Study of the Electrical Properties and Swelling Mechanism in Compressed Butyl Rubber Loaded with Carbon Black

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The dependence of both electrical conductivity "σ" and dielectric constant "ε" for samples containing different carbon black concentrations were studied at different loads. It was found that, "σ" and "ε" are nearly load independent at low concentration, however, they change at higher concentration of carbon black. Swelling of the samples in both benzene and kerosene was measured, and found to be dependent on both carbon black concentration and the type of solvent used. The diffusion coefficient, penetration rate and the molecular mass were calculated.

Introduction

Carbon materials are sometimes added to polymer in order to obtain composites with improved electrical and mechanical properties [1]. The dielectric properties and stress -strain characteristics of chloroprene rubber modified by different carbon black fillers were previously studied [2]. So that it was found that carbon black content exceeding ~ 60% MT did not lead to any improvement in dielectric properties [2]. This value was about 40% for SRF and 20% for both HAF and SAF blacks [2]. The dielectric constant ε and the modulus of elasticity were also previously studied [2]. Percolation concept and the dependence of electrical conductivity of the none crystallizable rubber (CR) on both carbon black concentration and temperature were studied [3].

The thermal and electrical conductivities of polyethylene and poly (vinyl chloride) filled with carbon materials over a wide range were measured in order to study the effect of formed conductive particle chains on them [4].

The swelling of polymer networks in suitable liquids was found to be large for three-dimensional network polymers. The study of the swelling process and its kinetics, favours the estimation of the degree of cross-linking of a given polymer [5].

In fact the ability of polymers to dissolve or even swell is usually determined by many factors [6]. The mechanism and growth of limited swelling of linear high-density polyethylene (LHDPE) in some industrial solvents were studied [7].

The equilibrium solvent uptake has been used to determine the cohesive energy density of a given polymer [7]. In their context the dynamic and equilibrium swelling behaviour of polystyrene microparticles cross-linked with divinyl benzene was investigated in methyl ethyl ketone and cyclohexane [8].

A general measurement theory for determining the diffusion coefficient “D”of small molecules in polymer matrices was made [9]. The theory was tested in the light of the results of water diffusion into polyacrylonitrile and poly (vinyl toluene). The diffusion coefficients determined with the general theory agreed well with the results achieved by using more complicated calculations. The diffusion and sorption of organic liquids through polymer membranes have also been studied [10]. The absorption and desorption of organic fluids in both amorphous and crystalline poly (Aryl-ether-ether-ketone) were investigated [11].

The present work is aimed to show the effect of different degrees of compression on the dielectric constant and the electrical conductivity of butyl rubber filled with different carbon black concentrations. Besides, it is used to investigate the swelling of these samples in benzene and kerosene.

Experimental

Sheets of butyl rubber (IIR) were prepared according to standard methods [12]. Appropriate samples in form of discs of area 0.78cm^2 and thickness of 0.3 cm were cut from these sheets. The dielectric constant was determined using a Phillips programmable automatic RCL bridge (Type PM6304) for samples containing different carbon black concentrations at constant frequency of 1 KH$_z$ and under different values of uniaxial stress by applying loads of 1,2,3,4,6Kgm respectively.

The D.C. electrical conductivity "σ" was obtained by measuring the current (I) flowing through the sample using digital picoammeter type Keithley 617. Figure (1) represents a schematic diagram for the cell used in measurement.

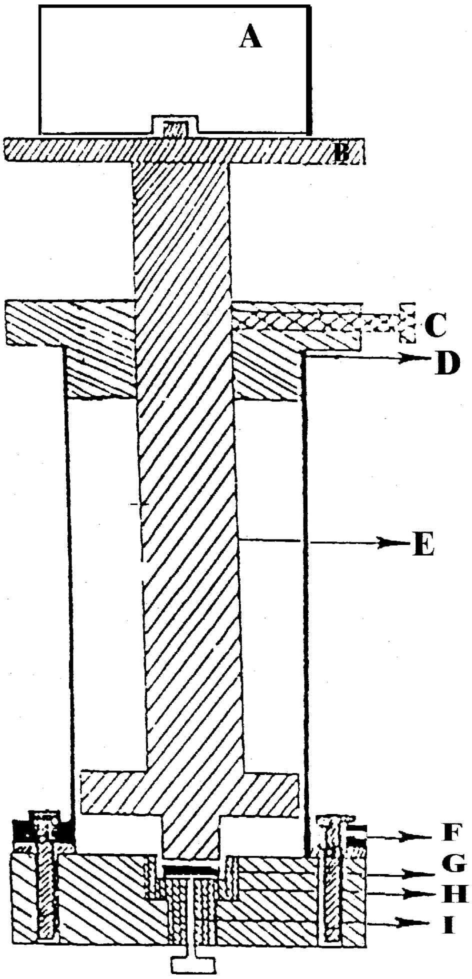

Fig. (1) :
Schematic diagram for the device used to carry out the electrical conductivity measurement for precompressed samples.

) Loads.
(B) Pan.
(C) Screw bolt (for changing the piston).
(D) Container.
(E) Piston terminal.
(F) Screw bolt.
(G) Specimen.
(H) Teflon gasket.
(I) Terminal.

Swelling measurements of the vulcanizates (IIR) were carried out using both kerosene and benzene as solvents. Square samples of side 0.5cm and 0.3cm thickness were cut from the rubber sheets. Each sample is weighted by a sensitive balance of least count of 10^{-4} gm. The test pieces were immersed in solvents, for different periods of time (15, 30, 60, ….min), wiped thoroughly and reweighed. It was found that, the equilibrium degree of swelling was attained after an immersion time of 24 hours. The degree of swelling was calculated according the relation [11]:-

$$Q = \frac{m - m_0}{m_0}$$

where m_o is the weight of the unswelled sample, and m is its weight after swelling in solvent.

Results and Discussion

One of the important features of polymers, is their ability to change their physical properties when exposed to mechanical stress. This has actually an inpart of their use in different technical applications. Figure (2) represents the load dependence of dielectric constant "ε"for butyl rubber loaded with different (HAF) carbon black concentrations (from 0 to 105 phr*).

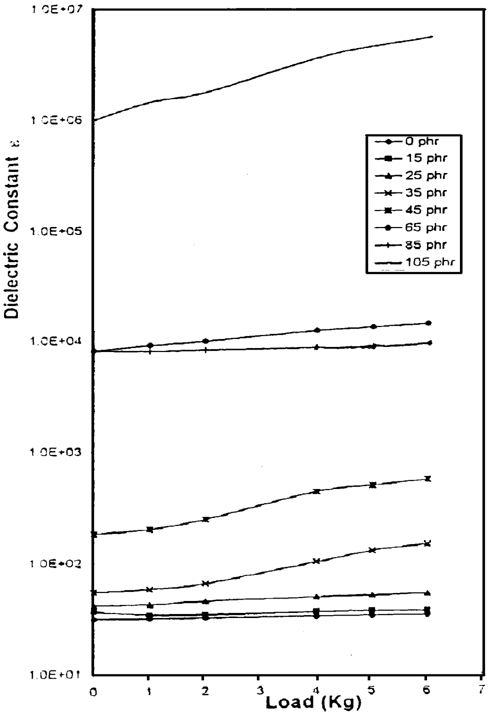

Fig. (2) : Load Dependence of dielectric constant for carbon black loaded Butyl rubber.

The behavior of the dielectric constant is determined to a great extent by the mode of dispersion of carbon black in the matrix. In fact, butyl rubber loaded with low concentration of carbon black (0-25 phr) have dielectric constant ε values which are nearly load - independent in the load range up to 6 kgm. This is probably because the carbon black dispersed in the polymer matrix as individual spherical particles which are at a large distances between each other. The small concentration of dispersed carbon black does not reveal the effect of space charge on the value of the dielectric constant. In the case of moderate concentration, however, (35 and 45phr) of HAF carbon black, there seems to be a contact between carbon particles, i.e. the beginning of formation of carbon black aggregates between rubber chains. This structure is liable to be affected by load, which tends to make the carbon particles come closer to each other, and enhance the space charge polarization. This in turn would raise the dielectric constant of butyl rubber. As the carbon black concentration gets higher (e.g. 65,85 phr), the structure becomes rich in carbon black aggregates separated by thin layer of rubber. This yields a high dielectric constant and slightly is affected by load again. Finally ε becomes completely load dependent when the carbon black content is 105 phr.

Figure (3) illustrates the dependence of dielectric constant of butyl rubber on the volume fraction of carbon black at low concentrations at different loads. The volume fractions are calculated by knowing the mass fraction of each component and its density. This dependence is appreciable affected by load and can be described by the relation

$$\varepsilon = \varepsilon_o \, (1 + \alpha_1 C + \alpha_2 C^2 + \ldots\ldots) ,$$

where ε_o is the dielectric constant of unfilled sample, α_1 and α_2 are constants, depending on the load used in measuring the dielectric constant and C is the volume fraction of carbon black.

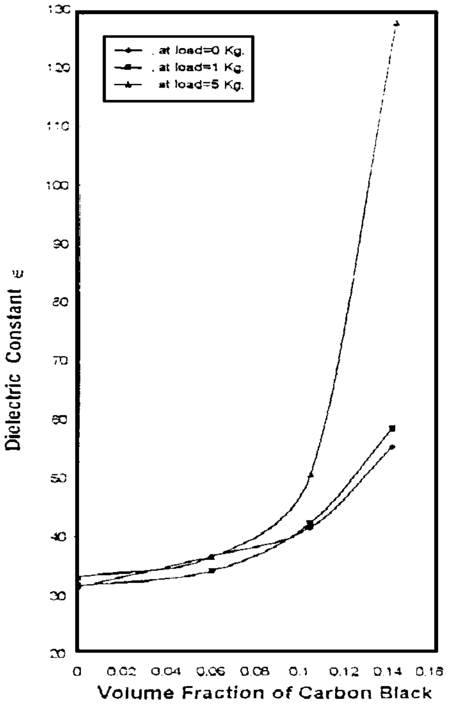

Fig.(3)

The dependence of dielectric constant on volume fraction of carbon black.

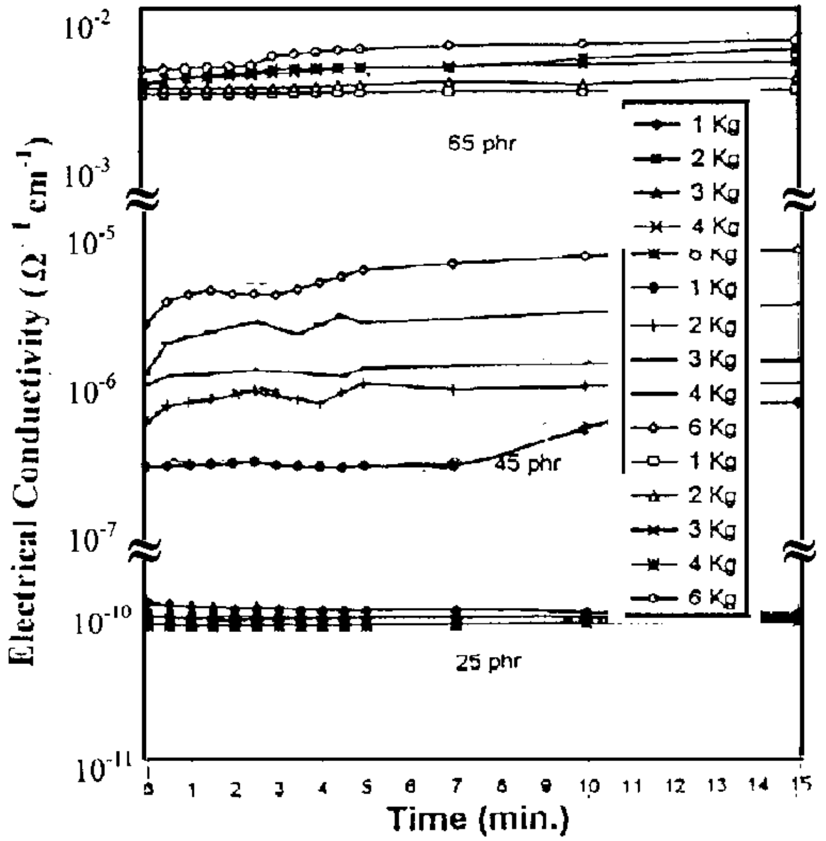

Fig. (4): The dependence of electrical conductivity on time for butyl rubber loaded with 25, 45 and 65 phr carbon black at different loads.

The time dependence of the electrical conductivity of carbon black loaded butyl rubber was studied under different selected loads as shown in figure (4). It is found that for the low and high concentrations, the loads did not affect the electrical conductivity, while for the moderate concentration (45 phr) a slight increase is observed with the increase of both load and time.

This is also evident in Fig. (5) which shows that the phase between dispersed and attached system is unstable and affected by load and time. The higher conductivity with the nearly high concentration of carbon black (~65phr) is due to the formation of physical or chemical cross-links between macromolecules through the carbon black aggregates. This can be established by measuring the cross-linking density, which is considered to be inversly proportional to the degree of swelling of rubber in some solvents. Figure (6,7) represent the time dependence of the degree of swelling for butyl rubber loaded with different concentration of carbon black in benzene and kerosene respectively. The degree of swelling increases progressively with time, especially at low concentration of carbon black, whence a sharp rise in “Q” appears at the early stage of swelling. This sharp value is smoothered as the carbon black increases and shifts to higher times. This could be explained in terms of the catastrophic rupture of the elastomer networks due to the increases of internal stress caused by the diffused liquid. i.e., the internal stress is high compared with the force between macromolecules. By increasing carbon black (HAF), which is considered as a high reinforcement filler, the formation of aggregates increases the force between macromolecules by forming a physical bond (adhesive) and resists the effect of internal stress of liquid, so such anomaly in “Q” % with (t ½) disappears at higher concentrations of carbon black. It is noticed from the two Figures (6 and 7) that, the value of the degree of swelling in kerosene is smaller than that in benzene. This is due to the high molecular weight of kerosene. Table(1) summarizes this effect and contains the calculated values of each of the penetration rate (p) , the diffusion coefficient (D) of solvent in carbon black loaded rubber and the molecular mass (M_c) by using the following formulae [13]:

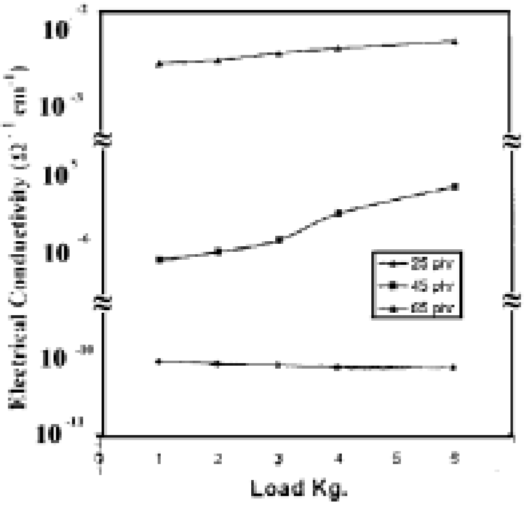

Fig.(5)
The dependence of electrical conductivity on carbon black concentration .

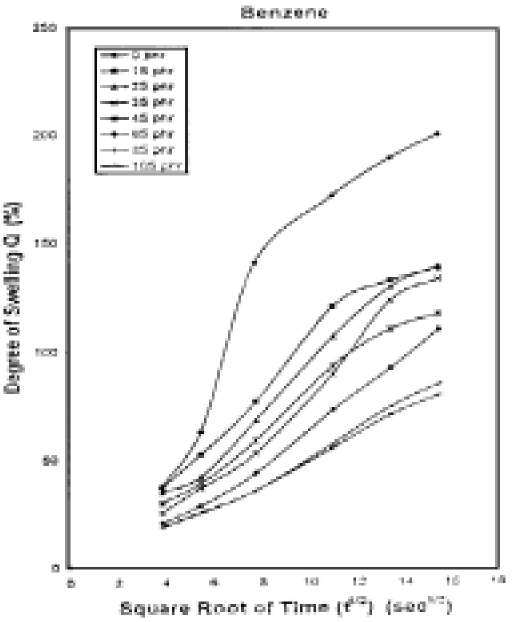

Fig.(6)
The dependence of swelling degree on carbon black concentration .

The penetration rate is calculated using the relation

$$p = \frac{d}{2Q_m}\frac{dQ}{dt^{\frac{1}{2}}}$$

where d is the thickness of the sample, Q_m is the maximum degree of swelling and Q is the swelling after time t.

The average diffusion coefficient can be calculated from the relation:-

$$D = \pi / 4 \ (P^2)$$

and the molecular mass M_C which is defined as the molecular weight of the segment between successive cross-links and is given by the relation:

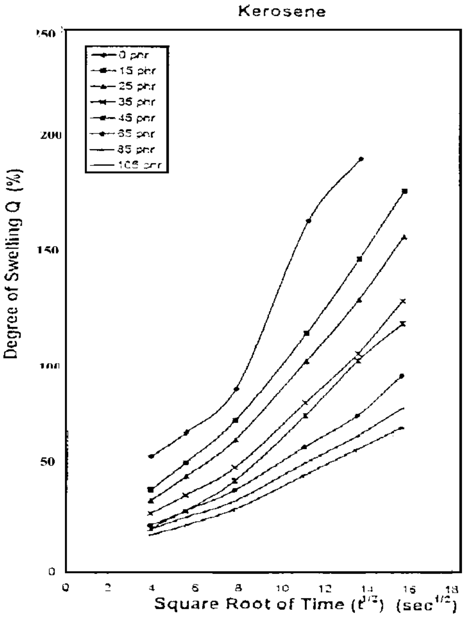

Fig.(7)
The dependence of degree of swelling on time for carbon black loaded butyl rubber in kerosene.

$$M_C = \frac{pRT}{G}$$

(G) is the elastic constant of rubber loaded with carbon black which is measured in previous work, [12] (ρ) is the density, (T) is the absolute temperature.

Table (1)

Values of the penetration rate P, the diffusion coefficient D and the molecular mass M_c for benzene and kerosene

Carbon Black Concentration	$P\times10^3$ Benzene	$P\times10^3$ Kerosene	$D\times10^5$ Benzene	$D\times10^5$ Kerosene	M_C
0	5.9	6.5	9.5	3.3	7389
15	5.9	4.4	8.63	1.5	5319.46
25	6.4	4.5	4.6	1.6	3256.53
35	5.8	3.8	4.6	1.13	2713.76
45	3.9	4.3	7.7	1.45	4711.72
65	8.6	3.9	5.5	1.19	3657.42
85	8.4	3.8	5.5	1.13	1620.6
105	8.4	3.6	5.8	1.62	1681.99

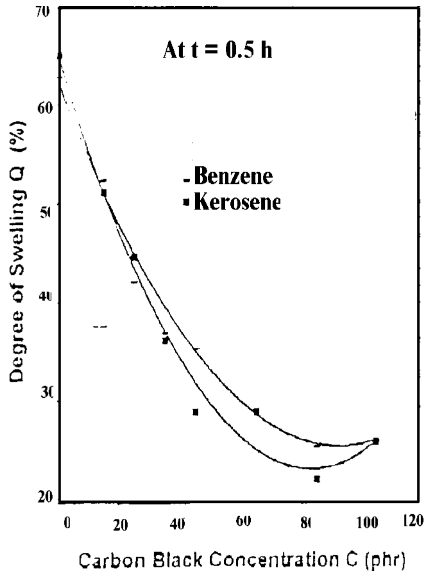

Fig.(8)
Degree of swelling after ½ hr.

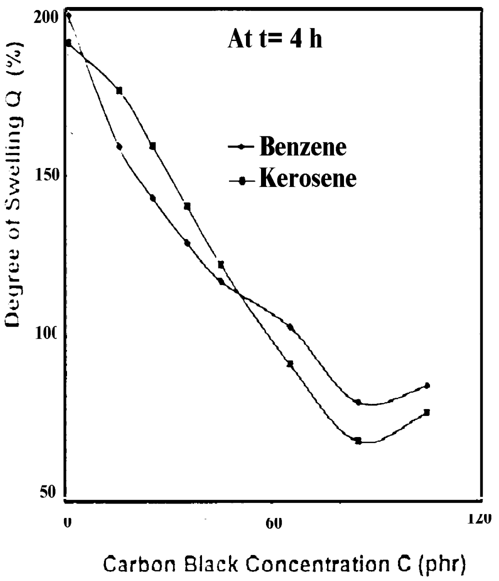

Fig.(9)
Degree of swelling after 4 hr.

From this table, we notice that, the molecular mass M_C of the polymer decreases as the carbon black content increases. This means that high degree of cross-linking is formed. Figures (8,9), which represent the dependence of the degree of swelling on carbon black concentrations in kerosene and benzene after half an hour and four hours are another confirmation of this result. It was noticed that the degree of swelling decreases as carbon black increases. This means that, the molecular weight between two successive cross-links decreases.

Conclusion

Combined measurements of electrical and physico-mechanical quantities are very instructive in understanding different mechanisms taking place when rubber articles are immersed in different solvents.

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