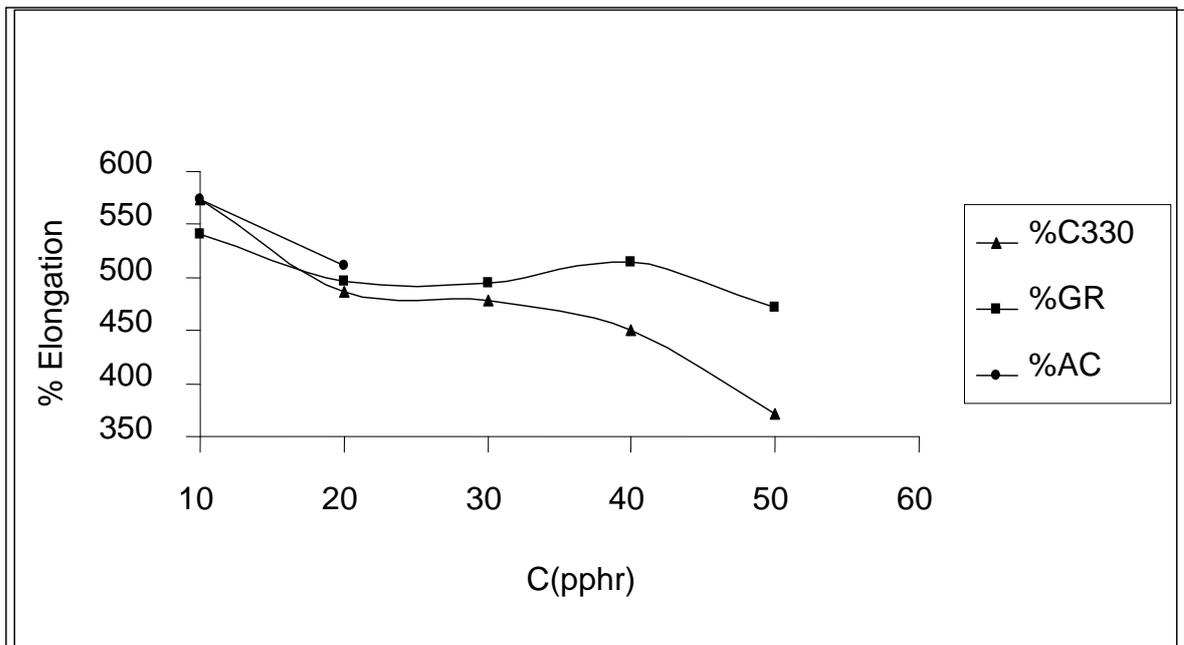


**Fig. (5): Effect of carbon percentage on viscosity of rubber**



**Fig. (6): Effect of carbon percentage on resilience of rubber**

### Elongation



**Fig. (7) Effect of carbon percentage on elongation of rubber**

## **5- References:**

- A. P. Legrand, N. Lecomte, A. Vidal, B. Haidar, and E. Papirer, "**Journal of Applied Polymer Science**": Appl. Polym. Symp. 46, 2223 (1992).
- CPL Caron Link, accessed 2008, "**Properties of Activated Carbon**", .
- E. J. Bottani and J. M. Tascon, "**Adsorption by Carbons**", Instituto Nacional del Carbon, CSIC, Oviedo, Spain, First edition, 2008.
- H. O. Pierson, "**HANDBOOK OF CARBON, GRAPHITE, DIAMOND AND FULLERENES Properties, Processing and Applications**", NOYES PUBLICATIONS Park Ridge, New Jersey, U.S.A.1993.
- P. Delhaes, "**Graphite and Precursors**", CRC Press, (2001).
- International Carbon Black Association,"**What is Carbon Black**". [http://www.carbon-black.org/what\\_is.html](http://www.carbon-black.org/what_is.html). Retrieved 2009-04-14.
- J. B. DONNET and E. CUSTODERO "**Reinforcement of Elastomers by Particulate Fillers**", **1999**.
- J. E. mark, "**POLYMER DATA HANDBOOK**", UNIVERSITY OF CINCINNATI, published by oxford university press, 1999.
- J. E. Mark, B. Erman and F. R. Eirich, "**Science and Technology of RUBBER**",\_Third edition, Elsevier Academic Press, 2005.
- L. L. Ban,W. M. Hess, and L. A. Papazian, "**Rubber Chemical Technology**", (1974).
- L. Simonot,T. Chartier, and E. Custodero, "**Rubber composition made with diene elastomer and a reinforcing silicon carbide**" (2002); WO2004003067, L. Simonot, A. Lapra, A. Veyland, and E. Custodero, "**Rubber composition based on diene elastomer and a reinforcing silicon nitride**" (2002).
- S. Blow, "**Testing and Identification of Rubber**", Galgatia publication Pvt. Ltd, 1998.
- Timothy D. Burchell "**Carbon Materials for Advanced Technologies**", Fourth edition, 1999.
- "**World of Carbon**", <http://invsee.asu.edu/nmodules/Carbonmod/point.html> Retrieved 2008-10-09.