Effect of Graphite on the Properties of Natural Rubber

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Abstract

Natural rubber-graphite composites (0, 1, 2, 3, 4 pphr graphite) were prepared on a laboratory two-roll mill. Swelling measurements were used to evaluate the impacts of graphite on the properties of natural rubber.

Swelling results showed that the volume fraction of natural rubber in the swollen gel, the interaction parameter, and the cross-link density decreased by increasing graphite loadings, while the average molecular weight of natural rubber between cross-links increased.

Vulcanization results showed that only scorch time parameter increased with increasing graphite loadings, while other parameters (Max. torque, Min. torque, cure rate and cure rate index) decreased. Both thermal and AC conductivities increased.

Key words: Graphite….Natural rubber…..Interaction parameter…π electron….. Swelling…..Cross-linking density…..Flory-Rehner equation.

الخلاصة

تم تحضير متراكبات من المطاط الطبيعي والكرافيت(pphr٠،١،٢،٣،٤ كرافيت) بأستخدام العصارة المختبريه ذات الرولتين. استخدمت قياسات الانتفاخ لرصد تأثير الكرافيت على خصائص المطاط الطبيعي. أظهرت نتائج الانتفاخ تناقص كل من حجم المطاط في المادة المنتفخه، عامل التجاذب، كثافة التشابكات فيما ازداد معدل الوزن الجزيئي للمطاط الطبيعي بين نقاط التشابك.أظهرت نتائج الفلكنه ان زمن الاحتراق يزداد بزيادة الكرافيت فيما تتناقص بقية عوامل الفلكنه كالعزم الاقصى ، العزم الادنى، معدل الانضاج ومؤشر معدل الانضاج. كما ازدادت كل من الموصليهالحراريه والكهربائيه.

كلمات المفتاحيه: الكرافيت، المطاط الطبيعي ، عامل التجاذب، باي الكترون،الانتفاخ، كثافة التشابكات العرضية، معادلة فلوري رينير

Introduction

Natural rubber (NR) is a high molecular weight polymeric substance with viscoelastic properties. Structurally it is cis 1,4-polyisoprene. Isoprene is a diene and 1,4 addition leaves a double bond in each of the isoprene unit in the polymer. Therefore, NR shows all the reactions of an unsaturated polymer. Besides to its renewability, NR combines several outstanding properties, such as high mechanical strength, low heat build-up, excellent flexibility, and resistance to impact and tear [Onyeagoro, 2012].

Unfortunately, NR in its original gum state cannot be used. Therefore, many additives were employed to improve its properties. These additives include vulcanizing agents (such as sulfur), accelerators, activators, retarders, fillers, anti-degradants. Fillers (such as carbon black) are often used in rubber compounding to obtain the desired properties for certain applications [Igwe and Ejim, 2011].

Swelling behaviors are used to determine crosslink density (v). The lowerthe crosslink density of the rubber, the higher the swelling for a certain solvent as expressed by the Flory-Rehner equation [Ahmed *et. al.*,2013]:

$$v = \frac{-\ln(1-V_r) + V_r + \chi V_r^2}{\rho_o V_s V_r^{\frac{1}{3}} - \frac{V_r}{2}} = \frac{1}{M_C} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1)$$

Where: V_r stands for volume fraction of rubber in the swollen gel, V_s stands for the molar volume of the toluene(106.2 cm^3 mol^{-1}), χ stands for NR-solvent interaction parameter (it can be determined from the cohesive energy density of solvent and polymer and is usually of the order of 0.4 in good solvents), ρ_o stands for the density of the polymer, ν stands for cross-link density of the rubber ($mol.cm^{-3}$) and M_C stands for the average molecular weight of the polymer between cross-links ($g\ mol^{-1}$).The value of χ can be calculated as:

$\chi_{NR} = 0.44 + 0.18\ V_r$……………………………………………………………(2)

V_r can be calculated from swelling data as:

$$V_r = \frac{\frac{W_{rf}}{\rho_1}}{\left[\left(\frac{W_{rf}}{\rho_1}\right)+\left(\frac{W_{sf}}{\rho_o}\right)\right]} \quad \ldots\ldots\ldots (3)$$

where W_{sf} is the weight fraction of solvent,$W_{rf}$is the weight fraction of thepolymer in the swollen specimen, ρ_1 is the density ofthe polymer (NR) which was taken as 0.9125 g/cm^3,and ρ_s is the density of the solvent (0.867 g/cm^3 fortoluene).

Based on swelling measurements, there are several relations used to evaluate the interaction between filler and rubber such as Lorenz and Park equation,Cunnen-Russel equation and Kraus equation.

Lorenz and Park equation studies the rubber-filler interaction through measuring the swelling of pure gum(Q_g) and filled (Q_f) vulcanizates in toluene solvent[Lorenz andParks, 2003]:

$$\frac{Q_f}{O_g} = a.e^{-z} + b \quad \ldots\ldots\ldots (4)$$

Where **f** and grefer to filled and unfilled (gum), respectively.**Z** is the weightfraction of filler in the polymer, while **a** and**b** are constants which depend on thefiller activity.

High value of **a** and low valueof **b** indicate strong polymer attachment[Costa *et al*., 2001].The lower value of swelling ratio (Q_f/Q_g) indicatesbetter interaction between the filler and therubber matrix:

The weight of toluene absorbed per one gram of vulcanized material(Q) was calculated by the following equation[Wu et al.2015]:

$$Q = \frac{Swollen\ weight - Dried\ weight}{Original\ \ weight} \quad \ldots\ldots\ldots (5)$$

Cunnen-Russel equation represents a variant of the originally derived Lorenz-Parks equation [Costa et al., 2001].

$$\frac{V_{ro}}{V_{rf}} = a.e^{-z} + b \quad \ldots\ldots\ldots (6)$$

Where V_{r0} and V_{rf} stand for volume fractionsof the rubber in pure and filled vulcanizates,respectively, swollen in a solvent.

Kraus model which is based on the Lorenzand Parks model [Costa et al., 2001] determines quantitatively the effect ofparticles bonded tothe polymer.

$$\frac{V_{ro}}{V_{rf}} = 1 - \frac{m\Phi}{1-\Phi} \quad \ldots\ldots\ldots (7)$$

Where

$$m = 3C\left(1 - V_{ro}^{\frac{1}{3}}\right) + V_{ro} + 1 \quad (8)$$

C is aconstant for given filler and Φ is the volumefraction of filler in the vulcanizate.

The slope of the plot V_{r0}/V_{rf} versus Φ/(1-Φ) equals to the m parameter, which measures the carbon-polymer interaction during the swelling process. V_{r0}determinesthe polymer-solvent interaction[Costa et al., 2001].

Aim of research

This research aims to employ the swelling measurements to interrupt the effect of graphite on the properties of natural rubber.

Experimental Part

NR-graphite composites were compounded on a laboratory two-roll mill and mixing schedule was done according to the ASTM D 3182-2001, then cured in a compression molding device at 140°C with pressure reaches to 10 MPa. These composites are 0, 1, 2, 3, 4 pphr graphite.

Several techniques were used to evaluate graphite's effects on the NR's properties, while swelling measurements were done by measuring toluene uptake at room temperature for six days. A.C conductivity was measured by using conductivity meter HIOKI 3532-50 LCR Hi TESTER at frequency of 5MHz.

The vulcanization properties were determined using the REHO + MOONEY mv Rheometer according to ASTM D-2084.

Results and discussion

Figures 1-4 show the swelling measurements in toluene solvent for six days at room temperature. It is clear that the volume fraction of NR in the swollen gel (V_r), the interaction parameter (χ), and the cross-link density (v) decreased by increasing graphite loadings due its delocalized π electrons, while the average molecular weight of NR between cross-links (M_C) increased.

These behaviors are due to those graphite particles reduce the interaction among NR chains which means that both the cohesive energy density (CED) and the solubility parameter (δ) decreased. Indeed, CED represents a quantitative measure of the magnitude of secondary bonding forces, which is the total energy per unit volume needed to destroy all intermolecular contacts among NR chains [Wu *et al*.,2015].

Graphite particles make NR chains more flexible and easy to be separated without a large expenditure of energy. These new flexible chains, separated from an adjacent chain penetrate easily into solvent and the diffusion occurs at the expense of sequential transition of links[Igwe and Ejim, 2011].

The presence of graphite particles facilities chain separation and polymer diffusion into solution, thus toluene solvent can diffuse into NR and cause swelling. Also, graphite through its lubricant property enhances the compatibility between NR and toluene[Wu *et al*.,2015].

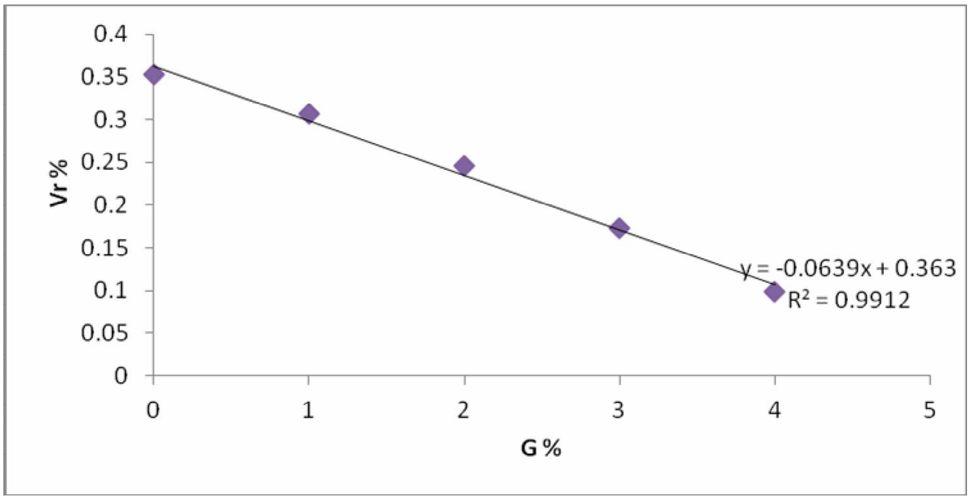

Fig.1 NR volume fraction in the swollen gel as a function of graphite percent

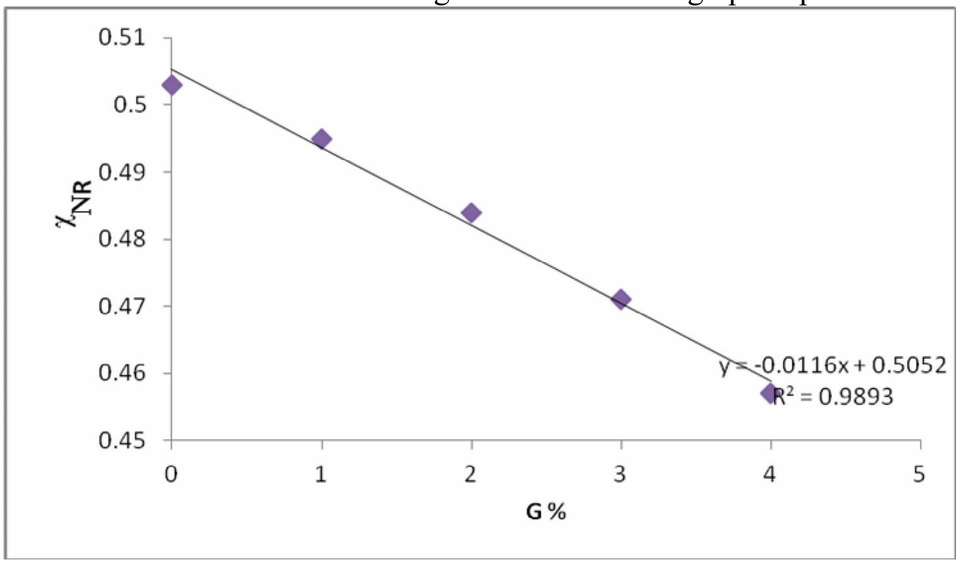

Fig.2 The interaction parameter as a function of graphite percent

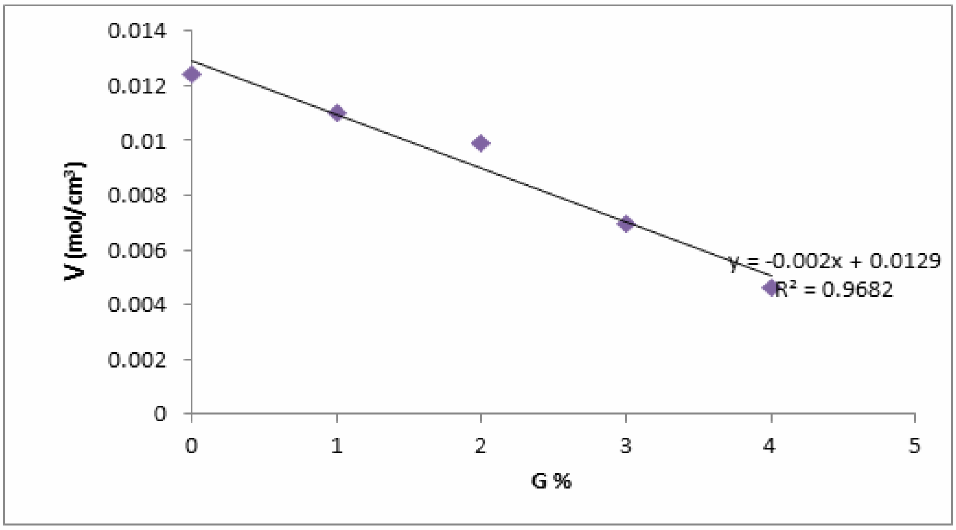

Fig.3 The cross-linking density as a function of graphite percent

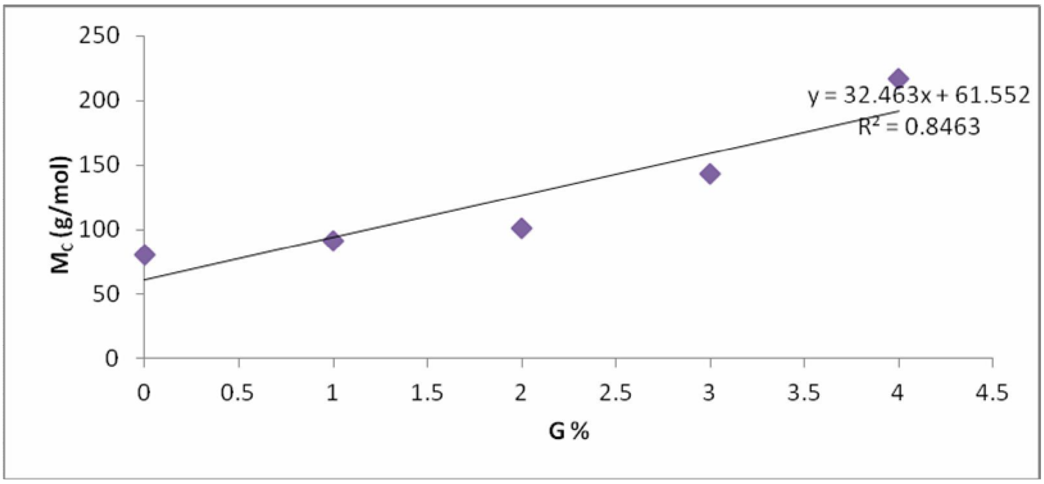

Fig.4 The average molecular weight of NR between cross-links as a function of graphite percent

Figures 5-9 show the vulcanization parameters for NR compounds. Only scorch time increased with increasing graphite loadings, while other parameters (Max. torque, Min. torque, cure rate and cure rate index) decreased. The scorch time (ts_2) is the time required for the minimum torque value to increase by two units and measures the premature vulcanization of the material [Rohanaet al., 2011]. The decline in torque values is due to the graphite structure. This structure consists of many flat layers of hexagons. The bonding energy between these flat layers reaches only 2% of that energy exist within these layers. Therefore, these layers can easily slide over each other making graphite soft and slippery and an excellent lubricant.

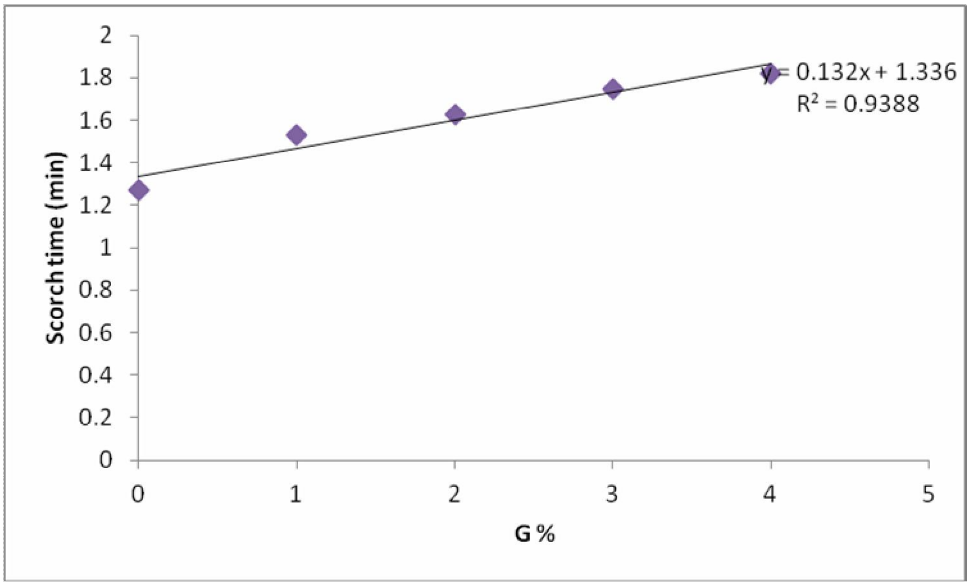

Fig.5 Scorch time of NR compound as a function of graphite percent

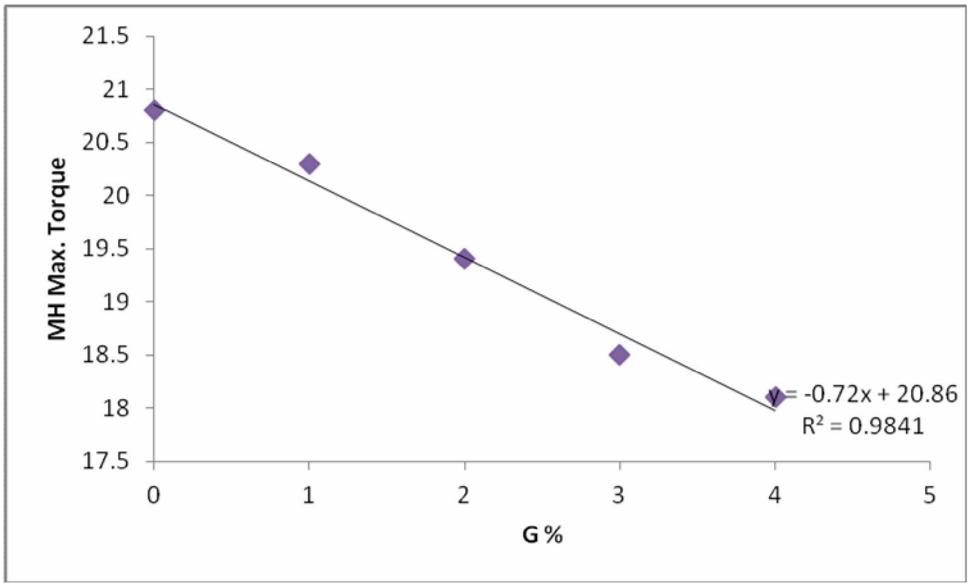

Fig.6 Maximum torque of NR compound as a function of graphite percent

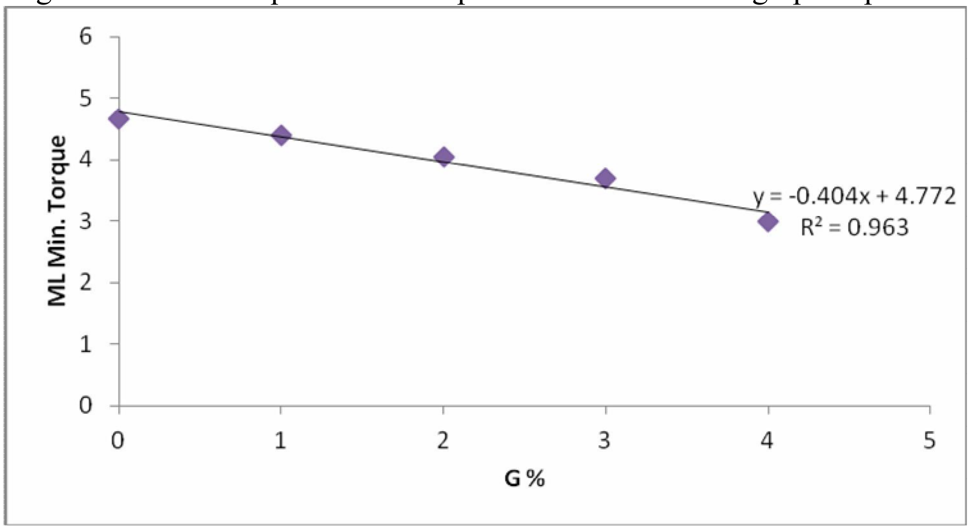

Fig.7 Minimum torque of NR compound as a function of graphite percent

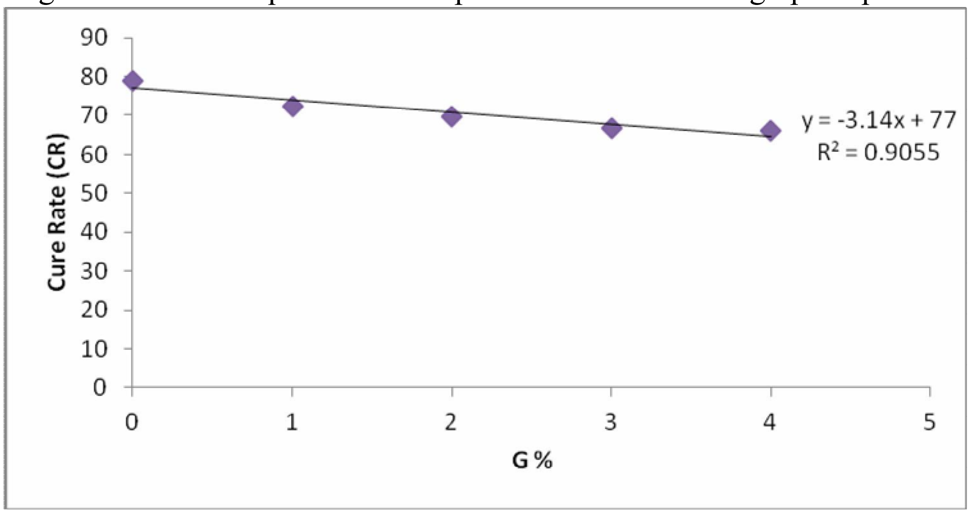

Fig.8 Cure rate of NR compound as a function of graphite percent

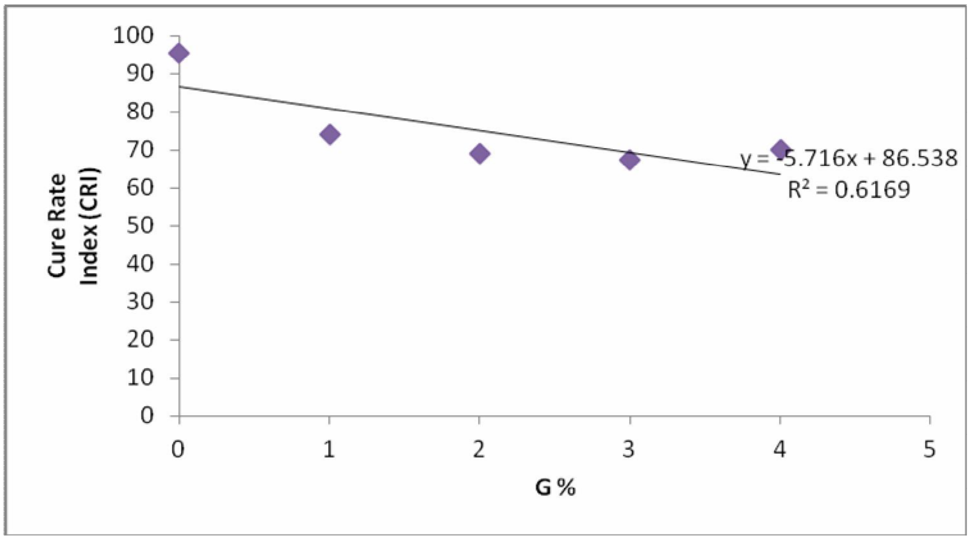

Fig.9 Cure rate index of NR compound as a function of graphite percent

Figures 10 and 11 show the thermal and AC conductivity respectively. Both these conductivities increased due to the graphite structure. Each carbon atom in the layer is joined by strong covalent bonds to only three other carbon atoms. Three of these electrons are used for covalent bonding in the graphene sheet. The fourth electron between the layers is delocaliz1ed. It is a free electron and these free electrons between the layers allow graphite to conduct electricity and heat [Entegris, 2013].

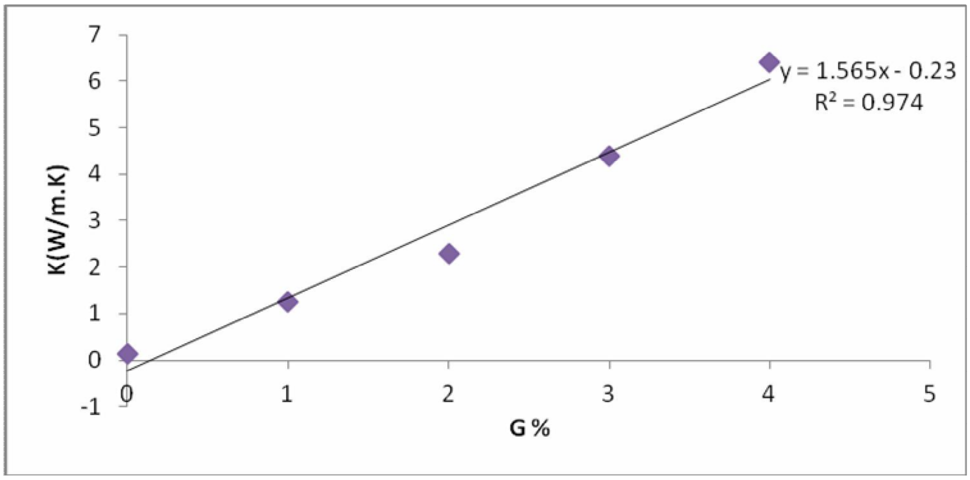

Fig.10 Thermal conductivity of NR compound as a function of graphite percent

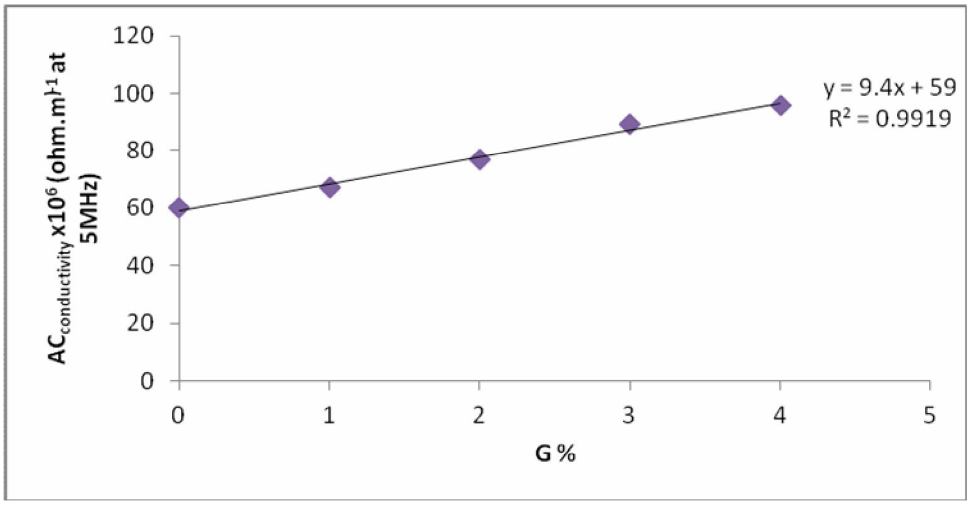

Fig.11 AC conductivity of NR compound as a function of graphite percent

Conclusions

Swelling measurements approach can be employed to investigate the influence the graphite addition on the properties of natural rubber. With graphite structure as hexagon layers and its lubricant character, results show clear effects on the vulcanization parameters, thermal and electrical properties of NR.

References

Ahmed, K., Nizami, S. S., Razak, N. Z. , Mahmood, K. ,2013," Effect of Micro-Sized Marble Sludge on Physical Properties of Natural Rubber Composites"Chemical Industry & Chemical Engineering Quarterly 19 (2) , pp: 281−293.

da Costa, H. M., Nunes, R. C. R., Visconte, L. L. Y., Furtado, C. R. G., 2001, "Physical Properties and Swelling of Natural Rubber Compounds Containing Rice Husk Ash"KGK KautschukGummiKunststoffe 54. Jahrgang, No.5.

Entegris" Properties and Characteristics of Graphite for Semiconductor Industry" 2013.

Igwe, I. O., and Ejim, A. A. , 2011" Studies on Mechanical and End-Use Properties of Natural Rubber Filled with Snail Shell Powder" Materials Sciences and Application, 2, pp: 802-810

Lorenz, O., and Parks, C. R., 2003, "The crosslinking efficiency of some vulcanizing agents in natural rubber "Journal of Polymer Science, Volume 50, Issue 154, pp: 299–312.

Onyeagoro, G.N., 2012,"Cure Characteristics and Physico-Mechanical Properties of Carbonized Bamboo Fibre Filled Natural Rubber Vulcanizates" International Journal of Modern Engineering Research (IJMER), Vol.2, Issue.6, pp: 4683-4690

RohanaYahya, Y. S., Azura, A. R., Ahmad, Z., 2011"Effect of Curing Systems on Thermal Degradation Behaviour of Natural Rubber (SMR CV 60)" Journal of Physical Science, Vol. 22(2),pp: 1–14.

Wu, X., Lin, T. F., Tang, Z. H., Guo, B. C., Huang, G. S., 2015,"Natural rubber/graphene oxide composites: Effect of sheet size on mechanical properties and strain induced crystallization behavior "eXPRESS Polymer Letters Vol.9, No.8,pp: 672–685.

www.gcsescience.com/a34-structure-graphite-giant-mol., 2015.