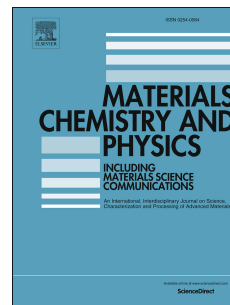


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Comparative study of LIBS and mechanically evaluated hardness of *graphite/ rubber* composites

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Abstract

Graphite is a crystalline form of carbon which has attracted the academic and industrial interest. It has been used as reinforcing filler that can produce highly effective improvement for rubber. This article presents and discusses the development of graphite-based rubber composites and their applications in industries which have been used extensively as reinforcing fillers. Increasing reinforcement of the rubber material leads to an increase in stiffness, modulus, tear strength, cracking resistance, tensile strength, abrasion resistance, and fatigue resistance. Laser-Induced Breakdown Spectroscopy (LIBS) technique has been utilized for determination of hardness and analysis of rubber polymers doped with Graphite filler. Different samples of natural rubber with different graphite filler concentration have been measured. A linear relationship between sample hardness and filler concentration is shown by the conventional hardness measurement techniques and has been demonstrated by LIBS technique too. Other laser-induced plasma parameters such as the electronic density and temperature as a function of time are determined. The same selectivity and ability to excite emission were revealed through measurements using LIBS, and thus the qualitative analysis capability of other techniques was confirmed.

Keywords: Hardness, LIBS, Rubber

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1. Introduction

Natural rubber/ graphite compositions are widely applied in several technological purposes because of their high durability, high elastic deformation, and their capability to be repeatedly strained to high levels without destruction, extrudate distortion or permanent deformation [1]. The mechanical behavior of rubber is affected by various internal and external parameters which produce changes in its chemical and physical composition. In accordance, this will lead to a discrepancy in the mechanical properties of the rubber.

Among the external factors that may cause variations in the physical or chemical behavior are the environmental conditions of time, pressure, temperature and radiation. Chemical structure and composition, the degree of crystallinity besides the size and degree of copolymerization are among the internal factors [2].

Testing mechanical properties of rubber is an area of interest. Numerous parts of tire manufacturer, need specific rubber composites with different mechanical properties to meet these applications. The mechanical properties of natural rubber are refined by graphite filler matrix reinforcement. Developing graphite filler inclusion increases the tensile strength of the composites by sharing the applied load among a group of chains, thus lowering

the unfortunate of a break to propagate. The variation in the mechanical properties is due to the change in the microstructure of rubber/ graphite filler matrix reinforcement [3].

Hardness is the capability of the composite material to resist abrasion or indentation. It is the most appropriate characteristics of rubber's mechanical properties. It is depending on measuring the permanent size of indentation by a rigid ball under a spring load [4]. Graphite is the most prevalent and lightest reinforcing agent used to increase the polymer hardness. It has been noted that the filler of relatively finer particle size exerts relatively more effect on hardness. To increase the hardness to certain limit, the required quantities of graphite filler are altered according to the type of used rubber [5].

Several methods are used to determine the hardness of rubber/graphite composites, among these methods are Shore Hardness Tester and LIBS technique.

Shore Hardness Tester is an International Standard Instrument used to measure the hardness of rubber or rubber-like materials [4]. It is designed to measure the penetration hardness of rubber, elastomers and other rubber-like substances. It can also be used for leather, soft plastics, and similar materials.

LIBS is an acronym of Laser-Induced Breakdown Spectroscopy [6]. It is one of the growing techniques used for elemental analysis because of being fast, simple and non-invasive technique [7]. This technique based on laser ablation to generate a micro-plasma with spectroscopic signatures of atomic and ionic lines of the matter (solid , liquid or gas) and the surrounding environments. LIBS is a non-destructive method to determine the material hardness for all samples. The intensity ratio of the ionic to atomic spectral emission lines of the solid targets is proportional to the target material compressive strength [8].

The aim of the present work is to evaluate the hardness of graphite/rubber composites via LIBS technique and Shore Hardness Tester. The addition of the graphite concentrations ranges from 0 to 100 parts per hundred parts of rubber by weight (phr). Ten different loadings in the rubber matrix were included in the study to evaluate the optimum concentration for composite hardness that sets the limit to its practical applications. Other laser-induced plasma parameters such as the change of the electron number density and the plasma excitation temperature with time were determined.

2. Materials and Methods

2.1 Materials

The preparation technique including the order of adding the ingredients, mixing and processing time greatly affecting the different characteristics of the rubber/graphite composites. [9], So, all the prepared samples must have the same preparation procedure in the same circumstances. The compositions of the tested materials are shown in Table 1. They were prepared from commercial ingredients according to standard procedures [10] by using the facilities of the "Transport and Engineering (Rubber Manufacturing) Company" (Trenco), Alexandria, Egypt. The rubber/graphite composites were prepared by utilizing a two-roll mill of 30 cm length, 17 cm diameter with speed of slow roll 1080 rev./sec and gear ratio 1.4.

The prepared rubber composites were left for at least 24 hours in advance of vulcanization. The vulcanization process was conducted at 413°K under a pressure of 40 kg/cm² for 1800 sec. Samples were subjected to thermal aging at 343 °K for 25 days in an electrical oven [2] before measurements were performed to ensure reasonable stability and reproducibility of the measured parameters.

Table 1: Composition of Natural Rubber composite

Ingredients	Types	Quantity (phr ^a)
Rubber	Natural Rubber	100
Filler	Graphite	0:10:100
Plasticizer	Processing oil	10
Activator 1	Stearic acid	1.5
Activator 2	Zinc Oxide	5
Accelerator	MBTS ^b	1.5
Age resisters	PBN ^c	1
Vulcanizing agents	Sulfur	2

2.2 Experimental setup

The LIBS experimental setup was similar to the one used before in ref. [11] It included the use of a Nd: YAG pulsed laser (Brio – Quantel, France), delivering laser energy of 50 mg/pulse, at 1064 nm wavelength with 5 ns pulse duration and 20 Hz repetition rate in open air. Laser radiation was focused onto the target surface using a 10 cm planoconvex quartz lens. The sample was mounted on a computer-controlled x-y micrometric translation stage. Optical emission from the plasma plume was collected by an optical fiber of diameter of 1mm held at a distance of 20 mm above the plasma at an angle of 35° concerning the target surface. The collected plasma was fed to an echelle spectrometer (Mechelle 7500, multichannel, Stockholm, Sweden) having a spectral resolution of 0.1 nm. The spectrometer was coupled with a controlled ICCD camera (DiCAM-PRO, PCO-Computer Optics, Kelheim, Germany) with its relevant software for dispersion and detection. LIBS spectrum is the average of 10 spectra taken at 5 different positions on each rubber/graphite composite sample. The obtained spectra have been displayed on a PC for further spectroscopic analysis adopting the LIBS++ software. The echelle spectrometer was calibrated before measurements, and the spectral lines identified via LIBS++ software were compared to NIST spectra database to ensure that a given emission line is the accurate element. LIBS measurements were performed on all samples under identical experimental conditions.

The Shore hardness test is a fast and suitable method to measure the hardness of rubber. The operation handles have evenly applied the force to the sample; adjust the testing height to obtain the measurement of different sample thickness. The Shore hardness tester comes with a measurement component and a digital display with a resolution of 0.1 hardness units. The hardness tester can be calibrated according to the ISO standard and includes an ISO calibrating certificate. This device with integrated refraction impact allows taking measurements in the absence of cables which may interfere with the results. Same measurements can be taken using the minimum

amount of force without affecting the level of accuracy. The tested samples were 0.6 cm thick. The measured hardness for each rubber/graphite composite sample was the average of five measurements taken at five different positions.

3. Results and Discussions:

3.1. Measured Spectral Lines of Interest.

In figure 1, we show the emission spectra of natural rubber/ graphite composite samples with different graphite concentrations ranging from 10 to 100 phr besides a one with zero analyte concentration covering the spectral region from 240 to 300 nm. We can notice the variation of the peak or integral of the line signal of C(I) 247.857 nm increases gradually from 0 to 100 phr. The line spectra show a variation of Mg(I) 285.2 nm and Mg(II) 280.27 nm with different graphite concentration.

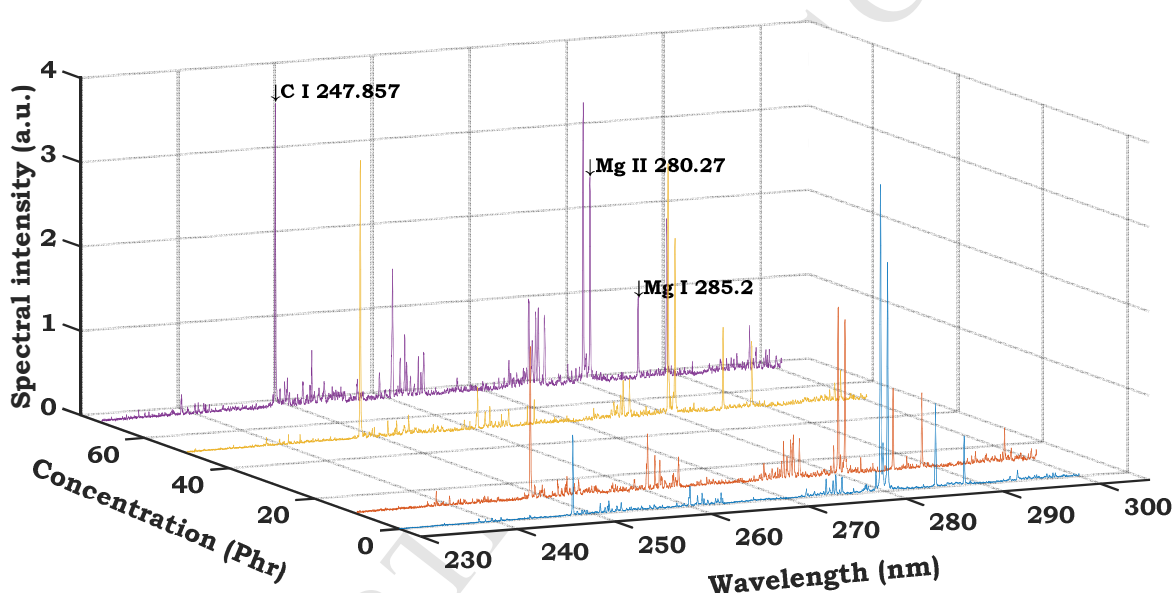


Fig.1 A sample of emission spectra from the laser-induced plasma (a) at different graphite concentrations showing different lines of C (I), Mg (I), and Mg (II)

3.2. Quantitative analysis and calibration curves

The recorded calibration curve at different graphite concentrations ranging from 0 to 100 parts per hundreds (phr) was constructed using C(I) 247.857 nm spectral line. The relative intensity is plotted against the relative concentrations of the graphite as shown in figure 2. As obvious from the figure, the calibration curve is well characterized by a straight line with a percolation threshold around 50 phr. The regression coefficient value of the linear fit equals 0.95 indicating a good linearity.

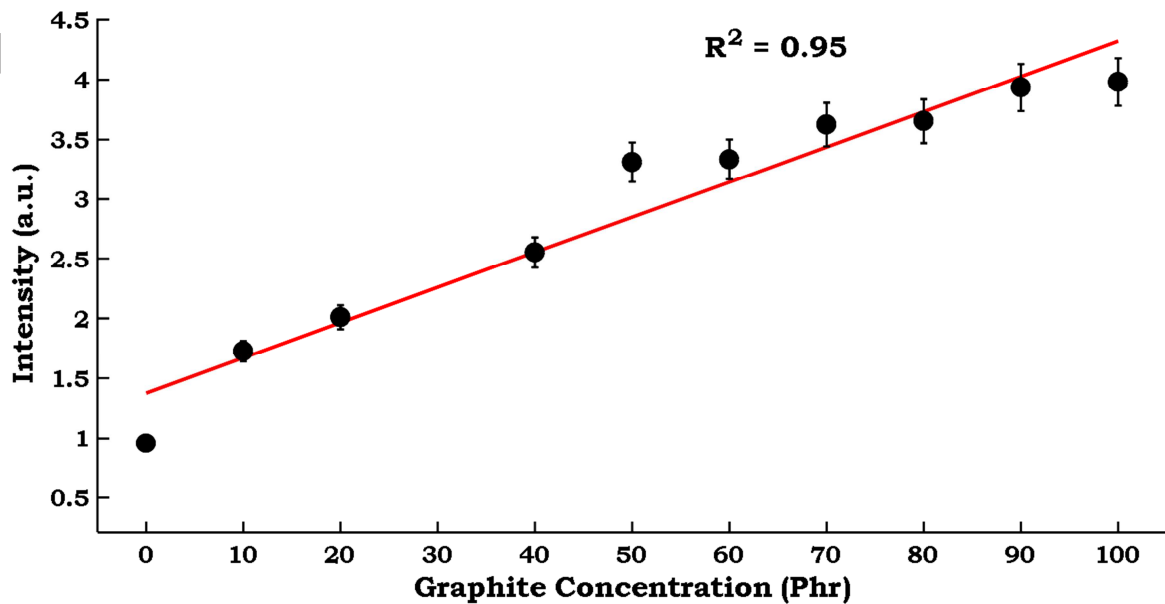


Fig. 2 The correlation between the intensity of carbon 247.857 nm emission line and the graphite concentrations in parts per hundred (phr). The points are the measured values, and the line is the linear fitting.

In the selection of the appropriate wavelength of the elements we have to avoid interference between spectral lines for different elements, and avoiding the possibility of self-absorption.

The limit of detection (LOD) was calculated from the formula

$$LOD = 3\sigma/S \quad (1)$$

Where σ is the standard deviation of the spectrum background and S is the calibration line slope.

The minimum concentration at which we can decide whether a carbon element is present or not and we can distinguish a signal from the background which significantly different due to the use of different measurement parameters. LIBS spectra were recorded from these graphite/rubber samples using a laser energy of 50 mJ/pulse at a delay time 1500ns. The LOD and the relative standard deviation (RSD %) were calculated and give the values of 363 ppm and 1.081 % respectively.

3.3. Effect of self-absorption on the spectral lines:

Self-absorption is defined as the absorption of the emitted light resulted from the hot parts of plasma in their path to outside by some cold species of atoms and molecules. This type of absorption results in a decrease in the intensity of the spectral line and increase in the Lorentzian full width at half maximum (FWHM).

Self-absorption coefficient at the line center (λ_0) is defined as the ratio of the spectral line radiance in the presence of self-absorption $I(\lambda_0)$ to that of the same line without self-absorption $I_0(\lambda_0)$. It is also expressed as the ratio of the

Lorentzian (FWHM) components of the same spectral line. An extended calculation for self-absorption coefficient is obtained from the ratio of the electron density of the line suffering from self-absorption to that of the optically thin H α - line. The self-absorption coefficient ranges from zero for completely optically thick spectral line to unity for completely optically thin line [12].

$$SA = I(\lambda_o)/I_o(\lambda_o) = (\Delta\lambda/\Delta\lambda_o)^{1/\alpha} = \left(n_e(\text{line})/n_e(H\alpha) \right)^{1/\alpha} \quad (2)$$

Where $\alpha = -0.54$, $\Delta\lambda_o$ is the Lorentzian component of the optically thin spectral line, and $\Delta\lambda$ is the Lorentzian component of the same line resulted from self-absorption (optically thick).

Figure 3 shows the variation of the intensity of C (I) emission line at 247.857 nm with the graphite concentrations with Self-Absorption (red lower squares) and without Self-Absorption (black upper circles).

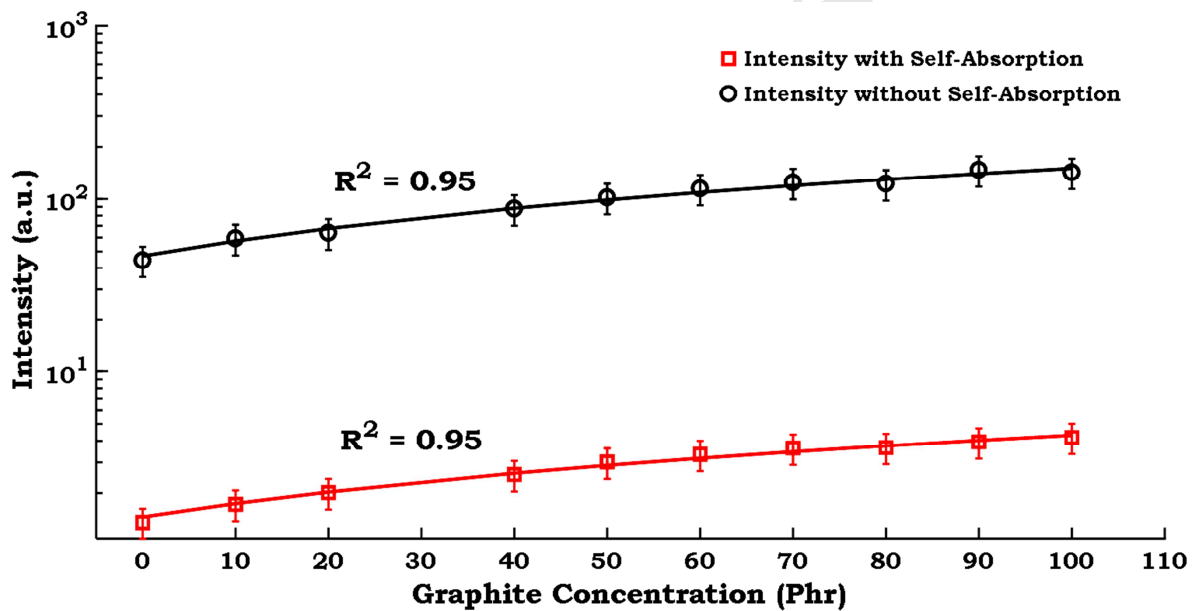


Fig. 3 Semiology plot between the intensity of carbon 247.857 nm emission line with the graphite concentrations (Phr) with and without line Self-Absorption, the points are the measured values, and the lines are the fitting.

3.4. Plasma Parameters

The measurement of the plasma parameters poses the most serious problem in plasma spectroscopy. Plasma state of thermodynamical equilibrium can be described via direct or indirect measurements of electron densities and temperature which are required to produce reliable spectral features [13]. The electron density term should specify the state of thermal equilibrium, i.e., LIBS plasma which has large electron densities satisfies the local thermal equilibrium state. The FWHM of Stark broadening of the spectral lines mainly depends on the electron density. Stark effect can be either linear or quadratic. The H-like ions and hydrogen atom exhibit the linear stark effect,

while other atoms exhibit the quadratic stark effect. Precise knowledge of electron temperature is another important factor that demonstrates the strength of variation of the different elementary distribution functions, and thus the plasma thermodynamic system will be clarified [13].

3.4.1. Measurement of Electron Density

The electron number density (n_e), related to the emitted radiation line by the plasma can be measured by exploiting the full width at half maximum (FWHM) $\Delta\lambda_o$ of the stark broadening, this broadening result from the ions and electrons collisions. Spectral line widths or spectral profile is a diagnostic tool for proper plasma identification [14]. The electron density of non-hydrogenic atoms can be related by FWHM of Lorentzian stark broadening with the following formula [14].

$$\Delta\lambda_{1/2} \approx [1 + 1.75A(1 - 0.75r)] \left(\frac{n_e}{N_r}\right) 2\omega \quad (3)$$

Where

$\Delta\lambda_{1/2}$ is the measured full-width at half maximum (FWHM), A is a parameter gives the ion contribution, r is the ratio of the mean distance between ions to the Debye radius, ω is the half width at half maximum (HWHM) Stark broadening parameter caused by the electron density and N_r is the reference electron density which is equal to 10^{17} cm^{-3} for ionic atoms and 10^{16} cm^{-3} for neutral atoms. By neglecting the ionic contribution broadening, equation (3) can be approximated to [15]:

$$\Delta\lambda_{1/2} \approx \left(\frac{n_e}{N_r}\right) 2\omega \quad (4)$$

Figure 4 shows the variation of the measured electron densities utilizing the $H\alpha$ line (red higher squares), and from the atomic C(I) line at 247.858 nm (blue lower squares) with graphite concentrations. The Measured electron density calculated from the C(I) line concerning that evaluated from the optically thin $H\alpha$ - line indicates that the C(I) at 247.858 nm is optically thin.

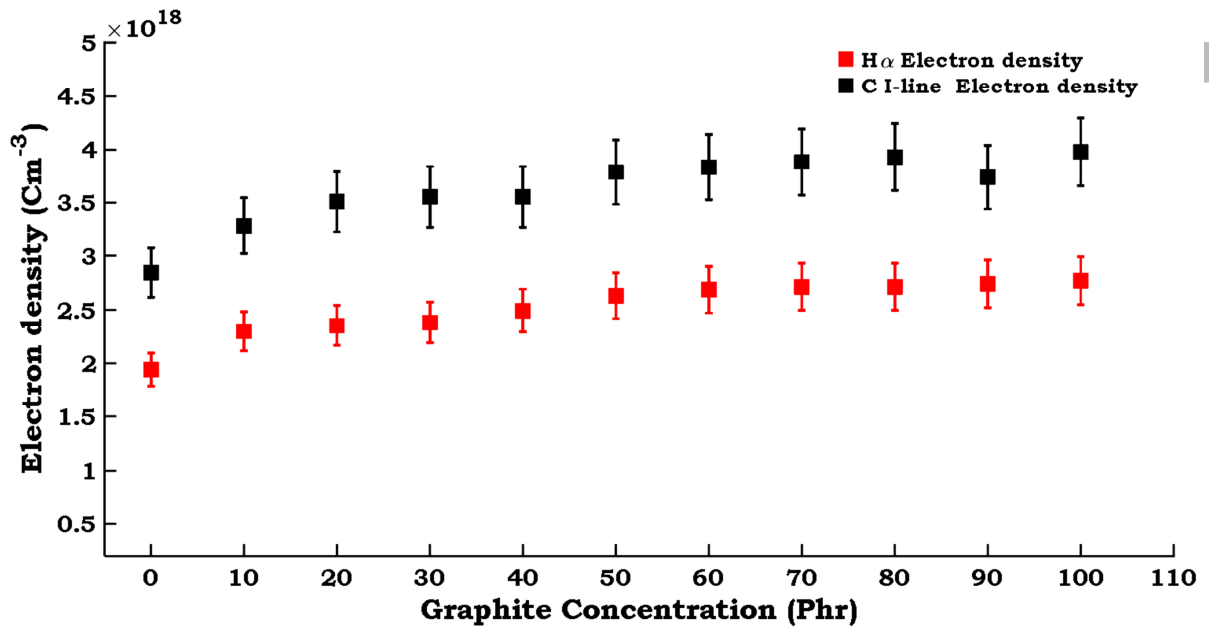


Fig. 4 Variations of the measured electron density utilizing the H α -line, and from the atomic C (I) line at 247.858 nm with graphite concentrations.

3.4.2. Measurement of Plasma Temperature

Plasma temperature of the specified composite is important in understanding the processes taking place in the plasma. The plasma temperature was calculated by plotting the spectral lines intensity of certain elements which must not be a resonant line relative to the energy of the upper level using the well-known Boltzmann method [15].

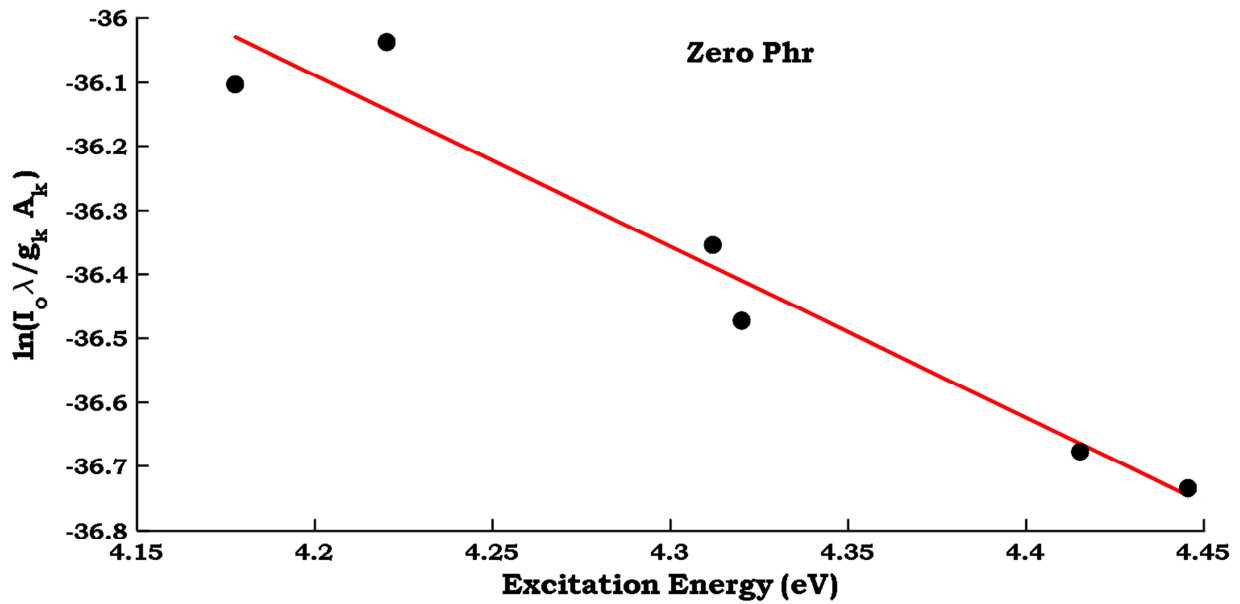
$$\ln\left(\frac{I_{ki}\lambda}{A_{ki}g_k}\right) = -\left(\frac{1}{kT_e}\right)E_k + \ln\left(\frac{C_s F}{U(T_e)}\right) \quad (5)$$

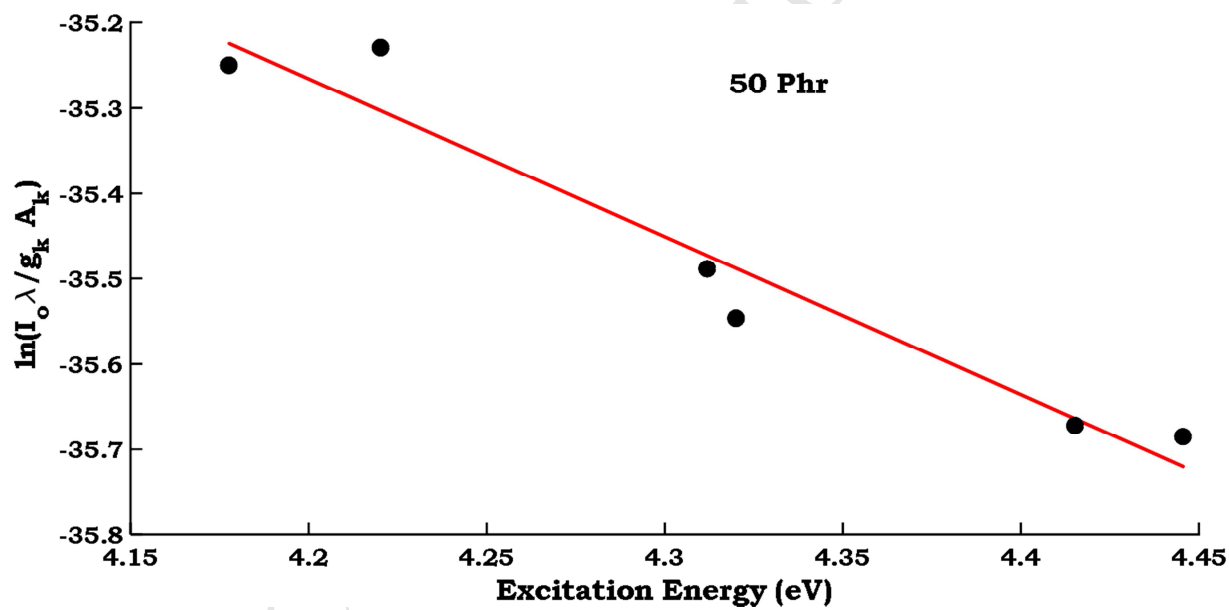
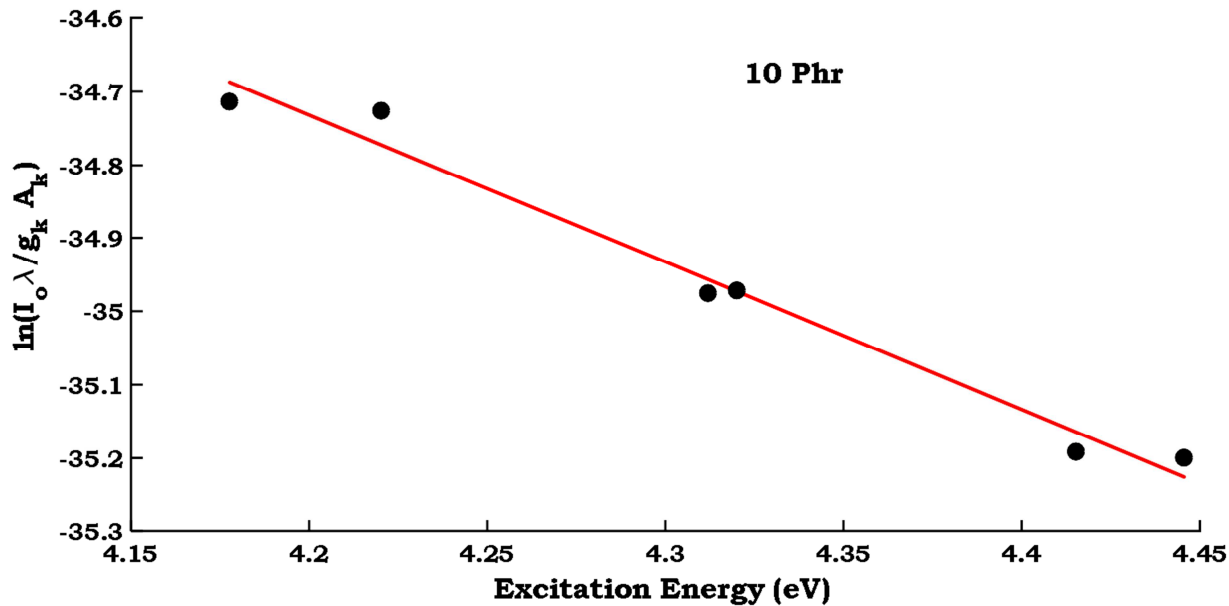
Where, λ is the wavelength of the transition, I_{ki} is the integrated line intensity of the transition, A_{ki} and g_k are the transition probability and the statistical weight of the upper level, E_k is the energy of the upper level, k is the Boltzmann constant and T is the plasma temperature, F is an experimental factor, C_s is the species concentration,

and $U(T)$ is the partition function. A plot of $\ln\left(\frac{I_{ki}\lambda}{A_{ki}g_k}\right)$ versus the energy E_k gives, a straight line with a slope equal to $(-1/kT_e)$ as shown in figure (5). Neutral Fe lines are used in figure 5 and listed with its spectroscopic data in Table 2. The chosen spectral lines should meet the conditions that they are interference free lines, well resolved and same ionization stage.

Table 2: Spectroscopic parameters of Iron lines used for the determination of plasma temperature

Element	Wavelength (nm)	g_i	g_k	$A_{ki} (s^{-1})$	$E_k (eV)$
Fe I	358.20	13	11	1.02E+08	4.32
Fe I	360.89	3	5	8.13E+07	4.44
Fe I	361.87	5	7	7.22E+07	4.41
Fe I	364.78	9	11	2.91E+07	4.31
Fe I	373.49	11	11	9.01E+07	4.17
Fe I	374.94	9	9	7.63E+07	4.22





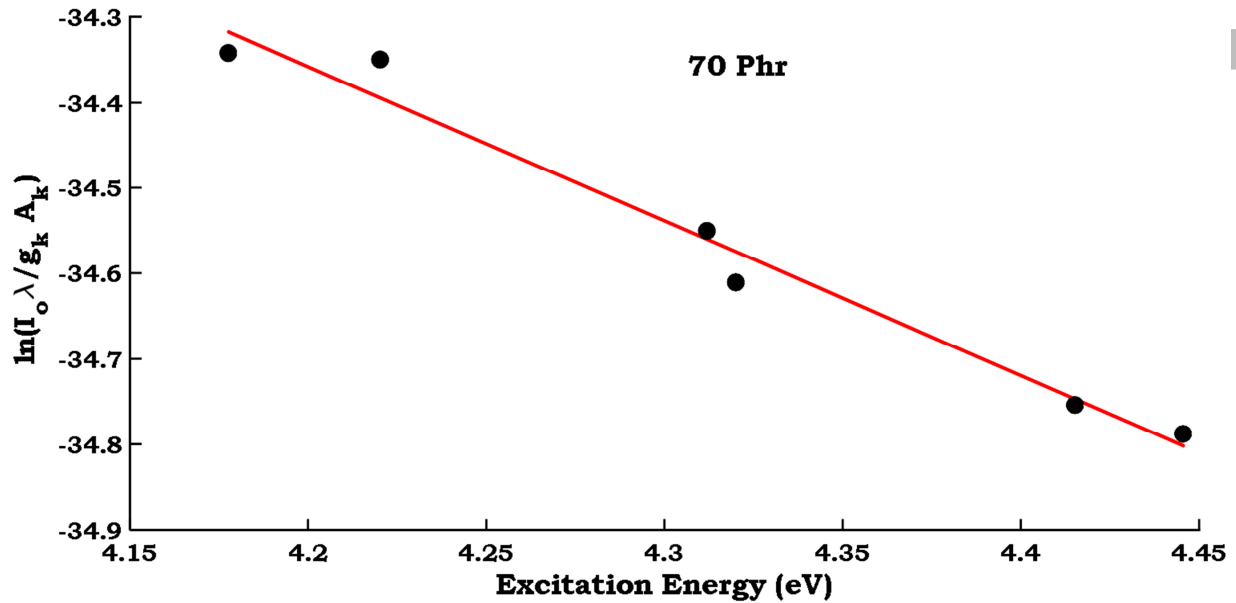
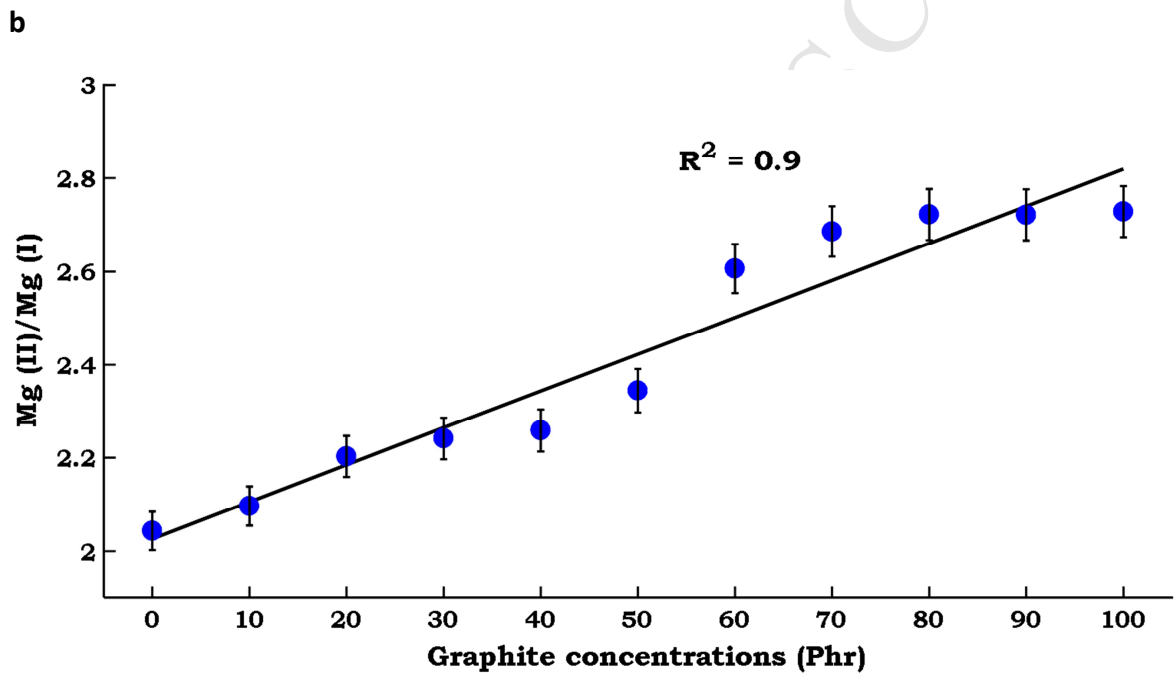
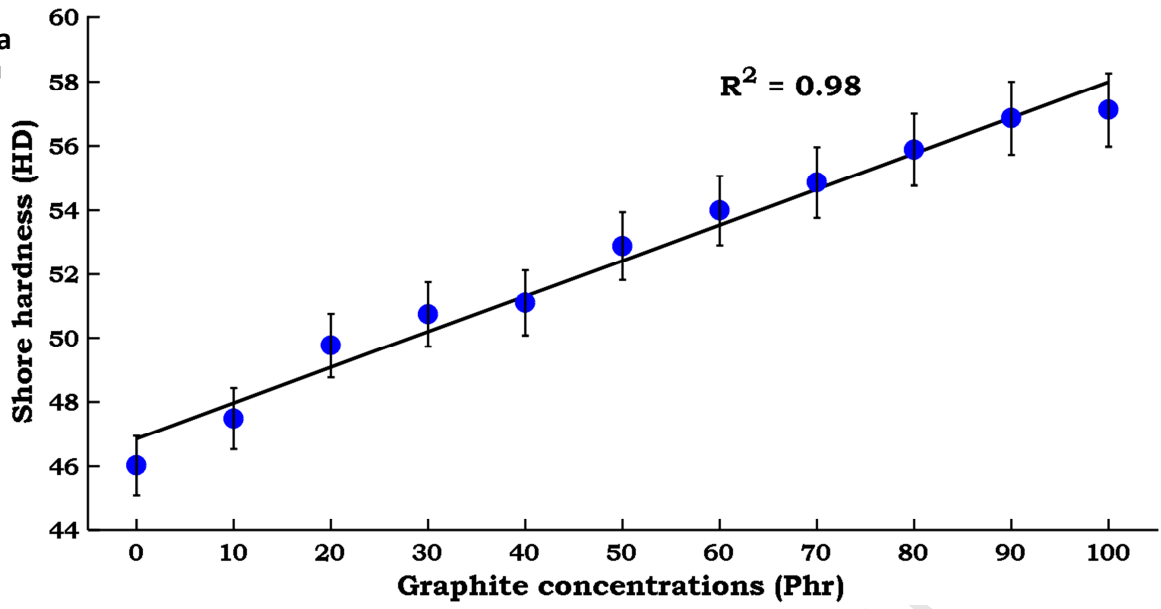


Fig. 5 Boltzmann plots utilizing the Fe(I) lines for different graphite concentrations.

3.5. Hardness Measurements:

Figure 6 shows the results of surface hardness measurements for different samples of natural rubber with different graphite filler concentration. The variation in the hardness between the samples is clear, measured and calculated by two different methods, the ratio Mg (II) / Mg(I) between the ionic Mg line at 280.2nm and the atomic Mg line at 285.2nm and the mechanical shore hardness test. The values of the Mg (II) / Mg(I) are achieved from the average of five spectral emission lines, the selections of the ionic magnesium line at 280.2 nm and the neutral one at 285.2 nm are due to the absence of self-absorption effect in these emission lines [16]. The trend of the mechanical shore hardness test shows a good agreement with the ratio of Mg(II) /Mg (I) which is found to be directly proportional to the target material hardness as shown in figure 6 which means the increase of the ionization rate in plasma plume [17]. The represented plasma temperature versus the calculated shore hardness values shows a direct proportionality as shown in figure 7. When the material is hard, there is a strong coupling efficiency between the laser and the material, which leads to more collisional ionization in plasma plume and consequently higher electron temperature. The plasma temperature increases from 0.37 to 1.17 eV from the low filler concentrations (soft) to the high graphite filler concentrations (hard). The plotted data are within the error range as given by the error bars. However due to the absorption of a part of the laser pulse by the plasma plume, the ablation rate decrease.



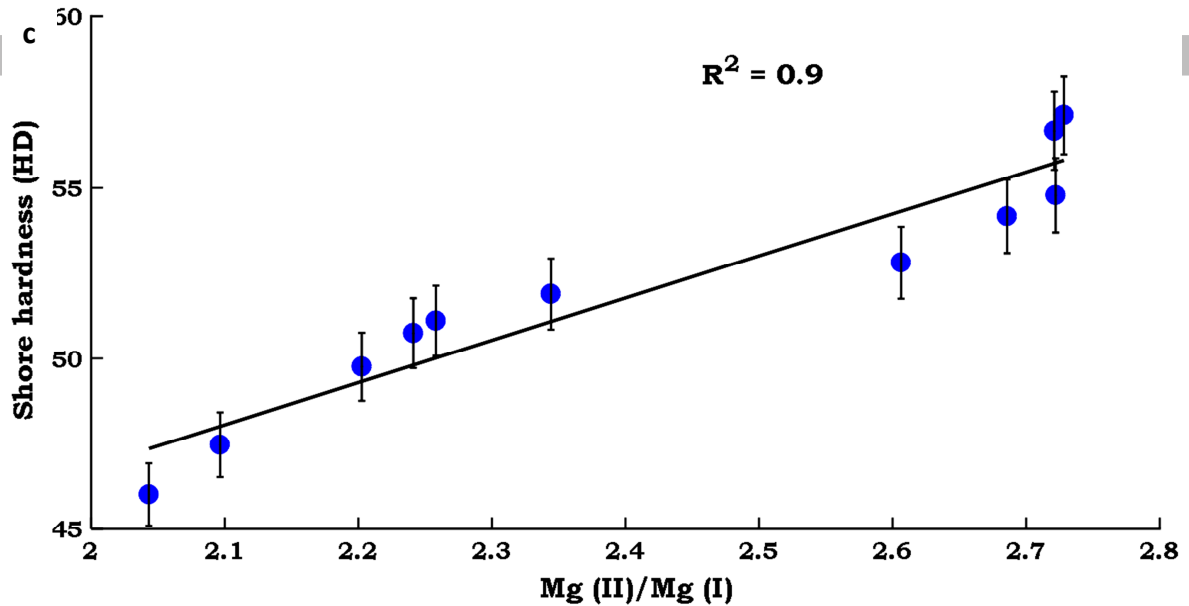


Figure 6 (a) The variation of the measured mechanical hardness with graphite concentrations, (b) The variation of the intensity ratio of Mg(II) 280.2 nm and Mg(I) 285.2 nm emission lines with the graphite concentrations. (c) The correlation between the hardness of different samples of natural rubber with different graphite filler concentration and the intensity ratio of Mg(II) 280.2 nm and Mg(I) 285.2 nm emission lines. The hardness of the samples was measured using a Shore hardness test.

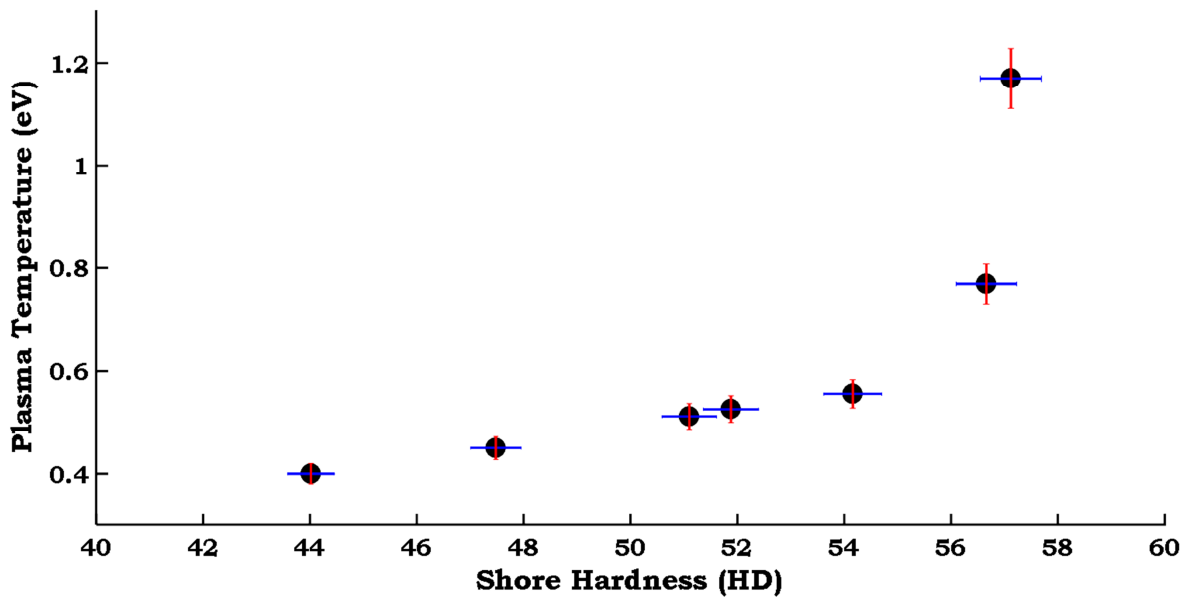


Fig.7 Plasma excitation temperatures versus shore hardness values. The error bars represent the standard deviation of the experimental data.

Conclusion:

In the present work, laser-induced breakdown spectroscopy has been used for estimating the surface hardness measurements of graphite/rubber composites with different graphite filler concentrations. The plasma electron density was also measured by utilizing the H α -line and the neutral C line for different graphite concentrations spectra. There is a direct relation between filler concentrations and electron density for both lines; the neutral C line was found to be self-absorbed in comparison to the H α -line. The neutral C line intensity was rectified using

the electron density ratio of neutral C line and the free self-absorbed H α -line. Also, it was shown that surface hardness is the most perceptible properties that can be affected, and will be marked up with increased cross-link density by increasing graphite filler concentration. This phenomenon designates that graphite fillers improve the chemical cross-linking of rubber chain. The results demonstrated that there is a direct proportionality of the laser-induced plasma temperature versus the shore mechanical hardness test. The reinforcing graphite filler used in the tire manufacturing compound is crucial to carrying out the required performance, besides the steadfastness and the overall load bearing. The obtained results display the credibility of using LIBS in industrial applications as an online and in situ demonstrative techniques to evaluate the surface hardness of tires.

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Footnotes

a Parts per hundred parts by weight of rubber

b 2,2"-Dithiobis(benzothiazole)

c Pheny 1- β -naphthylamine

Highlights

- Graphite has been used as reinforcing filler to improve the rubber.
- Hardness of composites was measured by the Shore Hardness Tester & LIBS technique.
- Plasma temperature is directly proportioned to the shore mechanical hardness.