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Research article

Conductivity Studies on Acrylonitrile Butadiene Rubber Loaded with different types of Carbon Blacks

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Abstract

The effect of three types of carbon blacks and namely: High abrasion furnace black (HAF), graphite and acetylenic carbon black on the electrical and mechanical properties of NBR composites was investigated. The conductivity of NBR composites is found to be 7 orders of magnitude higher than that of the filler-free NBR. It reaches~10^{-3} S cm^{-1} at 30°C in case of NBR composites loaded with acetylenic carbon black. The tensile strength of NBR/filler composites have been markedly increased, indicating high reinforcement efficiency i.e. good interaction between the fillers and NBR. The NBR/HAF composites have the highest tensile strength, then NBR/Acetylenic carbon black and then NBR/graphite composites. The elongation at break of NBR/ filler composites was found to decrease with increasing the filler content.

Keywords: Electrical conductivity; Dielectric; Acrylonitrile Butadiene Rubber NBR; Mechanical properties.

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1. Introduction

Rubber is an elastomer and the characteristic of rubber elasticity for practical application is provided by vulcanization and the formation of compounds with filler [1,2]. A vast number of products with specific properties of elasticity, stretch, tear resistance and abrasion resistance can be made of rubber. These properties can be achieved by the addition of various types of fillers and/or reinforcing additives. NBR vulcanizates, which have high physico-mechanical properties, are suitable for very special commercial applications such as oil resistant products. Fillers are generally incorporated to improve processability, reinforcement and cost reduction [3,4]. In general, rubbers are insulators because the atoms in the rubber chain are covalently bonded. In the covalent bonded molecules of organic carbon compounds, there is no scope of delocalization of the valence electrons. Consequently, the electron carrier path is not available.

One of the important methods to form carrier path in an insulating rubber matrix is the incorporation of conductive additives like carbon blacks, carbon fibers, metals or metal oxides [5,6].

Among different types of conductive additives, carbon blacks are the most widely used for rubber matrix. They not only provide high degree of conductivity, but also offer good reinforcement to the rubber matrix [6].Rubber/carbon black conductive composite materials are characterized by low cost, high flexibility, good physical and mechanical properties ,low density and in particular, specific structures that enable the formation of conductive network inside the polymer matrix at relatively low filler concentration[7-9]. Rubber/carbon black conductive composites are widely used for rubber contact switches, floor heating, electromagnetic interference shielding and various other electronic and electrical applications [10,11]. Carbon black (CB) is an amorphous form of carbon with a structure similar to disordered graphite. Carbon black as conductive filler is characterized by three major properties, particle size (surface area), structure and surface chemistry. Both high surface area and high degree of porosity are the critical of carbon blacks that impart electrical conductivity at lower loading in polymer composites. Examination under the electron microscope shows that carbon black is composed of prime particles fused into primary aggregates. The aggregate size, shape and the number of particles per aggregate affects the structure of carbon blacks. High structure of the primary aggregate is important in achieving high electrical conductivity. Carbon black is characterized by primary aggregates composed of many prime particles is referred to the high-structure black. If the primary aggregates consist of relatively few prime particles, the carbon black is referred to as a low structure black. High structure black has strong attractive forces between their aggregates. This means that the dispersion process should provide more energy to separate them. Since high structure blacks tends to produce large aggregates in contact as well as aggregates separated by smaller distance, this results in higher conductivity at the same loading [6].

Studies on electrically conducting polymer composites prepared by incorporation of metallic powders, flakes, whiskers, and other conducting fillers such as carbon black and graphite have attracted wide attention due to their effectiveness in such applications as electromagnetic interference (EMI) shielding [12-18], electrostatic charge dissipation [18] and sensors for vapors and chemicals [15,18]. Among the filled conducting polymer composites, however, those based on the use of different grades of carbon blacks [16-19] and carbon fibers [20,18] as filler have grown more in importance in respect of their physical, mechanical, conducting and noncorrosive property balance. Recent investigations on conducting polymer composites have led to some important revelations relating to attainable electrical conductivity range and trends of change in the conductivity parameter with variations in: (i) the loading level [18], (ii) nature of the matrix polymer [18,21,22], (iii) degree of filler dispersion [18] and (iv) temperature [18].

The aim of the present work is to study the effect of different types of carbon blacks in different concentrations as on the physico-mechanical and electrical properties of NBR composites

2. Materials and experimental techniques

2.1. Materials

- Nitrile Butadiene Rubber (NBR) a Bayer product, Perbunan N 3310 that is a Butadiene-acrylonitrile copolymer with 34% acrylonitrile content, sp.gr. 1.170 and Moony viscosity ML(1+4) at 100°C 45 ±5.
- High abrasion furnace black (HAF), with sp.gr. 1.78-1.82,pH 8-9.3, and particle size of 40 nm ,supplied by Transport and Engineering Company, Alexandria, Egypt.
- Graphite powder from Merck Co. (Germany) with a bulk density of 20-30g/100ml, and a particle size less than 50 µm.
- Acetylenic carbon black, particle size 42 nm, surface area 77(m2/g), obtained from Soltex Chemical Supplier, USA.

- All other ingredients such as N-cyclohexylbenzothiozyl sulfonamide (CBS), sulfur, zinc oxide (ZnO), stearic acid, Dioctylphthalate (DOP) and N-isopropyl-N`phenyl p-phenylene diamine (IPPD) are obtained from local rubber enterprises.

2.2. Experimental techniques

2.2.1. Samples preparation

Rubber was mixed with all compounding ingredients as shown in table (1) according to ASTM-D3182-07. Mixing was done on a laboratory two-roll mill. The speed of the slow roll is 24 rev/min and gear ratio is1:1.4. The compounded rubbers were left overnight before vulcanization. The vulcanization was carried out at 152 ±1°C for the pre-determined optimum cure time calculated from rheogram charts in an electrically heated press under a pressure of about 4 MPa.

2.2.2. Cure characteristics

M_L (minimum Torque), M_H (maximum Torque), tc_{90} (optimum cure time), ts_2 (scorch time) and cure rate index (CRI) were determined according to ASTM-D 2084-07 using a Monsanto (Akron, OH, USA) oscillating disc rheometer model 100. The measurements were carried out at 152 ±1°C.

2.2.3. Mechanical properties

The tensile strength and elongation at break were carried out at room temperature using tensile testing Machine, Zwick 1425, according to ASTM-D 412-06.

2.2.4. Electrical properties

The conductivity (σ), dielectric constant (ε`) of samples prepared were measured using LRC HiTester (HIOKI, 3532-50). Higher temperature was provided by increasing the input voltage of a variac transformer connected to the wire-wound resistance heater. The temperature was determined using a Copper/Constantine thermocouple in close proximity to the sample. The conductivity measurements were carried out over the temperature range from room temperature up to 110°C. Conductivity σ_{ac} (Ω^{-1}. cm^{-1}) was obtained using the equation:

$$\sigma_{ac} = \omega\, \varepsilon_o\, \varepsilon`$$

The dielectric constant (ε`) was obtained at frequency range from 0.1 KHz to 5 MHz using the equation:

$$\varepsilon` = C.d / \varepsilon_o.A$$

where: C= Measured capacitance of the sample(F), d = Thickness of the sample(m), ε_o= permittivity of free space equals $8.85X10^{-12}$ F m^{-1}, A= Sample surface area (m^2), ω = the angular frequency, $\varepsilon`` = \varepsilon`. \tan\delta$, $\tan\delta$ = the loss tangent, which is obtained directly from the instrument.

3. Result and discussion

3.1. Physico-mechanical properties

The rheometric and mechanical characteristics are given in Table 2, from which one can see that the M_L and M_H are increased as the loading of carbon black fillers are increased. On the other hand these fillers slightly increase the rate of vulcanization of NBR. These findings can be related to the surface activity of these fillers as they contain some functional groups, which are responsible for the noticed effect. The data in Table 2 showed also that HAF and acetylenic carbon blacks drastically improve the mechanical of NBR vulcanizates. The stress at rapture is increased from 1.8 MPa for unloaded NBR vulcanizates to about 20 MPa for the loaded ones, while the graphite black behaved as a weak reinforcing agent, since it has lost any function group on its surface during preparation. The optimum dose of such fillers is found to be 25 phr.

3.2. Electrical conductivity measurements

The dependence of conductivity on frequency of the studied rubber vulcanizates measured at 30°C is shown in Fig.1. The dependence of the ac conductivity on angular frequency is found to obey the relation:

$$\sigma(\omega) = \sigma_{dc} + \sigma_{ac}$$

A flat dc plateau can be observed at low frequencies. On the other hand, it can be noticed that, Log σ increases as the concentration of the filler increases and also as the frequency increases.

The temperature dependence of dc conductivity, σ_{dc}, for NBR/filler composites is shown in Fig. 2. It can be seen that σ_{dc} increases with the increase in temperature, indicating the semiconducting nature of the present vulcanizates [23]. It can be also noticed that the conductivity increases with the increase in concentration of the fillers. The conductivity in case of NBR/ Acetylenic carbon black can be noticed to be higher than that of both NBR/graphite and NBR/HAF composites. The plots show that the dc conductivity exhibits an Arrhenius-type temperature dependence given by the relation

$$\sigma_{dc} = \sigma_0 \exp(-E_{dc}/kT)$$

The activation energies of the studied samples and their conductivity values are listed in Table 3. Conduction through the composites can be explained on the basis of the formation of a continuous conductive network and a transport mechanism involving the tunneling of electrons across the gaps between two discontinuous conducting elements [24].

Dielectric constant (ε`) of the prepared composites was measured over the frequency range from 42 Hz to 5 MHz at temperature range from 30 to 110°C. The obtained data are illustrated graphically in Fig.3. It is clear that ε` has dispersion values, which were decreased by increasing the applied frequency. In such range the permittivity has contribution from orientation, atomic and electronic polarization [25, 26].The decrease of ε` values may be attributed to the lag of the molecule behind the electric field. Fig.4 shows the variation of dielectric constant with temperature. It is known that the dipolar groups, which are bound in the solid structures are structural elements of the solid lattice and the rigidity of the lattice hinders the orientation of the dipoles. At elevated temperatures, the dipoles acquire energy, which allows them to reorient; consequently an increase in the dielectric constant is achieved. This explanation is consistent with the found results, where the dielectric constant has increased with temperature [27].

It can be noticed also from (Fig.4) that, ε` increases by increasing the filler content. This increase could be attributed to the increase in the polarity due to the function groups (OH, C=O) on the filler surface, which leads to an increase in the orientation polarization and also to the presence of interfacial polarization. The observed decrease of $E_{a(dc)}$ (Fig. 5, Table 3) of NBR composites loaded with 50 phr of different fillers are accompanied by a decrease in the height of the free energy barriers has made the jump process easier and therefore, contributing to a higher mobility. This leads to increase in conductivity. The results suggest that the charge carriers are decoupled from the segmental motion of the polymer chain and the transport occurred via an activated hopping mechanism [28]. Figure 6 shows the electrical conductivity for NBR composites as a function of the carbon filler concentrations. It is clear that, as the carbon filler increases, the conductivity σ increases for all filler types (HAF, graphite and acetylenic carbon blacks). This increase in conductivity was attributed to the increase of conductivity chain formation through the aggregation of the carbon black particles network, while with low concentration; the particles of the filler are widely dispersed through the polymeric matrix [6].

These results are in accordance with the dielectric data (Table 3). The conductivity of NBR composites is several orders of magnitude higher than that of the filler free NBR. NBR composites exhibit an enhancement in electrical conductivity by 7 orders of magnitude, where it is increased from $\sim 10^{-10}$ to 3.5×10^{-3} S cm^{-1} at 30°C [29]. The value 10^{-3} $\Omega^{-1}cm^{-1}$ is found to be in the order of those for semi-conducting materials, which can help to use such materials in power cables to prevent partial discharge at the interface between insulation and conductor as the conductivity range for such application should be in that range [30]. The highest range of σ was found to be in the order of 10^{-5} and10^{-6} $\Omega^{-1}cm^{-1}$, which is suitable for electrostatic dissipation applications as the range of conductivity for such application should be in the range $10^{-5} \sim 10^{-9}$ $\Omega^{-1}cm^{-1}$ [30].

4. Conclusions

- The conductivity of NBR composites is found to be 7 orders of magnitude higher than that of the filler-free NBR. It reaches$\sim 10^{-3}$ S cm^{-1} at 30°C in case of NBR composites loaded with acetylenic carbon black.
- The Reinforcing efficiency of the studied fillers in NBR greatly depend on their types and can be arranged as follows:
  High abrasion black > Acetylenic black > Graphite > without filler
- The recommended dose for both HAF and graphite is 50 phr, but for acetylenic black is 25 phr in order to achieve good physico-mechanical properties.

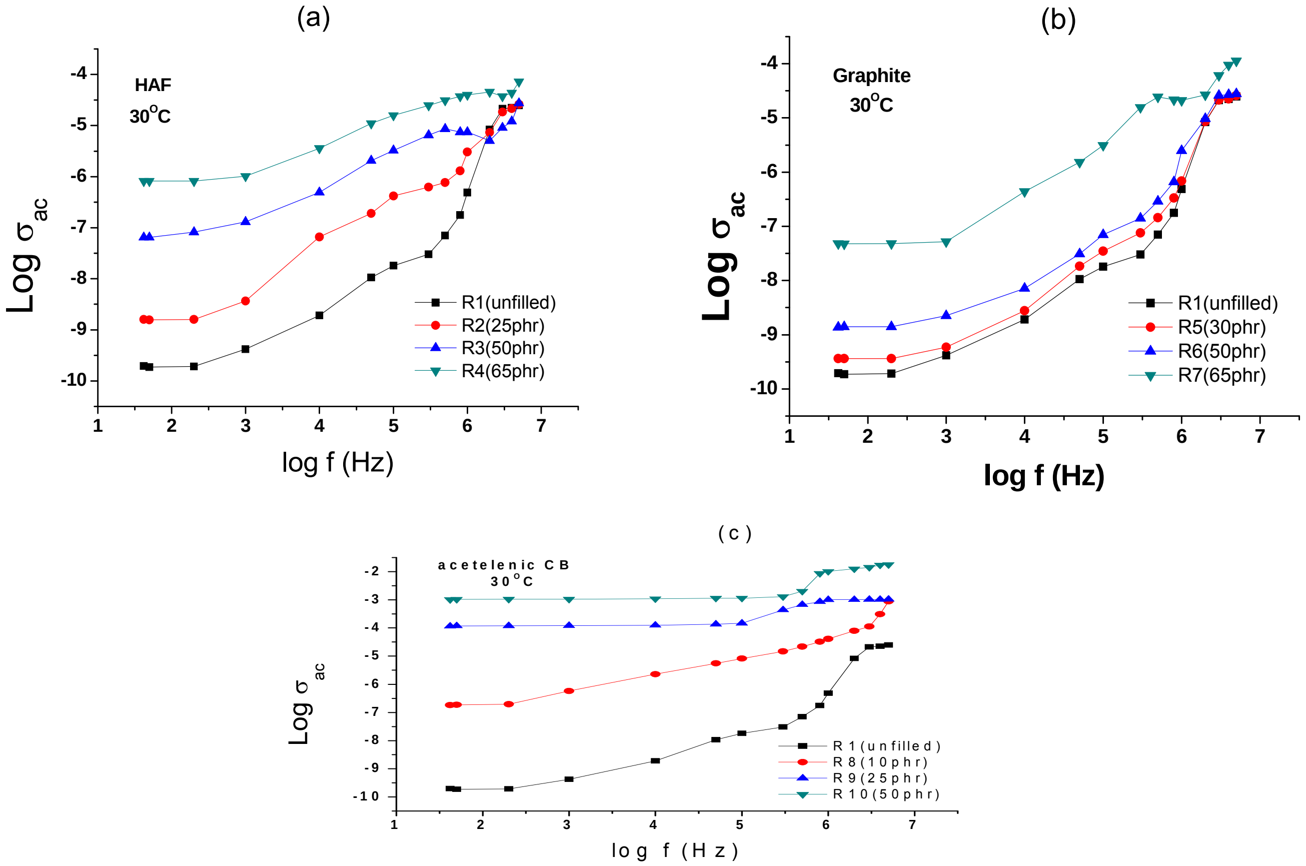


Figure1: Frequency dependence of conductivity for NBR composites containing different fillers of (a) HAF, (b) graphite and (c) acetylenic CB in comparison with filler-free NBR sample .

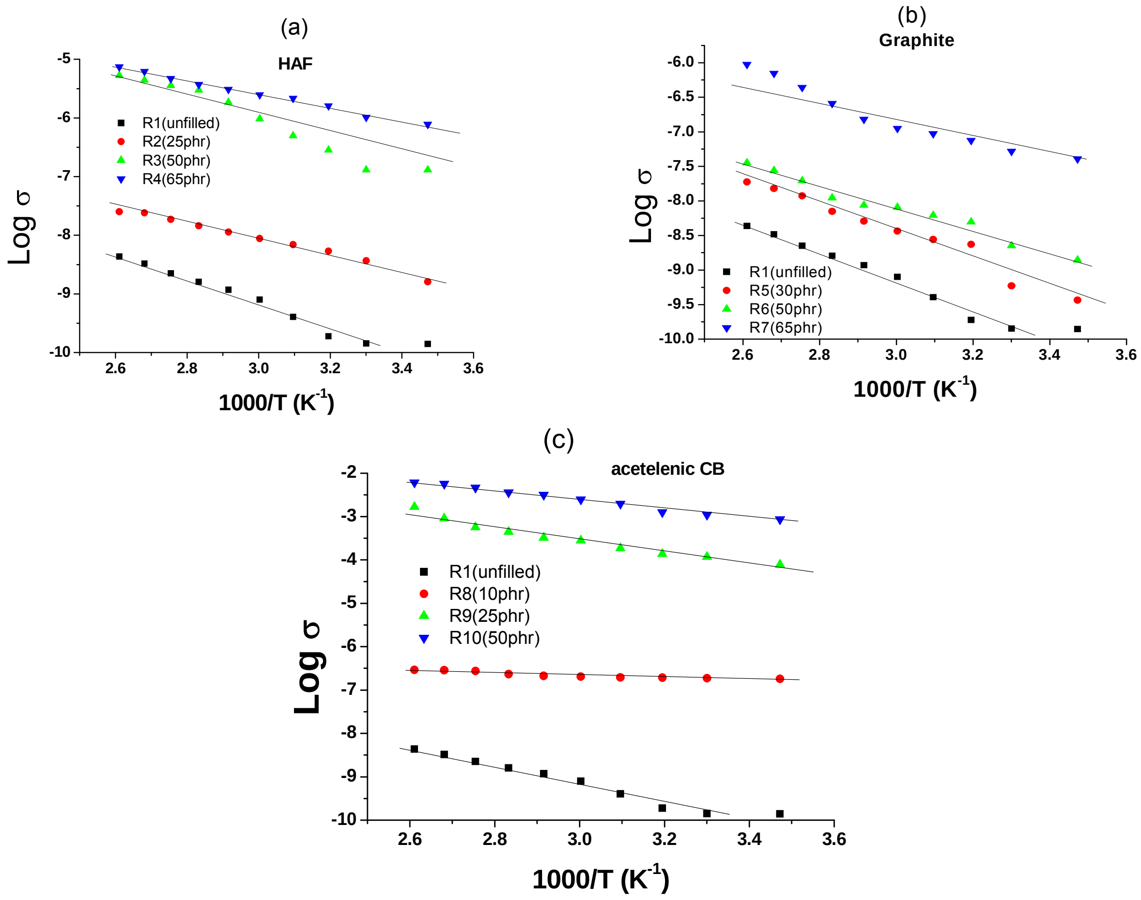


Figure 2: Temperature dependence of the conductivity for NBR composites containing different fillers of (a) HAF, (b) graphite and (c) acetylenic CB in comparison with filler-free NBR sample.

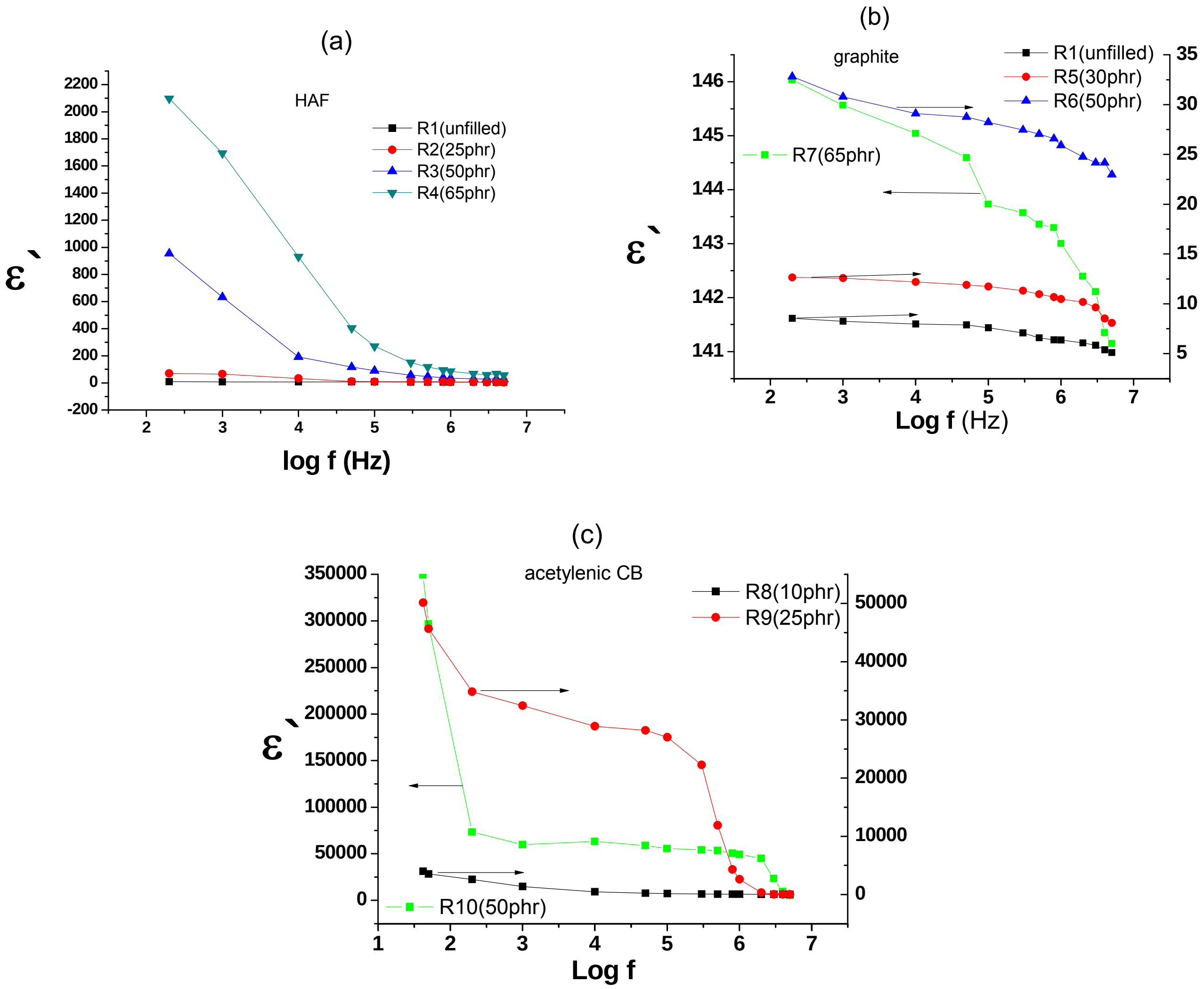
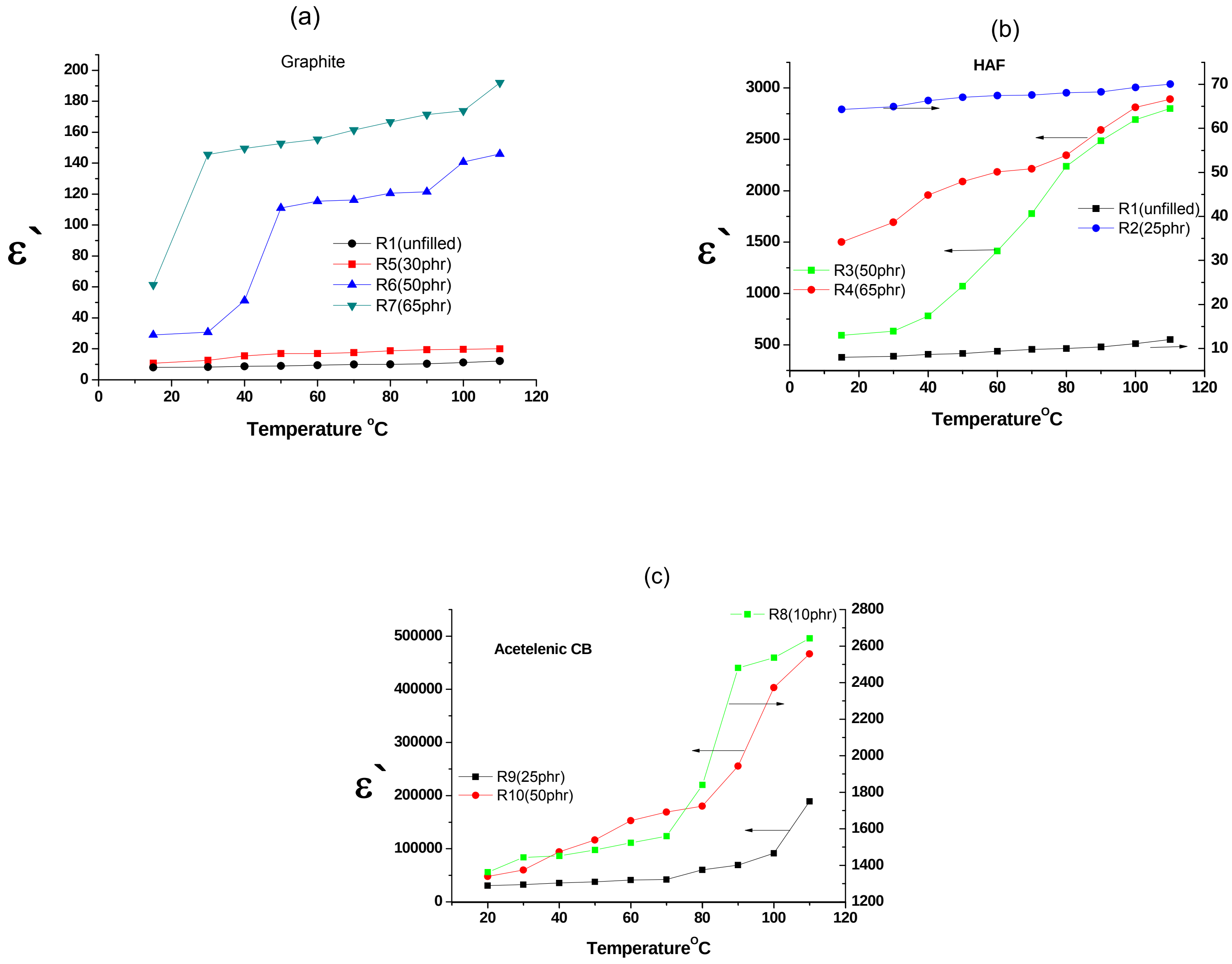


Figure 3: Dielectric constant as a function of frequency for NBR composites containing different fillers of (a) HAF, (b) graphite and (c) acetylenic CB in comparison with filler-free NBR sample at 30°C.



(a)

(b)

(c)

Figure 4: Variation of dielectric constant with temperature at 1KHz for NBR composites containing different fillers of (a) HAF, (b) graphite and (c) acetylenic CB

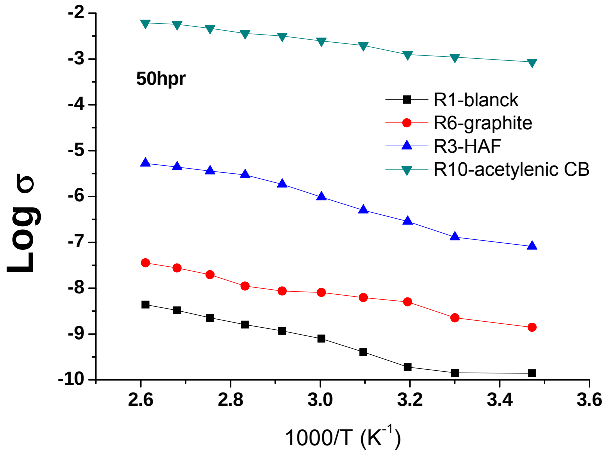


Figure 5: Temperature dependence of the conductivity for NBR composites containing 50 phr of different fillers

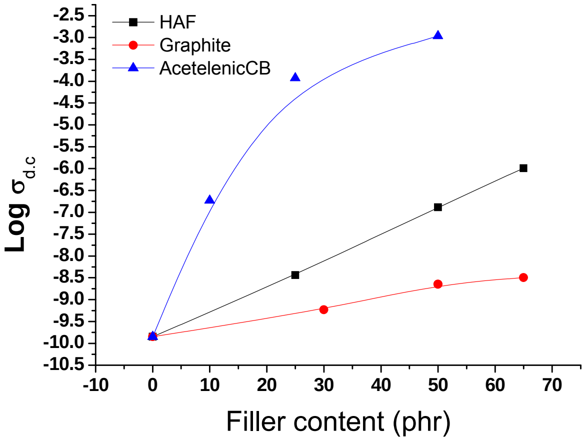


Figure 6: Dependence of conductivity on the filler content of the NBR composite samples measured at 30^{o}C.

Table1: Formulations of NBR / different types of carbon black fillers.

Formula no.	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**	**R8**	**R9**	**R10**
NBR	100	100	100	100	100	100	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
ZnO	5	5	5	5	5	5	5	5	5	5
DOP	10	10	10	10	10	10	10	10	10	10
HAF	-	25	50	65	-	-	-	-	-	-
Graphite	-	-	-	-	30	50	65	-	-	-
Acetylenic C	-	-	-	-	-	-	-	10	25	50
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CBS	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
IPPD	1	1	1	1	1	1	1	1	1	1

Table 2 : Cure and mechanical properties of NBR /different types of carbon black fillers.

Rheometric characteristics										
Cure preperation	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10
ML (Dn.m)	4	5	7	10	4	4	6	6.5	8.5	49.5
MH (dN.m)	30	44	54	62.5	30	38	44	29.5	39	68
MH-ML	26	39	47	52.5	26	34	38	23	30.5	18.5
t_{N2} ,min	6.25	4	3	3	6.25	5	4	4	7	8.5
t_{C90} ,min	12.5	9	11	10	12.5	11	10	15	15	14
CRI,min^{-1}	16	20	12.5	14.3	16	16.7	16.7	9.1	12.5	18.2
Physico-mechanical properties										
Tensile strength, MP$_a$	1.83	20.5	21.8	20.4	3.7	4.6	4.3	14.5	20.1	16.9
Elongation at break (%)	620	970	780	610	850	900	740	1000	900	400

Table 3: The conductivity(σ) , activation energies E_a (eV) and dielectric constant (ε `) of NBR /different types of carbon black fillers in comparison with filler-free NBR sample .

Filler type	Sample no.	Filler content (phr)	σ_{dc}	$E_{a(dc)}$	ε` (at 1KHz)
	R1	0	$1.4235\text{x}10^{-10}$	1.9852	8.28
HAF	R2	25	$3.6676\text{x}10^{-9}$	1.4820	65.02
	R3	50	$1.302\text{x}10^{-7}$	1.4961	632.35
	R4	65	$1.017\text{x}10^{-6}$	1.2214	1692.765
Graphite	R5	30	$5.91\text{x}10^{-10}$	1.9990	12.609
	R6	50	$2.25\text{x}10^{-9}$	1.6272	30.817
	R7	65	$5.222\text{x}10^{-8}$	1.1368	145.567
Acetylenic CB	R8	10	$1.87\text{x}10^{-7}$	0.2411	1446.687
	R9	25	$1.177\text{x}10^{-4}$	1.3462	32525.15
	R10	50	$1.09\text{x}10^{-3}$	0.9749	59938.003

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