



AL-TAHADY UNIVERSITY
FACULTY OF SCIENCE
CHEMISTRY DEPARTMENT

**STUDY OF
PHYSICO-CHEMICAL AND PHYSICO-MECHANICAL
PROPERTIES OF
RUBBER MIXTURES LOADED WITH DIFFERENT
CONCENTRATIONS OF CARBON BLACK**

A thesis submitted in partial fulfilment for the requirements of
the degree of Master of Science in Chemistry

BY
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SIRTE – LIBYA
2006 - 2007

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التاريخ :

الموافق : 16 - 4 - 2007

الرقم الاشاري : 411263/ع

Faculty of Science

Department of Chemistry

Title of Thesis

*((Study of Physico-Chemical and Physico-Mechanical
Properties of Rubber Mixtures Loaded with Different
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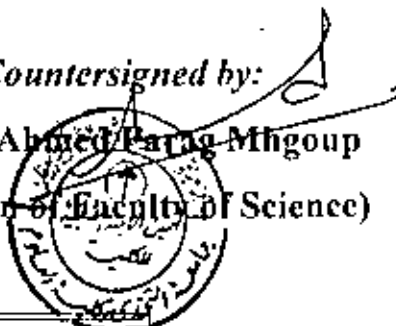
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Acknowledgment

First and foremost, my deep gratefulness and indebtedness is to ALLAH.

I wish to express my sincere appreciation to Prof. Dr. M. EL-MOBAYED, professor of Organic Chemistry, Faculty of Science, Al-Tahady University, Prof. Dr. H. M. OSMAN, professor of physics, Faculty of Science, Al-Tahady University, for suggesting the point of research, skillful technical assistance, useful suggestions, continuous encouragement, valuable interpretation, fruitful discussions during the progress and finishing of this research work.

I am grateful to the Al-Tahady University, Faculty of Science, and Chemistry Department; also all thanks and grateful to every one supported and advised me.

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List of Abbreviations and Symbols	
E	Young's modulus.
σ	nominal stress.
ϵ	nominal strain.
σ_R	tensile strength or The ultimate strength or rupture stress.
ϵ_R	strain at break or the percent ductility or rupture strain.
σ_y	yield stress.
ϵ_y	yield strain.
μ	Poisson's ratio
$\epsilon_{lat.}$	lateral strain
$\epsilon_{long.}$	longitudinal strain.
ΔV	the increase of volume.
V_0	initial volume.
E^*	the complex elastic modulus.
E'	the real part of the elastic modulus.
E''	the imaginary of the elastic modulus.
σ_T	true stress.
λ	the extension ratio.
ϵ_T	true strain.
G	rubbery modulus.
ϵ_0	the instantaneous strain.
$\epsilon_{el.}$	the elastic strain.
ϵ_u	unloading strain.
$\epsilon_{el,r}$	the elastic recoverable strain.
ϵ_r	the total recoverable strain.
ϵ_{irr}	the total irrecoverable strain.
E_1	conventional elastic modulus.
E_2	high elasticity modulus.
U	activation energy for steady state creep.
$\dot{\epsilon}_{st}$	strain rate at steady state creep.
q	activation volume for steady state creep.
η_2	viscosity for steady creep.
η_3	viscosity at plastic deformation (irrecoverable strain).
m	stress sensitivity parameter.
$\beta(t)$	memory function for recoverable deformation.
Δ	relaxation strength.
τ	retardation time for recoverable creep.
Δu	activation energy for recoverable creep.

List of Abbreviations and Symbols	
Q	the degree of swelling.
P	penetration rate.
M_e	the weight uptake of liquid at equilibrium.
M_t	the weight uptake of liquid after time t .
D	diffusion coefficient.
EPDM	Ethylene propylene diene monomer rubber.
NBR	Nitrile rubber.
HAF	High abrasion furnace carbon black.
TMTD	Tetramethylthiuram disulfide.
MBTS	2- Dibenzenothiazyle disulfide.
phr	Part per hundred parts of rubber by weight.
S_0	Sample of of (NBR/EPDM) blend free of HAF/black.
S_{10}	Sample of of (NBR/EPDM) blend loaded with 10 phr of HAF/black.
S_{30}	Sample of of (NBR/EPDM) blend loaded with 30 phr of HAF/black.
S_{40}	Sample of of (NBR/EPDM) blend loaded with 40 phr of HAF/black.
S_{50}	Sample of of (NBR/EPDM) blend loaded with 50 phr of HAF/black.
M_c	average molecular mass between two crosslinks.
ρ	density of rubber.
R	gas constant.
T	absolute temperature.
ν	degree of crosslinking (the number of gram moles of crosslinks per unit gram of rubber).
Q_e	degree of equilibrium swelling (measured after 24 hours).
Q_t	the degree of swelling after time t .
FEF	Fast Extruding Furnace.

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Summary

Polymer blending is one of the new approaches for the preparation of new materials from existing polymers. One obvious advantage is that it requires a lower cost relative to the production of new polymers. It is also possible to produce a range of materials with properties completely different from those of the blend constituents.

The blending of nitrile rubber (NBR) and ethylene propylene-diene monomer rubber (EPDM) was performed to achieve the best properties from each component. NBR has high resistance to swelling in oils and solvent but suffers from poor ozone resistance and heat aging properties. EPDM has good heat aging and ozone resistance (as its unsaturation sites are in the side chain and not in the backbone) but it possesses poor solvent resistance. Thus, the product of this blend will have excellent oil resistance, ozone resistance, heat resistance and mechanical strength. It could be used for the production of known rubber products requiring such properties, e.g. automotive brake hoses, automotive radiator hoses, motor mounts, transmission belts, conveyor belts, sheets and rolls.

The present study is concerned with NBR/EPDM blends loaded with different concentrations of carbon black; High Abrasion Furnace (HAF) N 330.

All test samples were prepared under the same conditions according to standard methods. The major goal of the study is to cover as far as possible some mechanical and physico-chemical behavior of the NBR/EPDM blends.

The relation between stress and strain gives a number of parameters such as rupture stress σ_R , rupture strain ϵ_R , Young's modulus E and the degree of crosslinking ν .

Creep and creep recovery relationships for some selected samples were inspected. It was found that, as the applied stress increases the instantaneous strain increases also at all HAF contents. The conventional elastic modulus, E_1 , high elasticity modulus, E_2 , and the viscosity for steady creep, η_2 , under different applied stresses increase with increase in carbon black concentration. Finally, useful parameters like activation volume, q , memory function, $\beta(t)$, the retardation time, τ , and relaxation strength Δ were deduced from the creep and creep recovery curves and study the effect of carbon black and/or applied stress on these parameters.

The time dependence of the degree of swelling in both gasoline and kerosene was analysed. The values of equilibrium swelling (Q_e) and the characteristic time (τ) were calculated. It was found that, both of Q_e and τ depend on the concentration of carbon black and type of solvent. The penetration rate, P , and consequently the diffusion coefficient, D , for some selected samples were calculated.

Chapter (1)

INTRODUCTION AND LITERATURE SURVEY

1.1 Introduction

Polymer blends have recently drawn considerable attention, due to the ease with which polymer properties can be modified to achieve characteristics that can not be achieved by a single polymer system. The most difficult task is the development of materials with a full set of desired properties. This has been achieved by selecting blend components in such a way that the principal advantages of the first polymer will compensate for deficiencies of the second one and vice versa⁽¹⁾.

In the following we present a brief overview of the properties and concepts that will be dealt with throughout the present work.

1.2 Polymer

Polymer is derived from the Greek poly and mer, meaning many and parts, respectively. Some scientists prefer to use the word macromolecule or large molecule, instead of polymer⁽²⁾. The difference between polymers, including plastics, fibers, and elastomers or rubbers, are determined primarily by the intermolecular and intramolecular forces between the molecules and within the individual molecule, respectively, and by the functional groups present.

One of the most significant parameters of polymers is their molecular mass, M , which is determined by the number of the repeating units, P , that makes up the macromolecule⁽³⁾:

$$M = M_0 P \quad (1.1)$$

Where M_0 is the molecular mass of the repeating unit, the parameter P is called the degree of polymerization, which may vary over a wide range, from a few units to 10^6 and more.

Polymers with high degree of polymerization ($P > 5000$) are called high polymers⁽⁴⁾. While those with lower degree of polymerization ($P < 5000$) are known as oligomers. Polymers consisting of identical monomers are called homopolymers, while those containing several types of monomeric units in their chains are known as copolymers or mixed polymers. Polymers are classified according to composition, origin, nature, formation, structure,etc. (4-6).

There are many reasons for using composite materials or blends rather than the simpler homogenous polymers⁽⁷⁾. Some of these reasons are: (1) increased stiffness, strength, and dimensional stability, (2) increased toughness or impact strength, (3) increased heat distortion temperature, (4) increased mechanical damping, (5) modified electrical properties, (6) reduced permeability to gases and liquids, and (7) reduced cost.

The properties of composite materials are determined by the properties of the component, the shape of the filler phase, the morphology of the system, and the nature of the interface between the phases.

Thus a great variety of properties can be obtained with composites just by alternation of one of these items. An important property of the interface that can greatly affect mechanical behavior is the strength of the adhesive band between phases.

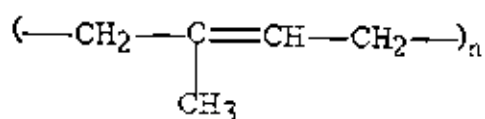
1.3 Rubber:

The original material of commerce known as rubber is obtained in the form of latex from the tree *hevea Braziliensis*⁽⁸⁾. The word rubber is derived from the ability of this material to remove marks from papers, to which attention was drawn by the chemist Priestly in 1770. In current usage the term rubber is not restricted to the original natural rubber (NR), regardless of its

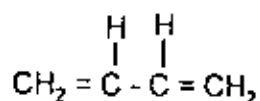
chemical constitution. The more modern term elastomers is sometimes employed in relation to synthetic materials having rubber-like properties, particularly when these are treated as a sub-class of a wider chemical group. Most synthetic rubbers are produced in two main stages; first, the production of the monomer(s), then the polymerization to form a rubber.

Rubbers^(4,8,9), as a high molecular weight polymers, have a lower temperature limit to their rubbery state. At the so called glass transition temperature (T_g) there is a fairly abrupt change to a glassy state. Materials in the class of polymers which are plastics, at normal temperature, become rubbery like as the temperature is raised above their (T_g). For this reason their (T_g) marks the upper temperature limit of their service properties, or their heat resistance.

Natural rubber (NR) is essentially a hydrocarbon, whose constitution was established by Faraday (1826) to be consistent with the formula $(C_5H_8)_n$ monomer, and has the following structure

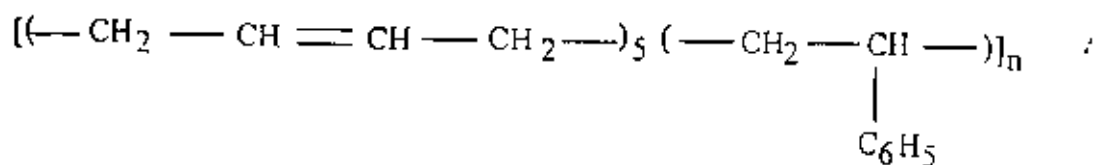


Butadiene rubber (BR) is now derived exclusively from petroleum fractionation of the products of cracking petroleum, which containing largely hydrocarbons of the butane and butene family. Butene is separated and catalytically dehydrogenated in the vapor phase to butadiene which has the formula

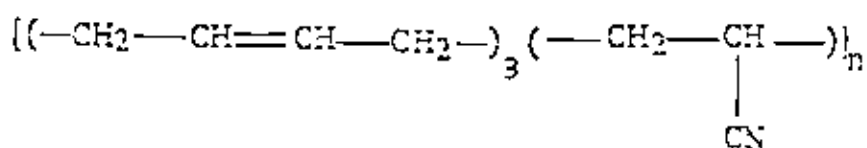


Styrene-butadiene rubber (SBR) is derived from butadiene. Its production begun in the United states during World War II. For many

mechanical goods SBR superior to NR and is preferentially used because of its easier processing and good quality and product. SBR is a random copolymer; i.e. a mixture of two monomers, butadiene and styrene, and has the formula

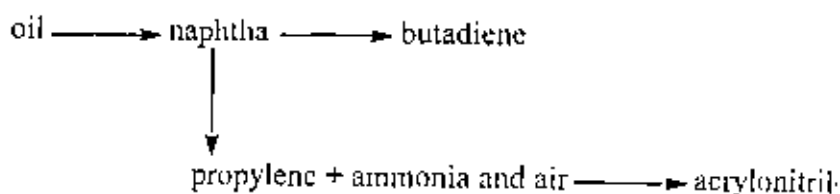


Nitrile rubbers (NBR) are polymers of butadiene and acrylonitrile, having the ratio of the two monomers similar to the ratio of butadiene to styrene in SBR; its formula is



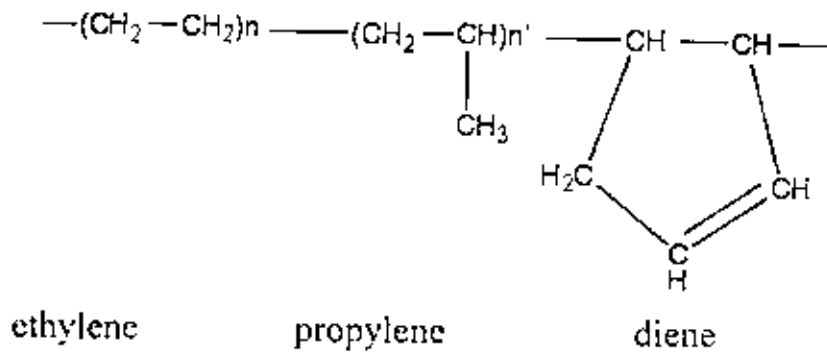
NBR is used for its oil resistance, low solubility, low swelling, and good tensile strength and abrasion resistance in gasoline or oils.

Basically, nitrile rubbers are manufactured by emulsion copolymerization of butadiene with acrylonitrile in processes similar to those used for other emulsion polymers, such as SBR⁽⁹⁾. The main raw materials required are the monomers butadiene and acrylonitrile. Both monomers may be synthesized from naphtha obtained from oil



Nitrile rubbers, suitably compounded, have a service temperature range of -50 to +1200 C° but temperatures as high as 1400 are frequently required. Whenever nitrile rubbers are used, a compromise between oil resistance and low-temperature properties is necessary.

Ethylene Propylene- Diene Monomer Rubber (EPDM) with the following chemical structure;



Where n and $n' = 10-20$

Ethylene-propylene rubbers and elastomers (also called EPDM and EPM) continue to be one of the most widely used and fastest growing synthetic rubbers having both specialty and general-purpose applications. Polymerization and catalyst technologies in use today provide the ability to design polymers to meet specific and demanding application and processing needs.

Ethylene-propylene rubbers use the same chemical building blocks or monomers as polyethylene (PE) and polypropylene (PP) thermoplastic polymers. These ethylene (C_2) and propylene (C_3) monomers are combined in a random manner to produce rubbery and stable polymers. A wide family of ethylene-propylene elastomers can be produced ranging from amorphous, non-crystalline to semi-crystalline structures depending on polymer composition and how the monomers are combined. These polymers are also produced in an exceptionally wide range of Mooney viscosities (or molecular weights).

The ethylene and propylene monomers combine to form a chemically saturated, stable polymer backbone providing excellent heat, oxidation, ozone

and weather aging. A third, non-conjugated diene monomer can be terpolymerized in a controlled manner to maintain a saturated backbone and place the reactive unsaturation in a side chain available for vulcanization or polymer modification chemistry. The terpolymers are referred to as EPDM (or ethylene-propylene-diene with "M" referring to the saturated backbone structure)⁽¹⁰⁾.

Ethylene-propylene rubbers are valuable for their excellent resistance to heat, oxidation, ozone and weather aging due to their stable, saturated polymer backbone structure. Properly pigmented black and non-black compounds are color stable. As non-polar elastomers, they have good electrical resistivity, as well as resistance to polar solvents, such as water, acids, alkalies, phosphate esters and many ketones and alcohols. Amorphous or low crystalline grades have excellent low temperature flexibility with glass transition points of about -60 C° . Heat aging resistance up to 130 C° can be obtained with properly selected sulfur acceleration systems and heat resistance at 160 C° can be obtained with peroxide cured compounds. Compression set resistance is good, particularly at high temperatures, if sulfur donor or peroxide cure systems are used. These polymers respond well to high filler and plasticiser loading, providing economical compounds. They can develop high tensile and tear properties, excellent abrasion resistance, as well as improved oil swell resistance and flame retardance⁽¹⁰⁾.

The blending of nitrile rubber (NBR) and ethylene propylene-diene monomer rubber (EPDM) was performed to achieve the best properties from each component. NBR has high resistance to swelling in oils and solvents but suffers from poor ozone resistance and heat aging properties^(11,12). EPDM has good heat aging and ozone resistance (as its unsaturation sites are in the side chain and not in the backbone) but it possesses poor solvent resistance^(13,14). The blend of such two polymers attracts the attentions of many

researchers to tailor a blend which withstands ozone, heat aging, oil and solvents swelling with desirable mechanical characteristics. Thus, the product of this blend will have excellent oil, ozone, heat resistance and mechanical strength. It could be used for the production of known rubber products requiring such properties, e.g. automotive brake hoses, automotive radiator hoses, motor mounts, transmission belts, conveyor belts, sheets and rolls.

1.4 Rubber Additives:

Additives are essential functional ingredients of polymers, and whenever possible, each should be used in optimum amounts for attainment of high quality products.

1.4.1 Fillers

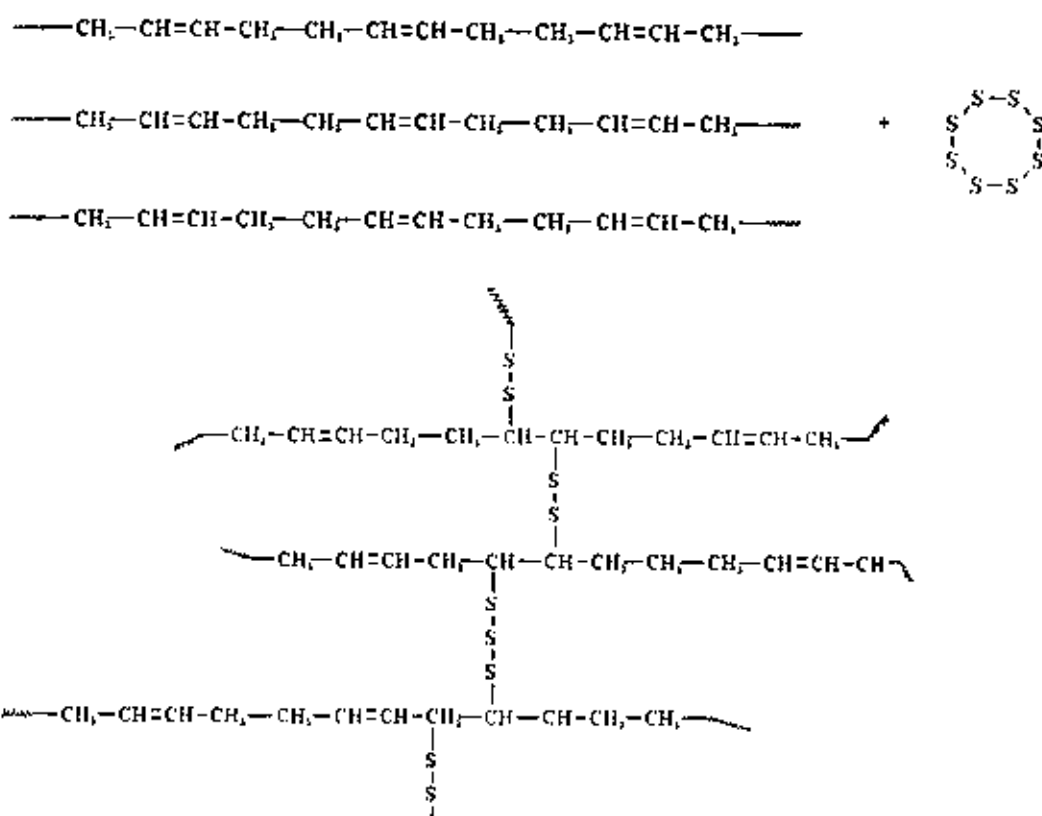
According to the American Society for Testing and Materials standard ASTM-D-833, filler is a relatively inert material added to a polymer to modify its strength, permanence, working properties or other qualities, or to lower costs.

Fillers may be black, like carbon black, or non-black. Calcium carbonate⁽¹⁵⁾ and oxide and barite (barium sulphate) used mainly to reduce cost. Antimony is a semi-reinforcing filler. Aluminum hydroxide, aluminum silicates, china clay, magnesium carbonate and titanium dioxide are used as a reinforcing filler to achieve high performance in non-black products.

In certain rubber articles, e.g. conveyor belting, textile rollers and spinning cots, and trolley wheels for use in hospitals, the build-up of static electricity is undesirable as an alternative to rubber compounded with conductive blacks, antistatic agents, which are frequently based on quaternary ammonium salts or ethylene oxide condensates, have been designed to assist in producing vulcanizates with low electrical resistance.

1.4.2 Vulcanizing Agents

many natural and synthetic rubbers are not in themselves thermosetting (materials that form three dimensional network). To form three dimensional network in them they are reacted with special vulcanizing agents, usually sulfur as shown.



Other vulcanizing agents are sulfur-bearing materials. Oxidizing systems, metallic oxides and polyamine without the chemical cross-linking reactions involving these agents; no improvement in physical properties of rubber mixtures can occur.

1.4.3 accelerators and Activators

the reaction between rubber and sulfur grows slowly⁽¹⁶⁾. The presence of accelerator increases the rate of cure, (reducing the time and / or the temperature of vulcanization), and this improves the physical properties of vulcanizates. Table (1.1) gives some indications of the improvement in properties of rubber compounds, by vulcanization.

Table (1.1): The improvement in properties of rubber compounds, by vulcanization.

Un-vulcanized material	Vulcanized material
Plastic Soft Low tensile strength Thermoplastic Tacky Non resistant to solvents Non resistant to oxidation	Elastic Hard High tensile strength Non thermoplastic Non tacky Resistant to solvents Resistant to oxidation

Zinc oxide and the fatty acids are vulcanization system activators⁽¹⁵⁾. These activators form a complex compound with the accelerator and thus aid obtaining the maximum benefits from an acceleration system by increasing vulcanization rate and improving the final properties of the products. Accelerators are classified and illustrated in table (1.2)

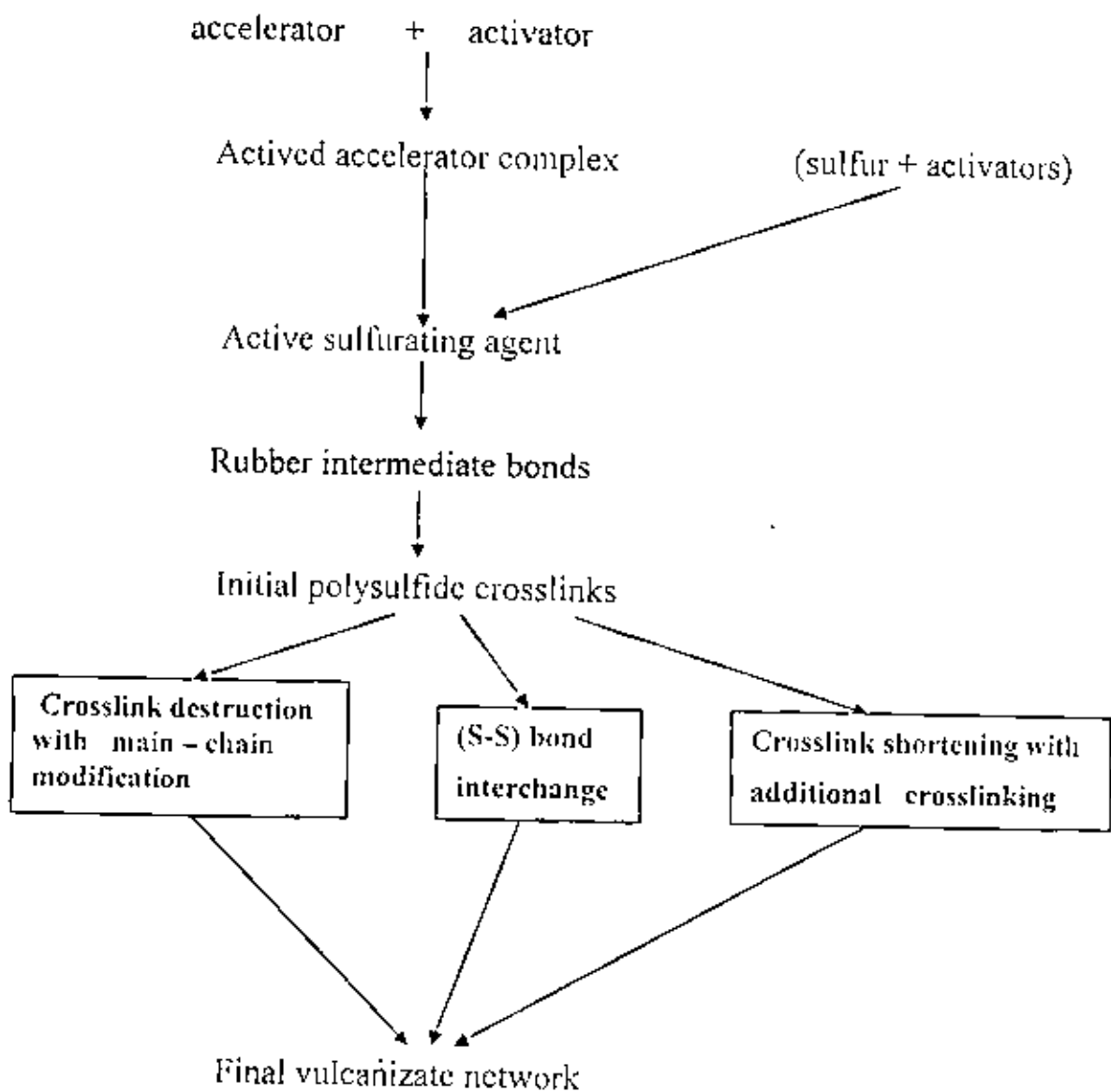
Table (1.2): Accelerators for sulfur vulcanization.

compound	abbreviation
2-Meracpto-benzothiazole	MBT
2-Dibenzothiazyle disulfide	MBTS
N-Cyclohexyl-benzothiazole-2-sulfinamide	CBS
N-t-Butylbenzo-thiazole-2-sulfinamide	TBBS
2-Morpholinothiobenzothiazole	MBS
N-Dicyclohexyl- benzothiazole-2-sulfinamide	DCBS
Tetramethylthiuram mono-sulfide	TMTM
Tetramethylthiuram disulfide	TMTD
Zinediethyldithiocarbamate	ZDES
Diphenyl-guanidine	DPG
Di-O-tolyguanidine	DOTG

1.4.4 Plasticizers

Plasticizer⁽⁶⁾ is a high molecular-weight solvent or low-melting solid which imparts flexibility to an amorphous polymer (improving its mechanical properties). Some types of plasticizers are paraffinic oil, dioctylphthalate, dihexylphthalate, dimethylphthalate and glycerol.

The schematic mechanism of crosslinking can be shown as follows ⁽¹⁷⁾ :



1.5 Mechanical Properties of Composites.

Polymer blends and composites are widely used in different technological purposes because of their high strength, elastic deformability, and ability to be strained repeatedly to high levels without destruction or permanent distortion. The mechanical behavior of rubber (polymers) is affected by many external and internal factors ⁽¹⁸⁾. The external factors are environmental factors including time, temperature, pressure and radiation that may cause changes in physical or chemical behavior. The internal variables are those, which produce changes in the chemical and physical structure of the polymer. Accordingly, changes of mechanical properties take place. Some of the important internal factors are chemical structure and composition, degree of crystallinity, polar nature of substituents, molecular weight diluents, such as water, monomer and plasticizer and the degree and extent of copolymerization.

For many uses, even vulcanized rubbers do not exhibit satisfactory tensile strength, modulus, hardness, abrasion resistance and tear resistance. These properties can be enhanced to suit several industrial applications by reinforcing with colloidal filler, such as carbon black, which has a large effect on the mechanical properties of rubber.

1.5.1 Tensile Strength of Rubber Composites.

The strength of a material is its ability to withstand under a load without breaking. Strength is usually characterized by the stress, which causes failure. This stress is called the fracture stress or tensile strength. The tensile strength of material is determined as a rule, from its stress-strain curve obtained under certain working conditions. It is the limiting stress or the ultimate stress at which the specimen fracture.

Tensile tests are the most widely used techniques for studying the mechanical properties of rubbers. It does not only give an indication of the strength of a material but also of its toughness. Usually, brittle materials have low toughness, while ductile materials are very tough because of their large elongation at break.

The mechanical properties of rubber vulcanizates are improved by the reinforcement with carbon black. The reinforcing carbon black inclusions increase the tensile strength of rubber by allowing the applied load to be shared amongst a group of chains⁽⁸⁾, thus decreasing a chance of a break to propagate.

In tensile test, the modulus of elasticity or Young's modulus (E) can be calculated from the slope of the initial linear portion of the stress-strain curve.

$$E = \frac{d\sigma}{d\varepsilon} \quad (1.2)$$

where σ is the applied stress and ε is the resulting strain.

1.5.2 Stress-Strain Relation

One of the most informative mechanical experiments of any materials is the determination of its stress-strain curve⁽¹⁹⁻²³⁾. This is usually done by continuously measuring the force developed as the sample is elongated at

constant rate of extension. The shape of the curve depends on the physical and phase states of polymer.

Figure (1.1) serves to define several useful quantities including modulus of elasticity, or stiffness, tensile strength σ_R , strain to break ε_R yield stress σ_y , and yield strain ε_y . The upper yield point is associated with the initiation

of a neck in the gauge length. The following region of low slope is associated with the process of cold drawing or the propagation of a necked region along the gauge length.

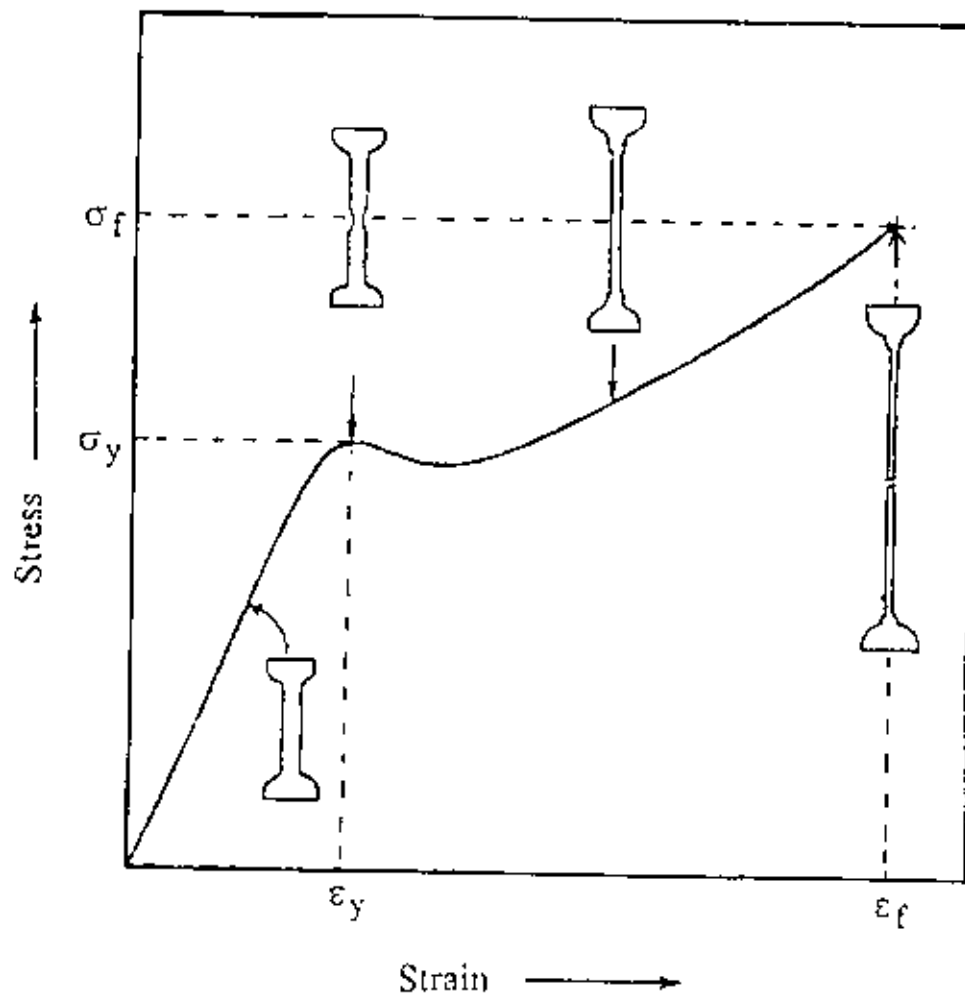


Fig. (1.1): Generalized tensile stress- strain curve for plastics⁽²⁴⁻²⁶⁾

Figure (1.2) is a typical stress-strain behavior for simple extension of an ideal rubber⁽²⁷⁻²⁹⁾. It can be seen that Hook's law is observed only for small strains, i.e., in the first section of the curve. In the second section minor changes of stress cause large strains (rubber-like deformation). The third section corresponding to a sharp increase in stress with insignificant changes in strain.

Films and sheets of elastomeric materials may have no discernible straight line portion of the stress-strain curve. Elastic modulus for these materials is usually defined as the stress divided by the value of the strain at 100 % elongation⁽³⁰⁾.

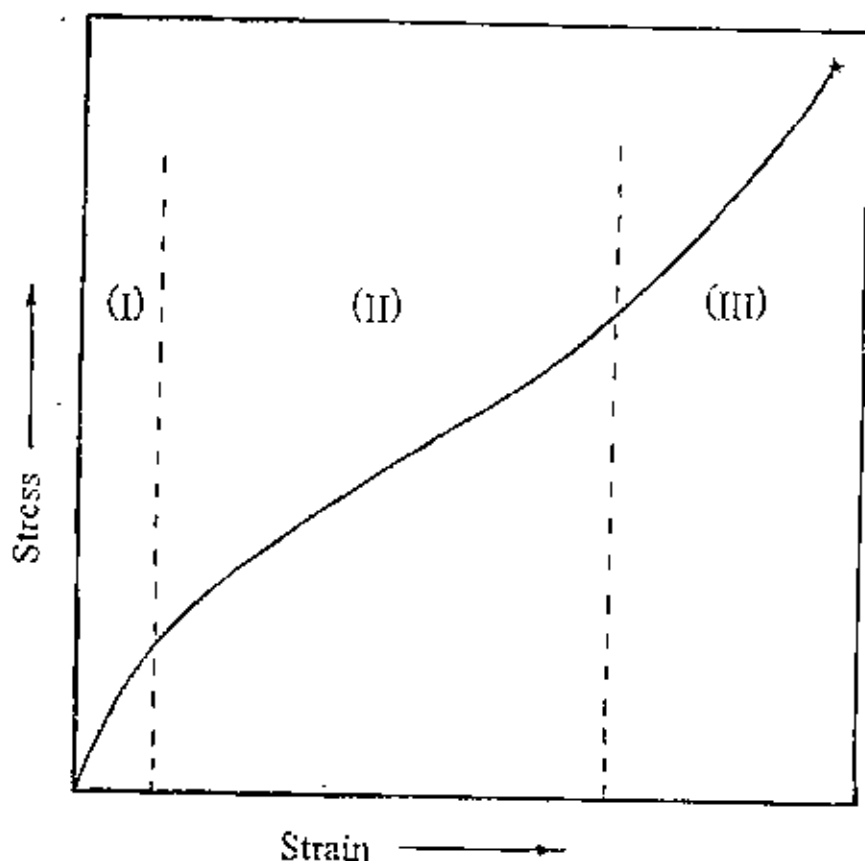


Fig. (1.2): Typical stress-strain curve for a rubber like polymer.

As an aid to the understanding of the shape of stress-strain curves, it is helpful to look at the curves of simple models. Four simple models are shown in Figure (1.3), along with their stress-strain curves for two rates of elongation. A spring has a constant modulus independent of the speed of testing, that is Hook's law holds, and the initial slope of the stress-strain curve is a constant proportional to the modulus. A dashpot on the other hand, has no modulus, but the force resisting motion is proportional to the speed of testing,

as shown in (case B) of Figure (1.3). The voigt or Kelvin model (case C) has a stress-strain curve given by.

$$\sigma = K\eta + E\varepsilon \quad (1.3)$$

where K is the speed of testing, $\frac{d\varepsilon}{dt}$ (strain rate), η is the viscosity of the dashpot. E is the modulus of the spring.

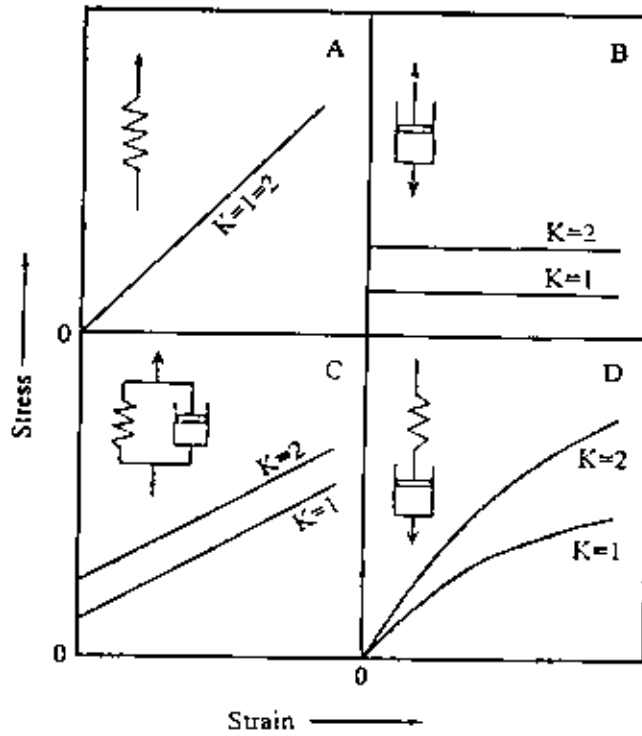


Fig. (1.3): The stress-strain behavior of simple models at two speeds of testing K_1 and $K_2=2K_1$. $K=d\varepsilon/dt$ ^(31,32)

The Maxwell model (case D) has a more complex stress-strain curve, which is given by.

$$\sigma = K\eta[1 - \exp(-E\varepsilon/K\eta)] \quad (1.4)$$

The initial slope gives the modulus which corresponds to spring stretching. At higher elongations the slope of the curves decreases, and their magnitude depends upon the speed of testing when the dashpot begins to relax out part of the stress. Eventually, the spring stops stretching and all

the elongation comes from the motion of dashpot. However, very brittle polymers have curves similar to spring (case A) up to the failure point.

Tensile stress-strain tests give another elastic constant called Poisson's ratio μ ⁽³¹⁾

$$\mu = \left| \frac{\epsilon_{\text{lat.}}}{\epsilon_{\text{long.}}} \right| = \frac{-\epsilon_{\text{lat.}}}{\epsilon_{\text{long.}}} \quad (1.5)$$

$\epsilon_{\text{lat.}}$ is the lateral strain in the width direction and $\epsilon_{\text{long.}}$ is the longitudinal strain.

Poisson's ratio is defined for very small elongations as the decrease in the width of the specimen per unit width divided by the length per unit length on the application of a tensile load. It can be shown that when Poisson's ratio is 0.5 for elastic material⁽³³⁾, the volume of the specimen remains constant while being stretched. This condition of constant volume holds for liquids and ideal rubbers. In general, there is an increase in volume, which is given by

$$\frac{\Delta V}{V_0} = (1 - 2\mu)\epsilon \quad (1.6)$$

where ΔV is the increase of the initial volume V_0 brought about by stretching the specimen.

In the case of viscoelastic bodies, the relation between the stress, which varies according to a sinusoidal law and the strain, may be written in the form:

$$\sigma = E^* \epsilon \quad (1.7)$$

where E^* is the complex elastic modulus⁽³⁴⁻³⁶⁾ defined by

$$E^* = E' + iE'' \quad (1.8)$$

The real part of the elastic complex modulus, $\text{Re } E^* = E'$, is known as the storage of dynamic modulus of elasticity which is a measure of the energy gained and lost by the volume element of the body per cycle, and the imaginary part, $\text{Im } E^* = E''$, is called the loss modulus which is a measure of the energy of elastic vibrations which is converted into heat per unit cycle of vibration under periodically varying stress.

1.5.3 The Kinetic Theory of Rubber Elasticity.

The classical kinetic theory of rubber elasticity was originally developed by Wall⁽³⁴⁾, Flory⁽³⁵⁾, James and Guth⁽³⁶⁾. The theory predicts the following relation in simple extension:

$$\sigma_T = NKT (\lambda^2 - \lambda^{-1}) \quad (1.9)$$

Where σ_T is the true stress, the force per unit area measured in the strained state, N is the number of effective plastic chains per unit volume, K is Boltzman's constant, T is the absolute temperature and λ is the extension ratio L / L_0 , L and L_0 being the present and initial length of the sample, respectively. The elasticity of different natural rubber and EPDM rubber has been studied in simple extension. The stress, σ_T has been plotted as a function $(\lambda^2 - \lambda^{-1})$ as suggested by the kinetic theory. A series of straight lines which do not pass through the origin have been obtained and consequently two parameters σ_0 and G have been introduced, these results allow Zang et al.⁽³⁶⁾ to hypothesize that the tensile stress is the sum of two terms: a Gaussian entropic contribution and further contribution reaching rapidly a steady state value σ_0 . The σ_0 term is found to depend only on the chemical nature of the rubber, whereas the value of G depends on the degree of the cross-linked and

seems to represent the rubbery modulus of the kinetic theory. They proposed the relation in the form

$$\sigma_T = \sigma_o + G(\lambda^2 - \lambda^{-1}) \quad (1.10)$$

1.5.4 Creep and Creep Recovery

The creep process can be studied by subjecting the specimen to a constant stress (σ) and observing the resulting time-dependent strain for relatively long periods of time. The total occurred deformation is a superposition of high elastic recoverable deformation (recoverable strain ϵ_r) and flow irrecoverable deformation (irrecoverable strain ϵ_{irr}) both of these develop in time. One can separate the two types of deformations by allowing the strained sample to relax fully after the removal of the applied load under specified conditions ensuring the highest rate of relaxation e.g., at elevated temperature.⁽⁶⁾ This removes the recoverable strain (ϵ_r), and hence, the residual deformation is the result only of the flow mechanism. Linear polymers in the high elastic state are capable of large irrecoverable strains. Proof of the separation of flow irrecoverable deformation and high elastic one is recovery of the initial structure of the material (the chains must acquire their initial deformation). If the structure of the material after relaxation is the same, as in the initial state while the shape of the sample is different, the residual deformation observed is irrecoverable. It should be noted that heating can be used to speed up relaxation only if it causes no chemical transformations (degradation or cross linking) in the polymer in question. Figure (1.4) represents the strain-time relationship for generalized mechanical model for creep combining elasticity, viscoelasticity and flow mechanisms⁽³⁴⁻³⁸⁾.

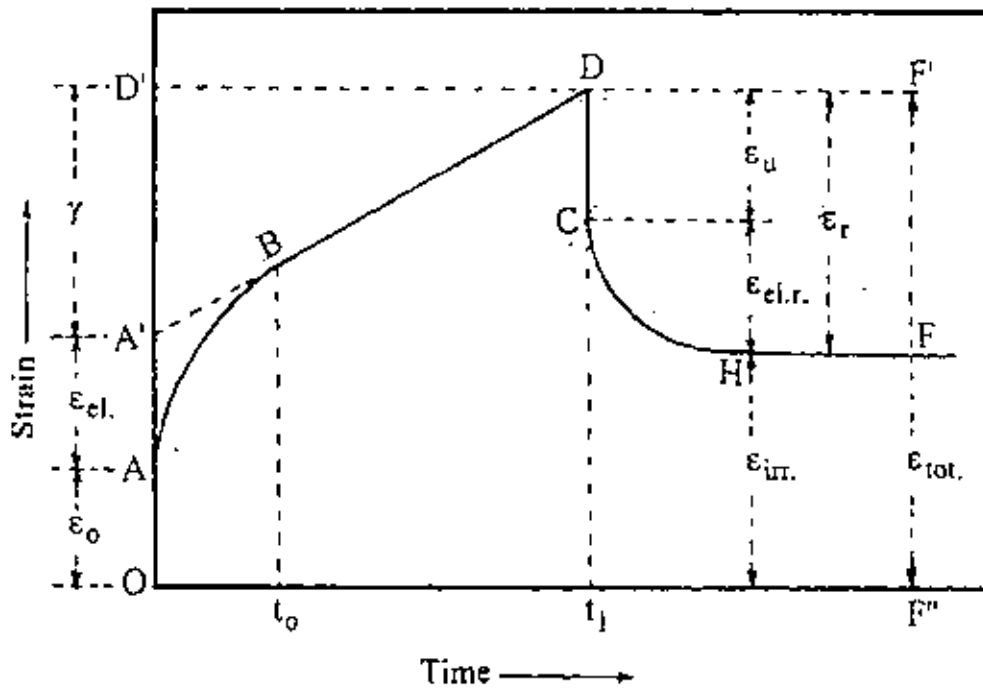


Fig. (1.4): Creep and creep recovery curve.

The section OABD represents the forward creep during loading.

DCF: represents the backward creep during unloading.

OA: is instantaneous strain (ϵ_0) which corresponds to elastic deformation and obeys Hook's law.

AB: characterizes the high elastic deformation developing simultaneously in time.

BD: straight line is associated only with steady flow creep, whose slope characterizes the change in the flow deformation per unit length in time.

OA': represents elastic deformation and is recoverable.

AA': represents high elastic deformation.

A'D': represents flow deformation (irrecoverable).

All the above is valid only if the high elastic strain has really reached its equilibrium value by the moment t_0 . Otherwise the relaxing elastic strain may

be mistaken for flow deformation. To avoid such a mistake it is necessary to analyze the unloading curve.

DC: corresponds instantaneous recoverable strain, it called unloading strain ϵ_u , it is time independent and equal to $OA = \epsilon_0$.

CH: is the elastic strain ($\epsilon_{el,t}$), it represents gradual time dependent decrease in the strain.

FF': is the total recoverable strain ϵ_r

FF'': is the total irrecoverable strain ϵ_{irr} .

Creep test gives extremely important practical information, at the same time, gives useful data to one interested in the theory of the mechanical properties of materials where it must sustain loads for long times. So the creep test must be performed at different parameters such as different temperatures, stress, etc., to get good information about the effect of these parameters on the material properties. One can deduce many useful parameters from creep curve as:

1- Conventional elastic modulus, E_1 ⁽⁶⁾

$$E_1 = \frac{\sigma}{\epsilon} \quad (1.11)$$

2- High elasticity modulus, E_2 ⁽³¹⁾

$$E_2 = \frac{\sigma}{\epsilon_{el}} \quad (1.12)$$

3- Activation energy for steady state creep, U ⁽³⁸⁾

$$\dot{\epsilon}_s = A \exp \left[-\frac{(U - q\sigma)}{kT} \right] \quad (1.13)$$

4- Activation volume for steady state creep, q ⁽³⁸⁾

5- Viscosity η_2 for steady creep ⁽⁶⁾

$$\eta_2 = \frac{\sigma}{(d\epsilon/dt)} \quad (1.14)$$

6- Viscosity η_3 at plastic deformation (irrecoverable strain) ⁽³¹⁾

$$\eta_2 = \frac{\sigma}{\epsilon_{irr}} t_1 \quad (1.15)$$

7- Stress sensitivity $m^{(39)}$

$$m = \left(\frac{\partial \ln \dot{\epsilon}_s}{\partial \ln \sigma} \right) \quad (1.16)$$

8- Memory function for recoverable deformation $\beta(t)^{(40)}$

$$\beta(t) = \frac{\dot{\epsilon}_s}{\epsilon_{elr}} \quad (1.17)$$

9- Relaxation strength $\Delta^{(41)}$

$$\Delta = \frac{\epsilon_{elr}}{\epsilon_r} \quad (1.18)$$

10- Retardation time for recoverable creep $\tau^{(6)}$

$$\epsilon_{elr} = A \exp \left(-\frac{t}{\tau} \right) \quad (1.19)$$

11- Activation energy for recoverable creep $\Delta u^{(6)}$

$$\tau = \tau_0 \exp \left(-\frac{\Delta u}{kT} \right) \quad (1.20)$$

1.6 Swelling:

The interaction of different solvents with polymeric materials is known as swelling. From the swelling process and its kinetics one can estimate the degree of crosslinking of a given polymer.

The degree of swelling of any polymer can be determined either by gravimetric or volumetric methods. In the case of gravimetric method, the degree of swelling $Q\%$ is given by:

$$Q\% = \frac{m - m_s}{m_s} \times 100 \quad (1.21)$$

where, m_s = weight of the dry polymer sample

m = weight of the swollen polymer sample.

The ability of polymers to dissolve or swell is determined by many factors such as ⁽⁶⁾:

- 1. Chemical nature of a polymer and solvent:** Swelling of non-crystalline polymers depends on the chemical composition of polymeric chain and also the properties of molecules of solvent, specially its polarity. If the polarity of polymeric chain is comparable with that of molecules of solvent, then the energy of interaction between the different molecules will be the same, thus the swelling process occurs. Conversely, if there is large difference between the polarity of both polymer and solvent molecules, there is no swelling appears.
- 2. Molecular mass of polymers:** The ability of polymers to swell decreases with increasing the molecular mass of polymers.
- 3. Flexibility of polymeric chain:** The mechanism of dissolve or swell of a polymer consists of two processes. Firstly, separation of the long polymeric chains from each other, secondly, penetration of these chains in between the molecules of solvent. These two processes depend upon the flexibility of polymeric chains.
- 4. Chemical composition of polymers:** The chemical composition differs from polymer to another due to the preparation conditions. The ability of these different polymers to swell in a solvent differs also due to presence of different effective groups such as ONO_2 , $-\text{OH}$, OCOCH_3 , etc.
- 5. Crystalline structure of polymers:** The ability of crystalline polymers to swell with a solvent is less than that of on-crystalline ones.
- 6. Chemical crosslinks:** The degree of swelling of a polymer in a solvent decreases with increasing the crosslinking density.

The diffusion theory in elastomers is based^(42,43) on the assumption that swelling commences by sorption of liquid in the surface of the sample to a certain concentration equal to that of the whole sample at equilibrium; then the swelling proceeds by increasing the depth of the swollen layers at a penetration rate, P ⁽⁴⁴⁻⁴⁶⁾ given by the equation.

$$P = \left(\frac{S}{2M_e} \right) \frac{dM_t}{dt^{1/2}} \quad (1.22)$$

where S is the thickness of the sample, M_e , M_t are the weight uptake of liquid at equilibrium and after time t , respectively.

The relation between the average diffusion coefficient, D , and the penetration rate, P , is expressed as⁽⁴³⁾.

$$D = \frac{\pi \cdot P^2}{4} \quad (1.23)$$

1.7 Literature Survey.

Porter⁽⁴⁷⁾ had pointed out that the presence of HAF black in the vulcanized rubber increases the yield of cross-links. Factors which affect the mechanical and physico-mechanical properties of an isobutylene-isoprene rubber (IIR) loaded with carbon black were studied by A. Abo-Hashem et al⁽⁴⁸⁾. The effect of carbon concentration and time of vulcanization on the elastic modulus, E , and the tensile strength of isobutylene-isoprene rubber (IIR) loaded with HAF carbon black have been investigated. It has been found that there is an optimum concentration at which modulus and strength attain their maximum values.

The physical and mechanical properties of crosslinked (IIR) elastomers blended with (NR,SBR,EPDM) rubber are significantly increased their aging performance and ozone resistance, but deteriorated some physical properties

as tensile strength, tear strength, elongation, compression set, maximum rheometric torque as observed by Banerjee et al⁽⁴⁹⁾. These properties varied according to the composition of rubber blends.

Bhowmick et al⁽⁵⁰⁾ measured the bond strength between natural rubber (NR) and each of ethylene-propylene-diene rubber (EPDM), Styrene-Butadiene Rubber - (SBR) and nitrile butadiene rubber (NBR) arising through vulcanization, and between (NBR) and SBR with reference to variation in the vulcanizing systems. They found that, the tensile strength of the blends decreases with increasing the incorporated component having lower tensile strength. The modulus and elongation at break follow the same trend.

The stress-strain measurements were carried out by Sobhy⁽⁵¹⁾ on ternary rubber vulcanizates. It has been found that natural rubber (NR) and Styrene Butadiene Rubber (SBR) are more sensitive to the vulcanizates agents than the butyl rubber (IIR). The molecular theories of rubber elasticity were used to discuss the obtained results. The Mooney- Rivlin relationship was used to describe the behavior of the ternary rubber matrix. The constants C_1 and C_2 have been calculated by use of the strain-amplification factor and the total crosslink density of the ternary rubber carbon black systems has been investigated.

Akovali et al⁽⁵²⁾ checked the limits of applicability of plasma surface modification of carbon black to be used in the tire manufacturing industry. For this purpose, RF range cold plasma has been utilized in Styrene or Butadiene atmospheres. Tensile strength and percent elongations of vulcanizates are found to respond differently if modified fillers are used as compared with those prepared by the unmodified fillers. Glass transition temperature of vulcanizates is found to correlate well with the results of mechanical properties.

Fahim⁽⁵³⁾ studied the effect of variation of PVC content on the elastic behavior of SBR-PVC conductive blends by carrying out equilibrium stress-strain measurements. The mechanical properties have been improved by addition of PVC weight fraction owing to the good interaction between the HAF carbon black filler and the SBR- PVC matrix. The Mooney-Rivlin relation was used to elucidate the behavior of the rubber - polymer blend and the constants C_1 and C_2 have been calculated by the use of the strain-amplification factor. He studied the dependence of these constants on the PVC concentration.

Abu-Abdeen⁽⁵⁴⁾ studied the degradation of the mechanical properties of composite of Styrene Butadiene Rubber (SBR) blended with natural rubber (NR) loaded with 40 phr of high Abrasion furnace (HAF) carbon black and loaded with different concentration of paraffin wax. From the Stress-Strain curves, Young's modulus was found to decrease with increasing the amount of added paraffin wax. The modified Mooney-Revlin equation was used to calculate the parameters C_1 , and C_2 . A plot between the true tensile stress as a function of $(\lambda^2 - \lambda^{-1})$ (λ , extension ratio) was used to calculate two parameters σ_e and G and then both the average molecular weight between crosslinks and the number of effective plastic chains per unit volume were also calculated.

Choi-sung-scen⁽⁵⁵⁾ observed an improvement of the properties of silica-filled Styrene Butadiene Rubber (SBR) compounds by using acrylonitrile-Butadiene Rubber (NBR). Viscosities and bound rubber contents of the compounds became lower by adding NBR to the compound. Cure characteristics of the compounds were improved by adding NBR. Physical properties such as modulus of elasticity, tensile strength, heat buildup, abrasion and crack resistance were also improved by adding NBR. Both wet

traction and rolling resistance of the vulcanizates containing NBR were better than those of the vulcanizates without NBR. The NBR effects in the silica-filled SBR compounds were compared with the carbon black filled compound.

Kumar-kamal et al.⁽⁵⁶⁾ found the improvement of mechanical properties and aging behavior of styrene-butadiene rubber (SBR) vulcanized by addition vinyl tri ethoxy silane (VTEOS) in range 0 to 2.73phr to SBR vulcanizates. The VTEOS increases, the fatigue - to failure (FTF) cycles of the vulcanizates and shows improvement of the other mechanical properties namely tensile, tear, compression, resilience and hardness at around 0.5 to 1 phr of VTEOS. Finally VTEOS plays the roles of coupling agent and softener.

Essawy et al.⁽⁵⁷⁾ used montmorillonite as reinforcing and compatibilizing filler for NBR/SBR rubber blend. Both the reinforcing and compatibilizing performance of the filler were investigated using rheometric measurements, physico-mechanical properties, scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). There was a remarkable decrease in the optimum cure time (t_{c90}) and the scorch time (t_{s2}), which was associated with an increase in the cure rate index (CRI), with filler loading up to 20 phr in the different blend ratios. The stress at yield was 2.5-5 times higher in the case of the filled blends, also the strain at both yield and rupture increased with the use of the filler for the different blend compositions, while the resistance to swelling in toluene became higher. SEM photographs show that the filler is located at the interface between the different polymers which induces compatibilization in the immiscible blends. DSC scans of the filled blends showed shifts in the glass transition temperatures T_g which can be attributed to the increased strength at the interface.

Creep relaxation in carbon black loaded NBR-Neoprene composite was studied by Fahim et al.⁽⁵⁸⁾. A four-element model has been tested to account

for the creep relaxation in a technological material composed of a common rubber and different ingredients. Interesting results have been obtained. A kink was noticed in temperature dependence of several parameters at about 353 K. All the obtained data are discussed within the frame of the above mentioned model.

Southern and Thomas⁽⁵⁹⁾ Studied the effect of constraints on the equilibrium swelling of rubber vulcanizates. The results showed that when a rubber vulcanizate is immersed in a solvent, the liquid diffuses into the bulk of rubber and the penetration rate depends on the type of solvent.

A mathematical model based on the Flory-Huggins interaction parameters was developed⁽⁶⁰⁾ to predict the behavior of vulcanizate-solvent systems at low and moderate degrees of swelling taking into account solvent adsorption on filler surfaces. Experimental calculations of the equilibrium sorption capacities of chalk kaolin, and aerosil in butadiene rubber, EPDM rubber, silicone rubber, and nitrile rubber vulcanizates showed that the contribution of filler to the sorption capacity of vulcanizates decreased with decreasing rubber polarity. The contribution of aerosil to solvent sorption by vulcanizates was significantly higher than that of chalk or kaolin.

Wolf et al⁽⁶¹⁾ studied the absorption and swelling of poly (ethyl-ether-ketone) PEEK in toluene in the temperature range (307 - 368 K). They observed that the rate of penetration of toluene into PEEK depend on temperature and crystallinity, and that small change in crystallinity may lead to large variation of the penetration rate.

Alex et al⁽⁶²⁾ investigated the swelling of self-vulcanizable ternary rubbers (epoxidized natural rubber, carboxylated nitrile and polychloroprene rubber) blend ratio and fillers in solvent properties. They used Ellis and Welding method to calculate the volume fraction of rubber in the swollen

vulcanizate and concluded that the crosslink density and physical properties depend on blend ratio and the used filler.

The properties and swelling characteristics of crosslinked poly (vinyl alcohol) / chitosan blend membrane were studied by Kim et al⁽⁶³⁾. The results indicated that crosslinking reduces the swelling capacity of the membrane due to the discounted ability of hydrogen bonding between water molecules and hydroxyl and amino groups in PVA and chitosan blend.

The maximum degree of swelling of polymers in liquid is the same as that in vapour but the rate of swelling depends on the solvent. When a crosslinked polymer is brought into contact with a solvent, the network absorbs a certain amount of liquid which depends strongly on the molecular weight of this liquid and the degree of cross-links⁽⁶⁴⁻⁶⁷⁾.

Nasr et al⁽⁶⁸⁾ studied the penetration of kerosene into carbon black loaded SBR vulcanizates. They observed that the penetration rate, P depends on the type and concentration of carbon black. It was also found that the penetration rate decreases with FEF (Fast Extruding Furnace) carbon black concentration due to the formation of carbon aggregations in SBR matrix.

1.8 Aim of This Work

The aim of this work is to carry out systematic study on NBR/EPDM blends loaded with carbon black. The effect of carbon black on the mechanical and physico-chemical properties is considered. Stress- strain and creep measurements are carried out to follow up the variation of mechanical properties. Swelling in different solvents, gasoline and kerosene, are used to study the diffusion and penetration of the solvent. Finally, a correlation between the studied properties is tried.

Chapter (2)

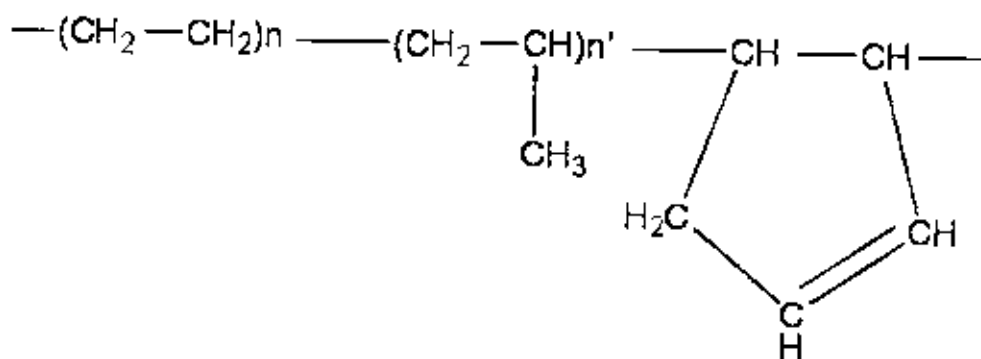
EXPERIMENTAL

2.1. Materials Used:

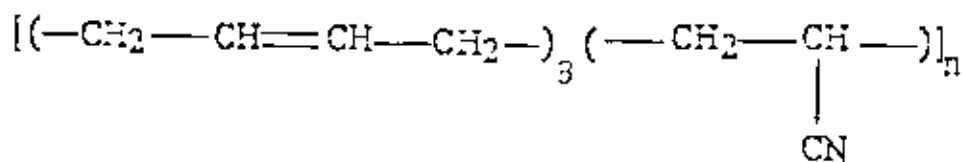
The materials used are:

2.1.1. Rubber:

- Ethylene propylene diene monomer rubber (EPDM): Mooney viscosity (ML 14) at 125 C°, 57; specific gravity 0.85; ethylene content 68 per cent. with the following chemical structure:



- Nitrile rubber (NBR): acrylonitrile content 33 per cent, Mooney viscosity at 100 C°, 45; specific gravity 1.17; ash content 0.5 %. The chemical structure of (NBR) is:



2.1.2. Fillers

High abrasion furnace carbon black, N-330 (HAF): Black granulated powder has a particle size of 40nm and specific gravity 1.78-1.82.

2.1.3. Activator

- Zinc oxide: fine powder; purity 99 % ; specific gravity 5.6.
- Stearic acid: melting point 67-69 C°; specific gravity 0.838.

2.1.4. Accelerators

- Tetramethylthiuram disulfide (TMTD).
- 2- Dibenzothiazyle disulfide (MBTS).

2.1.5. Vulcanizing agent

• Sulphur: Pale yellow powder of sulphur element; purity 99.9 %; melting point 1128 C° ; specific gravity 2.04-2.06.

All rubber ingredients are supplied by Transport and Engineering Company (TRENCO), Alexandria, Egypt .

2.2. Preparation of the Samples:

The rubber blends were prepared on a two rolls mill of 300 mm length, 170 mm diameter with speed of slow roll 18 r.p.m. and gear ratio 1.4. The prepared compounded rubber was left for at least 24 hour before vulcanization. The vulcanization process was conducted at $162\pm 1\text{ C}^{\circ}$ under a pressure of 40 kg/cm^2 for 20 min. The test materials have the compositions shown in Table (2.1).

They were prepared by using the facilities of the Transport and Engineering (Rubber Manufacturing) Company, Alexandria, Egypt.

Table (2.1): Composition of the test samples.

Samples Ingredients * (phr)	S ₀	S ₁₀	S ₃₀	S ₄₀	S ₅₀
<i>NBR / EPDM</i>	50/50	50/50	50/50	50/50	50/50
<i>Stearic acid</i>	1	1	1	1	1
<i>Zinc oxide</i>	5	5	5	5	5
<i>Processing oil</i>	10	10	10	10	10
<i>HAF/black</i>	0	10	30	40	50
<i>MBTS</i>	1.5	1.5	1.5	1.5	1.5
<i>TMTD</i>	1	1	1	1	1
<i>Sulphur</i>	2.5	2.5	2.5	2.5	2.5

* (phr): Part per hundred parts of rubber by weight.

2.3. Measurements

2.3.1 Mechanical Measurements:

The Sample Shape

Dumbbell shaped samples were cut from the vulcanized sheets by a fine edge steel die of constant width (5mm). The thickness of the test sample was determined by using a dial gauge.

The Apparatus

The apparatus used in stress-strain measurements is shown in Figure (2.1). The samples were stretched with different load. The corresponding

elongation was recorded continuously with constant stress rate throughout the extension until rupture of the samples took place.

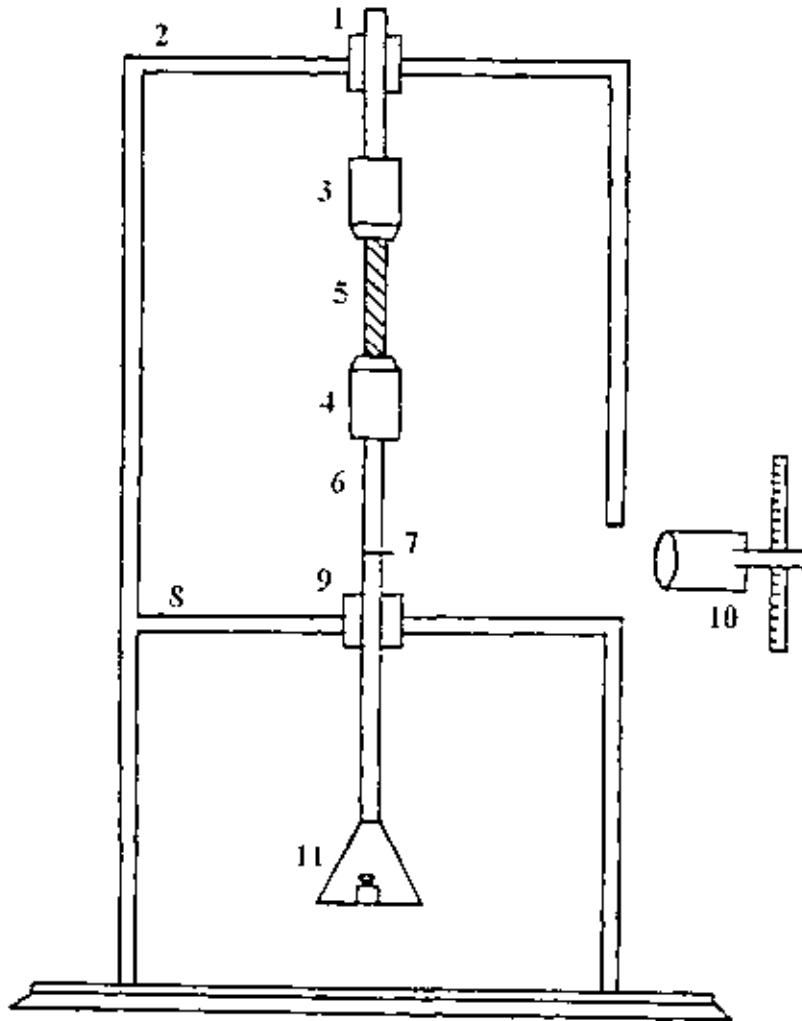


Fig. (2.1): Schematic diagram for stress-strain and tensile creep apparatus.

- | | |
|----------------------------|---------------------------|
| 1-Screw to fix upper grip. | 2-Stable frame |
| 3-Upper grip | 4-Lower grip |
| 5-Test specimen. | 6-Aluminium rod. |
| 7-Pointer. | 8-Stable shelf. |
| 9-Screw to fix lower grip. | 10-Travelling microscope. |
| 11-Pan. | |

By using the dimensions of samples the stress and strain were calculated. From these data, the true stress (σ_T) and true strain (ϵ_T) were calculated as follows⁽⁶⁹⁾.

$$\lambda = L / L_0 \quad (2.1)$$

$$\sigma = F / A_0 \quad (2.2)$$

$$\epsilon_T = \ln(\lambda) \quad (2.3)$$

$$\sigma_T = \sigma \lambda \quad (2.4)$$

where L_0 , L : are the lengths of undeformed and deformed samples, respectively, λ is the extension ratio, F is the force, σ is nominal stress, A_0 area of unstrained sample, σ_T true stress and ϵ_T true strain.

From stress - strain diagrams, we can deduce many useful parameters such as ⁽⁷⁰⁾:

- i- Young's modulus (E)
- ii- The ultimate strength or the rupture stress (σ_R)
- iii- The percent ductility or the rupture strain (ϵ_R).

2.3.2. Swelling Measurements

The test samples in the form of discs of radius 0.5 cm and thickness of about 0.1cm were weighed by using a sensitive balance (10^{-5} gm) and then inserted in stoppered-glass bottles containing the solvent, gasoline or kerosene. The samples were removed from the solvent at time intervals (15, 30,50,min.). The excess solvent on the surface of the test samples was removed by blotting with filter paper then the samples were weighed again to calculate the degree of swelling using equation (1.21).

Chapter (3)

RESULTS AND DISCUSSION

3.1. Static Mechanical Properties

(i) Stress-strain behavior :

The true stress-true strain characteristics of (NBR/EPDM/HAF) composites were measured and the results obtained are listed in table (3.1)

Table (3.1): The true stress-true strain characteristics of (NBR/EPDM/HAF) composites.

0(phr)				10 (phr)			
ϵ ($\Delta L/L$) (%)	ϵ_T (%)	σ (MPa)	σ_T (MPa)	ϵ (%)	ϵ_T (%)	σ (MPa)	σ_T (MPa)
0	0	0	0	0	0	0	0
40	33.65	0.10	0.14	20	18.23	0.10	0.12
60	47.00	0.20	0.31	40	33.65	0.20	0.27
80	58.78	0.29	0.53	48	39.20	0.29	0.44
120	78.85	0.39	0.86	60	47.00	0.39	0.63
160	95.55	0.49	1.27	80	58.78	0.49	0.88
270	130.83	0.78	2.90	120	78.85	0.98	2.16
430	166.77	0.98	5.19	200	109.86	1.47	4.41
				280	133.50	1.96	7.45
				310	141.10	2.16	8.84
				340	148.16	2.35	10.35
				360	152.61	2.55	11.72
				380	156.86	2.74	13.17
				400	160.94	2.94	14.70
30(phr)				40 (phr)			
ϵ ($\Delta L/L$) (%)	ϵ_T (%)	σ (MPa)	σ_T (MPa)	ϵ (%)	ϵ_T (%)	σ (MPa)	σ_T (MPa)
0	0	0	0	12	11.33	0.10	0.11
12	11.33	0.10	0.11	20	18.23	0.20	0.24
24	21.51	0.20	0.24	24	21.51	0.29	0.36
32	27.76	0.29	0.39	28	24.69	0.39	0.50
40	33.65	0.39	0.55	36	30.75	0.49	0.67
44	36.46	0.49	0.71	44	36.46	0.98	1.41
80	58.78	0.98	1.76	60	47.00	1.47	2.35
120	78.85	1.47	3.23	68	51.88	1.96	3.29
160	95.55	1.96	5.10	80	58.78	2.45	4.41
200	109.86	2.45	7.35	100	69.31	2.94	5.88
240	122.38	2.94	10.00	120	78.85	3.43	7.55
280	133.50	3.43	13.03	140	87.55	3.92	9.41
320	143.51	3.63	15.23	160	95.55	4.41	11.47
360	152.61	3.82	17.58	184	104.38	4.90	13.92
				204	111.19	5.39	16.39
				224	117.56	6.37	20.64
				12	11.33	0.10	0.11

Table (3.1): continue

50(phr)			
ε ($\Delta L/L$) (%)	ε_T (%)	σ (MPa)	σ_T (MPa)
0	0	0	0
8	7.70	0.10	0.11
16	14.84	0.20	0.23
40	33.65	0.29	0.41
60	47.00	0.39	0.63
68	51.88	0.49	0.82
80	58.78	0.98	1.76
120	78.85	1.47	3.23
180	102.96	1.76	4.94
280	133.50	1.96	7.45
340	148.16	2.25	9.92
420	164.87	2.45	12.74
460	172.28	2.74	15.37

Fig.(3.1) shows the stress- strain characteristics of (NBR/EPDM/HAF) composites. This figure shows the conventional behavior of thermosetting materials where each curve consists of two distinct regions; the linear (elastic) region and the plastic region. It is clear that in general, the stiffness, governed by the slope of the initial linear part increases with increasing carbon black concentrations, since it acts as a reinforcing filler. Accordingly, the elongation at break decreases.

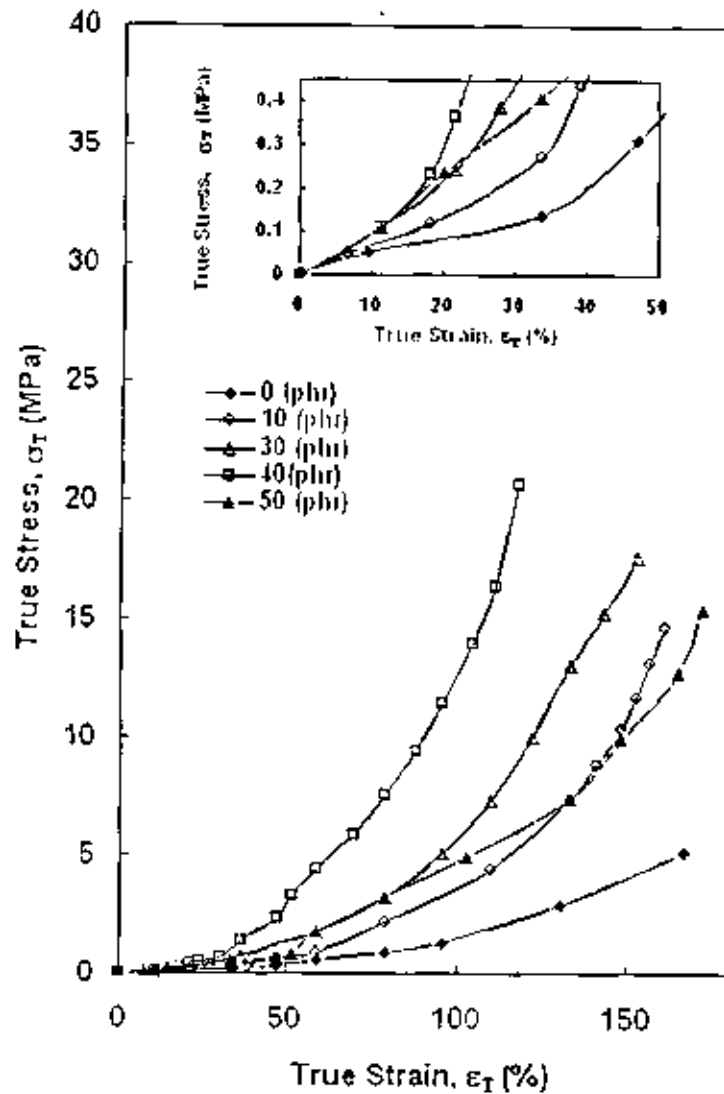


Fig.(3.1): Stress-strain curves for (NBR/EPDM) blends loaded with different concentrations of HAF black.

The stress-strain parameters; young's modulus (E), rupture strain (ϵ_R) and rupture stress (σ_R) of the samples are appreciably affected by increasing carbon black concentrations. Table (3.2) represents the variation of (E), (ϵ_R) and (σ_R) of the samples with HAF black contents.

Fig.(3.2) shows the relation between Young's modulus (E) and carbon black concentration for the tested samples. It is clear that in general, Young's modulus increases with increasing carbon black concentrations and shows a maximum around (40 phr) of HAF/black, followed by a decrease with further increase of HAF/black concentration.

Table (3.2): young's modulus (E), rupture strain (ϵ_R) and rupture stress (σ_R) of the samples.

Carbon black content (phr)	E (MPa)	σ_R (MPa)	ϵ_R (%)
0	0.84	5.19	166.77
10	1.27	14.7	160.94
30	1.59	17.58	152.6
40	3.44	20.6	117.55
50	1.45	15.36	172.2

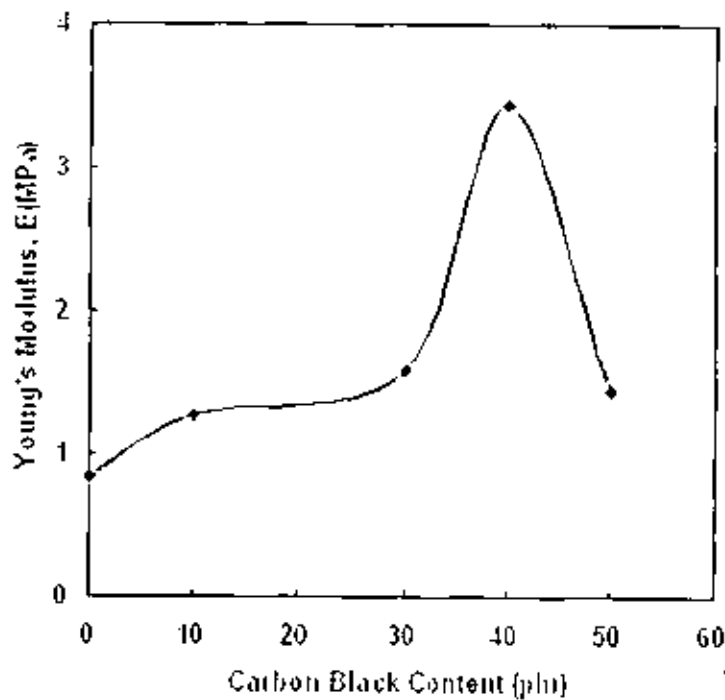


Fig.(3.2): Dependence of young's modulus, E on carbon black concentration for (NBR/EPDM) blends.

The dependence of (ϵ_R) and (σ_R) on the concentrations of carbon black yields a minimum ϵ_R around 40 phr of HAF/black [see Fig. (3.3)]. The value of rupture strain (ϵ_R) increases with a further increase of HAF/black concentration. The initial decrease in ϵ_R is probably due to entanglement of macromolecular chains by the introduction of some physical crosslinking between them and carbon black particles. The subsequent formation of compact structure⁽⁷⁰⁾ at

higher concentrations would be responsible for the decrease in (ϵ_R) . It is also noticed that the concentration dependence of rupture stress, σ_R , shows a maximum around (40 phr) of HAF/black, followed by a decrease with further increase of HAF/black concentration. This may imply that some sort of compact structure formation is behind this behavior. Such compact structure, would become more loose by adding excess carbon black⁽⁷⁰⁾.

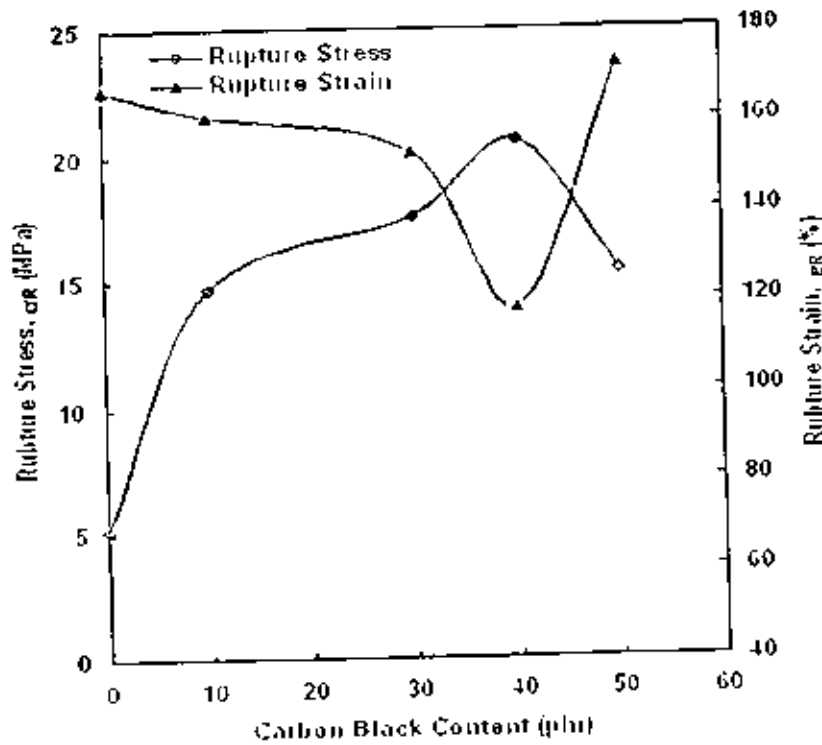


Fig.(3.3): Dependence of (ϵ_R) and (σ_R) on carbon black concentration for (NBR/EPDM) blends.

(ii) Determination of the degree of crosslinking:

The classical theory of elasticity⁽³⁷⁾, is described by the expression:

$$\sigma_T = \sigma_0 + G(\lambda^2 - \lambda^{-1}) \quad (1.10)$$

where σ_0 is the steady state component of σ_T which depends on the chemical nature of the rubber, and G is the rubbery modulus which depends on the degree

of crosslinking. The dependence of true stress σ_T on $(\lambda^2 - \lambda^{-1})$ for the tested samples are listed in table (3.3) and represented in figure (3.4).

Table (3.3): The true stress- $(\lambda^2 - \lambda^{-1})$ characteristics of (NBR/EPDM/HAF) composites.

0(phr)		10 (phr)		30 (phr)	
$(\lambda^2 - \lambda^{-1})$	σ_T (MPa)	$(\lambda^2 - \lambda^{-1})$	σ_T (MPa)	$(\lambda^2 - \lambda^{-1})$	σ_T (MPa)
0	0	0	0	0	0
1.24	0.137	0.60	0.117	0.36	0.109
1.93	0.313	1.24	0.274	0.73	0.243
2.68	0.529	1.51	0.435	0.98	0.388
4.38	0.862	1.93	0.627	1.25	0.548
6.37	1.274	2.68	0.882	1.38	0.705
13.42	2.900	4.38	2.156	2.68	1.764
27.90	5.194	8.66	4.410	4.39	3.234
		14.17	7.448	6.38	5.096
		16.56	8.839	8.67	7.350
		19.13	10.348	11.27	9.996
		20.94	11.720	14.18	13.030
		22.83	13.171	17.40	15.229
		24.80	14.700	20.94	17.581

40(phr)		50 (phr)	
$(\lambda^2 - \lambda^{-1})$	σ_T (MPa)	$(\lambda^2 - \lambda^{-1})$	σ_T (MPa)
0	0	0	0
0.36	0.109	0.24	0.105
0.61	0.235	0.48	0.227
0.73	0.364	1.25	0.411
0.86	0.501	1.94	0.627
1.11	0.666	2.23	0.823
1.38	1.411	2.68	1.764
1.94	2.352	4.39	3.234
2.23	3.292	7.48	4.939
2.68	4.410	14.18	7.448
3.50	5.880	19.13	9.917
4.39	7.546	26.85	12.740
5.34	9.408	31.18	15.366
6.38	11.466		
7.71	13.916		
8.91	16.385		
10.19	20.638		

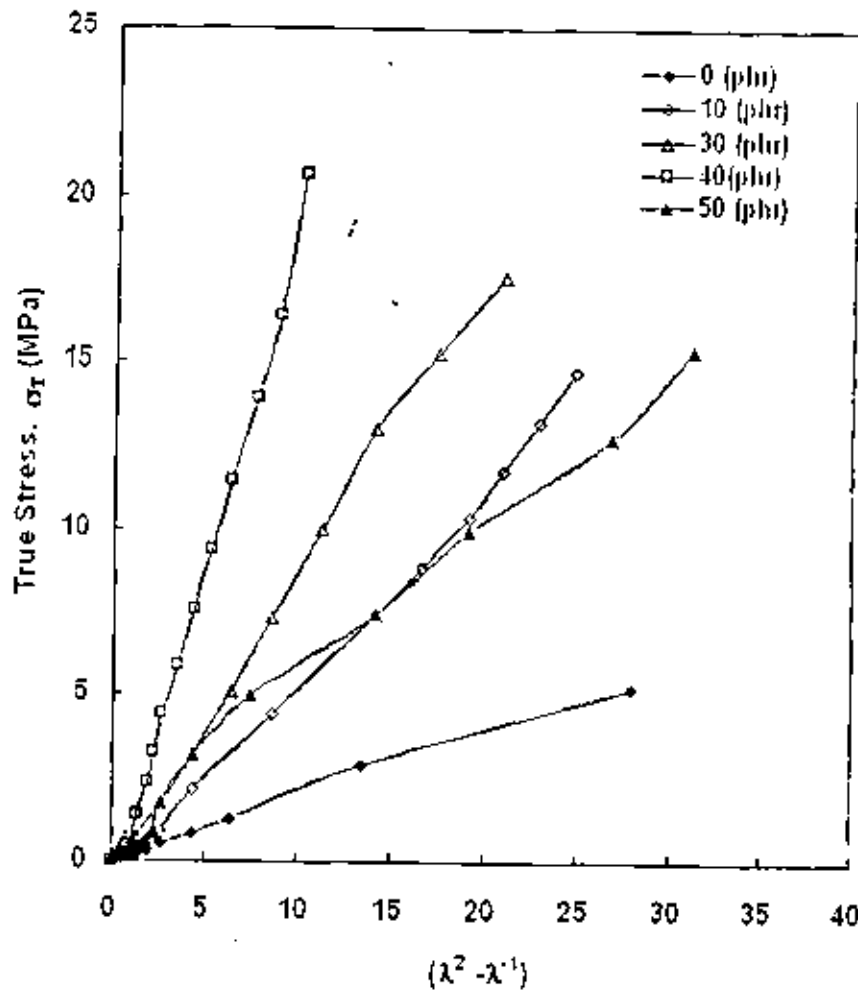


Fig.(3.4): Dependence of stress on $(\lambda^2 - \lambda^{-1})$ for (NBR/EPDM) blends loaded with different concentrations of carbon black.

The slope of the initial linear part of any of these curves gives the rubbery modulus, G . It was found that G depends on the carbon black content. The average molecular mass between two crosslinks, M_c , was calculated using the relation⁽⁷⁰⁾:

$$M_c = \frac{\rho RT}{G} \quad (3.1)$$

where, ρ is the density of rubber, R is the gas constant and T is the absolute temperature. The degree of crosslinking ν (the number of gram moles of

crosslinks per unit gram of rubber) was calculated by using equation in the relation⁽⁶⁾:

$$\nu = 1/(2M_c) \quad (3.2)$$

Table (3.4) represents the variation of ν with HAF black contents.

Carbon black content (phr)	ν (Mole X 10^5)
0	3.97
10	11.61
30	12.51
40	24.02
50	11.33

Figure (3.5) represents the variation of the crosslink density with increasing carbon black content. It is noticed that the ν increases with increasing carbon black content. It is worth-noting that the role of carbon black to create crosslinks is more effective for sample S_{40} which contains 40 phr of carbon black as clear from its higher level of crosslink density (see table (3.3)).

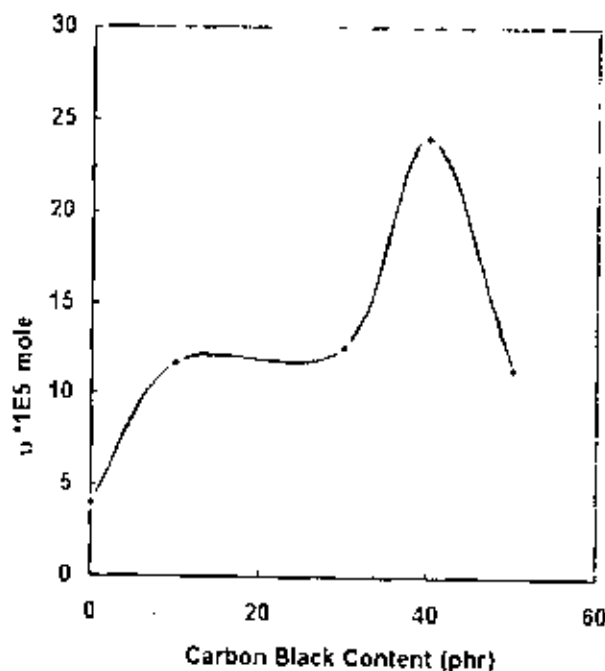


Fig.(3.5): Variation of the crosslink density with carbon black content.

3.2. Creep and Creep Recovery

Creep characteristics can be successively described in terms of the element model which is described by L.E Nielsen⁽³¹⁾, and the elastic, viscoelastic, and flow mechanisms in creep recovery, curve can be represented by the four elements model as shown in Figure (3.6).

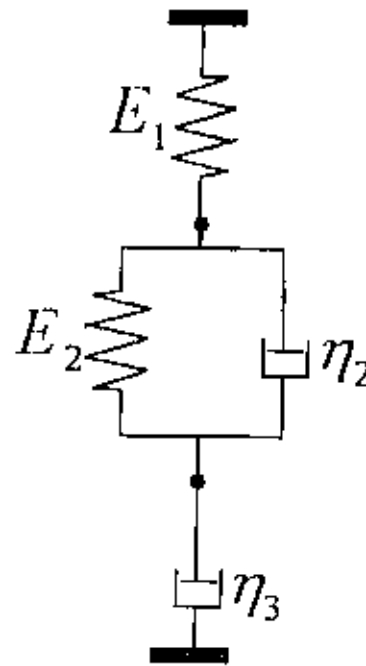


Fig. (3.6): The four elements model for creep.

The total elongation of the model which is equivalent to that of the test specimen may be considered as the sum of three components; i.e.

$$\epsilon = \frac{\sigma_a}{E_1} + \frac{\sigma_a}{E_2} (1 - \exp \frac{-t}{\tau}) + \frac{\sigma_a t}{\eta_3} \quad (3.3)$$

Where:

E_1 – modulus – intermolecular force.

E_2 – bond rotational energy.

τ - retardation time – flexibility.

η - viscosity – molecular weight.

The first term gives the initial elongation, the second one and the third give the later elongation from the spring of modulus E_2 and the dashpot of viscosity η_2 in parallel; moreover, it comes from the dashpot with viscosity η_3 in series. σ_0 is the applied stress, and the retardation time is given by:

$$\tau = \frac{\eta_2}{E_2} \quad (3.4)$$

When the stress is suddenly removed at an elevated time (t_1), the reduction in elongation is equal to what we call the instantaneous strain σ_0/E_1 , while the subsequent creep recoverable is given by:

$$\varepsilon = \varepsilon_2 \exp \frac{-(t-t_1)}{\tau} + \frac{\sigma_0}{\eta_3} t_1 \quad (3.5)$$

where t_1 is the instant when the stress is removed and ε_2 is given by:

$$\varepsilon_2 = \frac{\sigma_0}{E_2} \left(1 - \exp \frac{t_1}{\tau}\right) \quad (3.6)$$

The following section aims at studying the factors that affect the creep mechanisms, such as applied axial stress, carbon black concentration and vulcanization process. Observations were recorded during forward creep besides the mechanisms associated with backward creep, such as recoverable strain, memory function and finally the retardation time.

(i) Forward Creep:

Figures (3.7-3.10) represent a set of forward and backward creep curves at different values of applied stress (at room temperature 30°C) for different carbon black concentrations. The applied tensile stress ranging from (0.98 to 3.92 MPa).

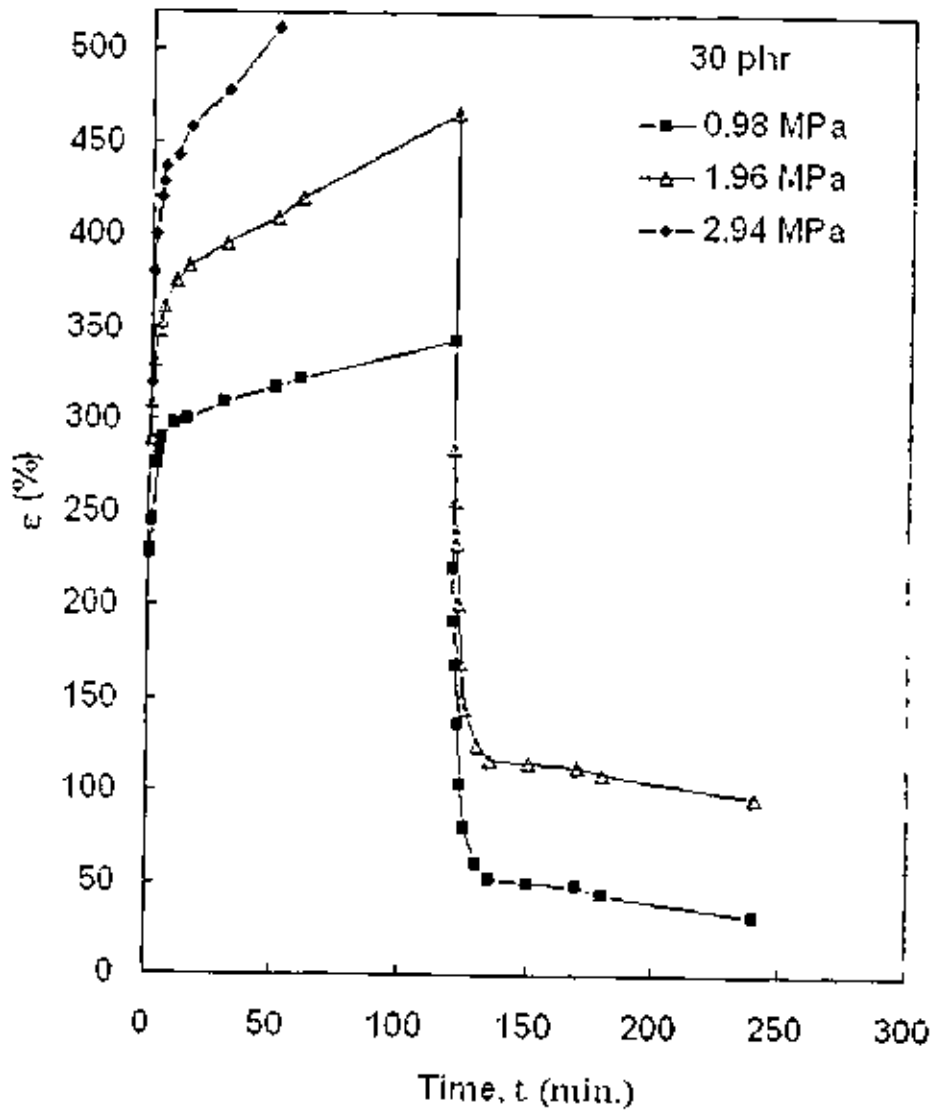


Fig. (3.7): Forward and backward creep curves for sample S₃₀ at different values of applied stresses.

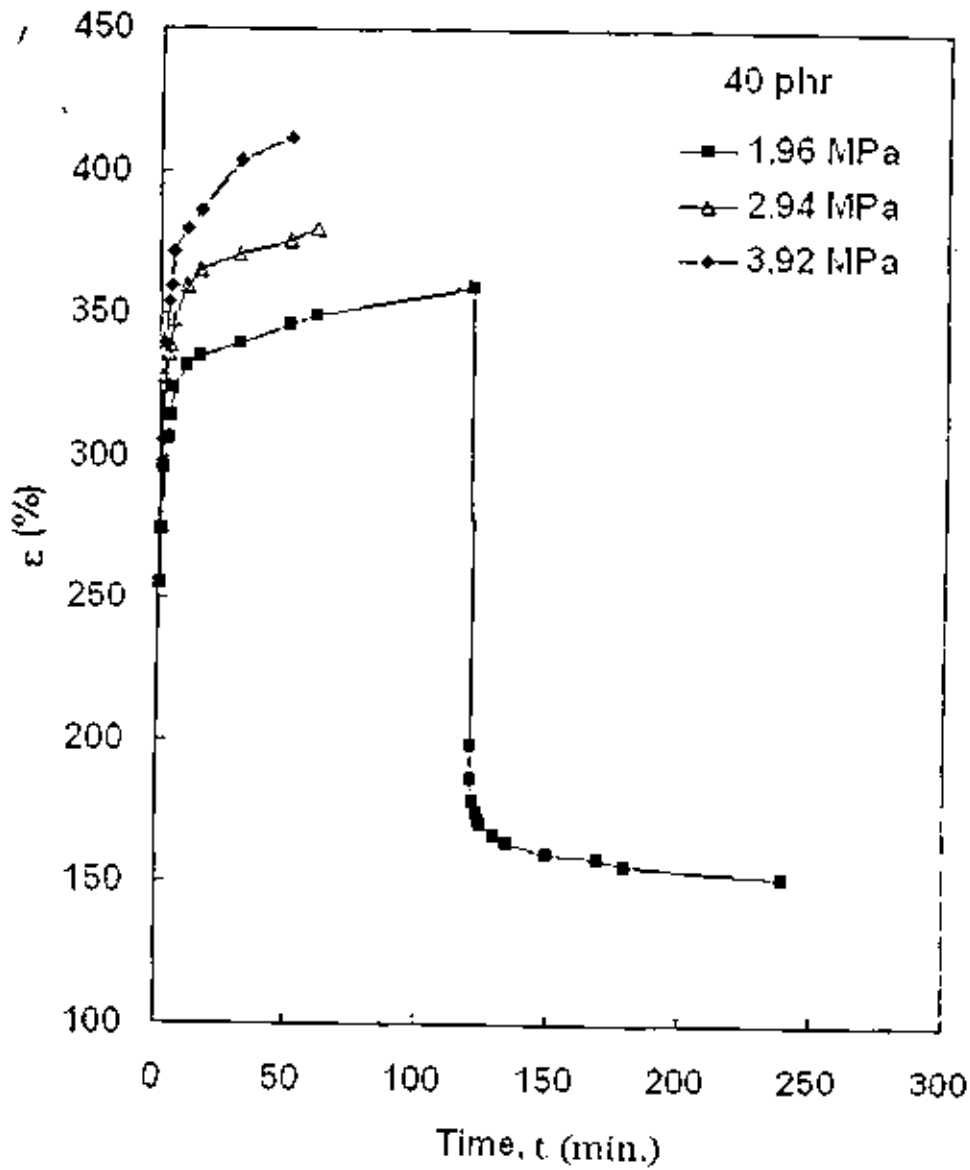


Fig. (3.8): Forward and backward creep curves for sample S_{40} at different values of applied stresses.

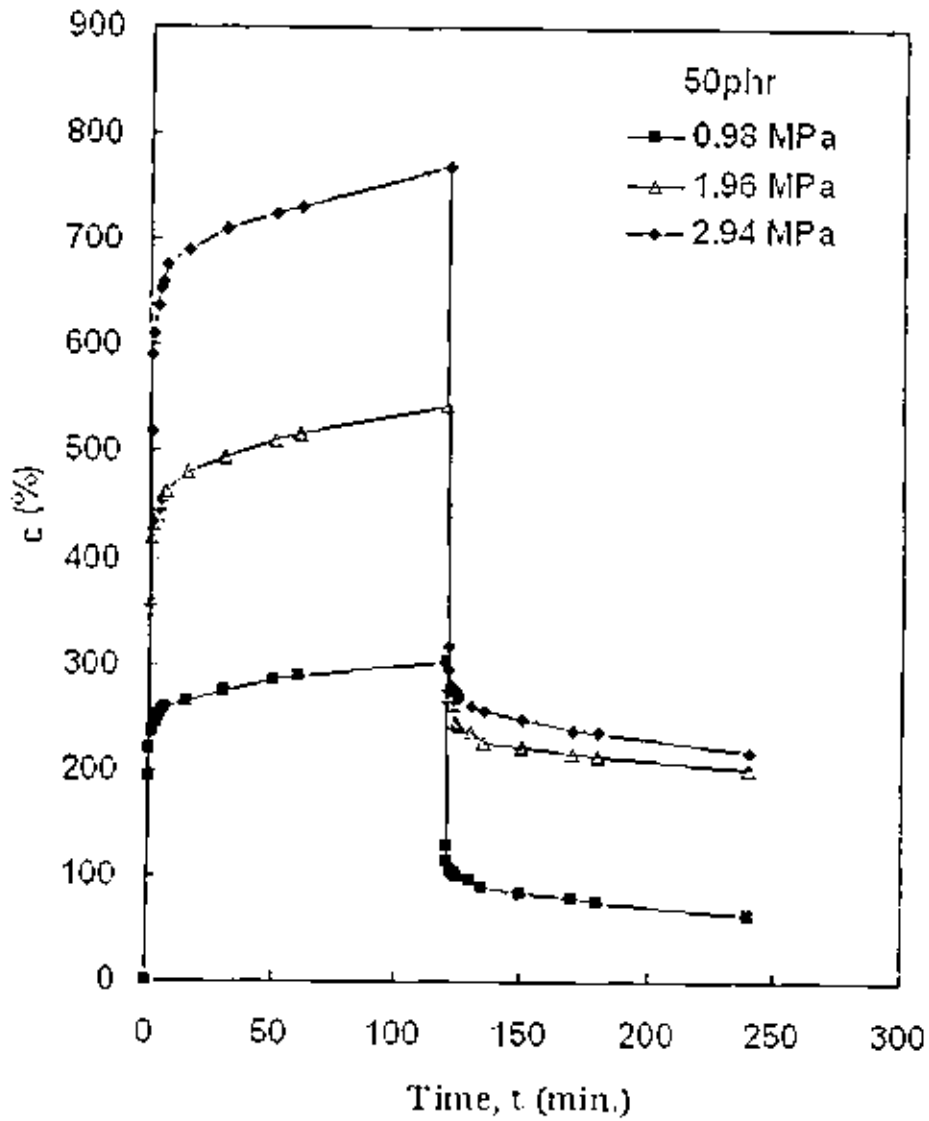


Fig. (3.9): Forward and backward creep curves for sample S_{50} at different values of applied stresses.

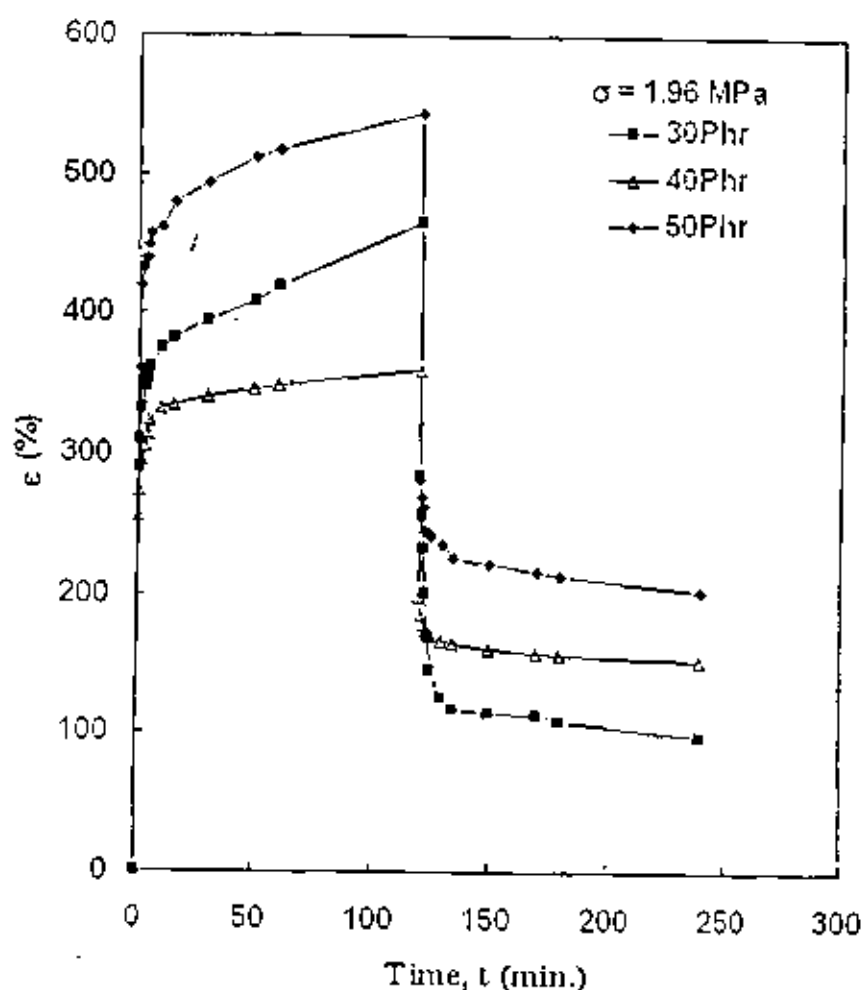


Fig. (3.10): Forward and backward creep curves for samples S_{30} , S_{40} and S_{50} at applied stress ($\sigma = 1.96$ MPa).

It is observed that, the increase of HAF black content largely affects the total resulting strain and some parameters, such as instantaneous strain

$$(\epsilon_0 = \sigma / E_1)^{(6)}, \text{ and the strain rate } \dot{\epsilon}_v$$

The applied stress has also an important reflection on the set of curves; it raises the instantaneous strain and the strain rate. After 120 minutes at which steady state is attained, the applied stress is removed and the subsequent strain is recorded with time under different conditions.

There was always a sudden drop in strain followed by exponential decrease tending eventually to the viscoelastic deformation (irrecoverable strain i.e. $(\sigma_0 / \eta_3) t_1^{(3)}$). Here, one discusses each parameter separately.

The increase in the creep strain by increasing the applied stress was attributed to the stress enhancement of the translational motion and increase the mobility of the flexible and rigid molecular chain segments. This enhancement has been achieved by the movement and arrangement of carbon black aggregates in the direction of creep strain.

Table (3.5) represents the variation of the conventional elastic modulus,

E_1 , high elasticity modulus, E_2 , the viscosity, η_2 for steady creep and the activation volume, q with HAF black contents under different applied stress.

Table (3.5): The dependence of E_1 , E_2 , η_2 and q on HAF contents under different applied stresses.

Carbon black content	σ (MPa)	E_1 (MPa)	E_2 (MPa)	η_2 (MPa.sec)	q (m ³)
30phr	0.98	0.43	1.56	17193	1.24E-27
	1.96	0.67	2.45	14962	
	2.94	0.92	2.60	11440	
40phr	1.96	0.77	2.68	64157	6.21E-28
	2.94	1.06	3.72	62553	
	3.92	1.31	4.08	65333	
50phr	0.98	0.50	1.48	29429	1.11E-27
	1.96	0.54	1.81	28823	
	2.94	0.57	1.84	26486	

From table (3.5), It is clear that E_1 , E_2 and η_2 increase with increasing carbon black concentration at constant applied stresses. Besides, show a maximum at carbon black 40 phr (sample S₄₀). This emphasized the reason

mentioned before, where a compact structure is believed to be formed at this concentration.

Figure (3.11) shows the stress dependence of strain rate $\dot{\epsilon}_s$, from which one can calculate the activation volume q (see table (3.5)).

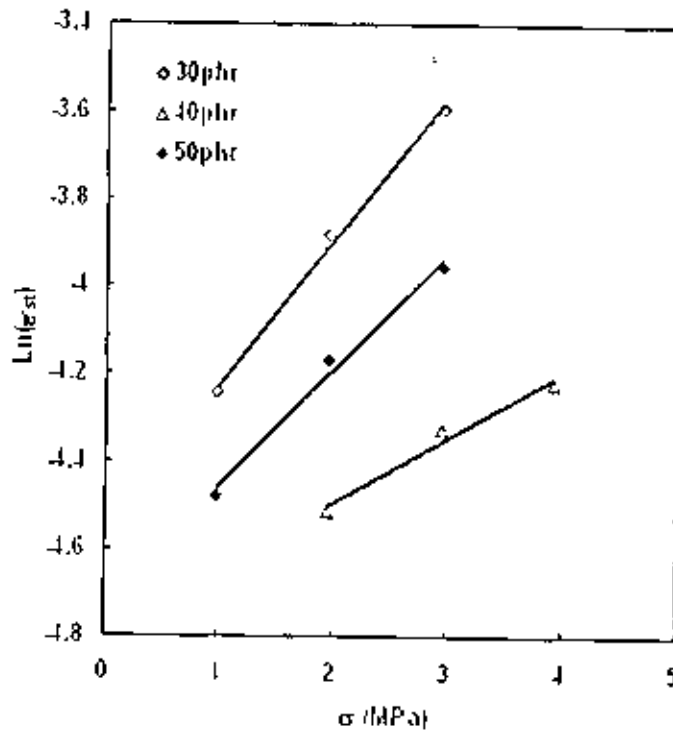


Fig. (3.11): The relation between the stress and strain rate, $\dot{\epsilon}_s$

From table (3.5), it is clear that, the addition of the fillers lowers the activation volume q , into which the macromolecular chain may be translated or slipped through it during the creep process. This is attributed to the formation of chemical and physical cross links with increasing HAF contents, which restricts the motion of macromolecules, i.e. formation of aggregates of carbon black between the flexible chains segments which causes obstacles to their sliding. So, the activation volume decreases with increasing HAF contents.

(ii) Backward Creep:

The backward creep ,i.e., creep after removal of the applied stress at a time t_1 in the steady state region, is also useful in deducing several important parameters by studying their dependence on carbon black concentration and applied stress as well as vulcanization process.

Table (3.6) represents the variation of the retardation time for recoverable creep τ , memory function for recoverable deformation $\beta(t)$, relaxation strength Δ and the viscosity η_3 at plastic deformation (irrecoverable strain) with HAF black contents under different applied stresses.

Table (3.6):The dependence of τ , $\beta(t)$, Δ and η_3 on HAF concentration under different applied stresses.

Carbon black content	σ (MPa)	τ (min.)	$\beta(t) \times 10^5$	Δ	η_3 (MPa.sec)
30phr	0.98	17.45	9.19	0.206	17210
	1.96	32.89	23.39	0.159	13067
	2.94	-	-	-	-
40phr	1.96	158.7	6.78	0.284	25658
	2.94	-	-	-	-
	3.92	-	-	-	-
50phr	0.98	84.03	6.05	0.229	9408
	1.96	113.63	7.15	0.295	6414
	2.94	156.25	13.05	0.158	8820

The retardation time τ increases with increasing carbon black concentration till 40 phr (sample S_{40}) and then begin to decrease once again with HAF contents under all different applied stresses, this is attributed to the compact structure attained at 40 phr as mentioned before which is responsible for the hindering of the sliding of macromolecules over each other.

Another parameter which gives an indication of the elasticity and the whole previous history of the deformation gradients is the memory function $\beta(t)$. It is manifested during the time dependent recoverable strain and is given by ⁽⁴⁰⁾. Since, the creep rate depends on the value of the applied stress, and carbon black concentration, the memory function should depend on them, beside the time of the creep process. From table (3.6), it is noticed that, $\beta(t)$ decreases with HAF contents at all applied stress owing to the increase of cross linking density .

Table (3.6) shows the variation of relaxation strength Δ with the HAF black content and different applied stress. It has been noticed that, Δ , increases with increasing carbon black concentration under all applied stresses and shows a peak for sample S_{40} which contains 40 phr of HAF black.

After long time (t_1) from application of stress (σ) the dashpot (η_3) becomes responsible for the creep rate and recoverable elastic strain, so the viscosity at plastic deformation η_3 can be calculated from the relation (1.15).

From table (3.6), it has been noticed that, η_3 , increases with increasing HAF black contents and again, the formation of compact structure is behind the maximum value of η_3 for sample S_{40} . In general, it is noticed that, the value of η_3 is small compared with η_2 (viscosity for steady creep), although the behavior of both quantities with carbon black concentration is nearly the same.

3.3. Swelling Behavior

With respect to the used solvents, gasoline and kerosene, it is necessary to indicate that, there are two ways to describe their behavior by their chemical composition or by their properties. Both viewpoints can be instructive. The most common way to characterize the properties of the solvent molecule is its

size which depends on its molecular weight. The molecular weight depends upon its carbon atom number. Gasoline is a complex mixture of hundreds of hydrocarbons vary by class – paraffins, olefins and naphthens enhanced with aromatic benzene (up to 5% by volume), trimethylbenzene (up to 7% by volume) – and within each class, by size, gasoline complex/mixture contains also rich – oxygenated compounds such as ethanole $\text{CH}_3\text{CH}_2\text{OH}$ (up to 10% by volume) and/or methyl tertiary butyl ether (MTBE) (up to 18% by volume) as well as some other sulphur compounds⁽⁷¹⁾. The average molecular weight of gasoline ranges from 92 to 95 corresponding to number of carbon atoms between 3 and 12. Gasoline can contain materials boiling from 40 C° to 200 C° . On the other hand, kerosene is a mixture of hydrocarbons consisting also of branched and straight chain, paraffins with some naphthenes and aromatics, in the $\text{C}_{10} - \text{C}_{16}$ carbon atoms range. Thus, the molecular size of gasoline molecule is relatively smaller than that of kerosene. Kerosene can contain material boiling from 150 C° to 300 C° . The swelling characteristics in both of gasoline and kerosene were discussed in the following sections.

(i) Degree of Swelling:

The dependence of the degree of equilibrium swelling, Q_e , (measured after 24 hours) in both of gasoline and kerosene on HAF black content is represented in figure (3.12).

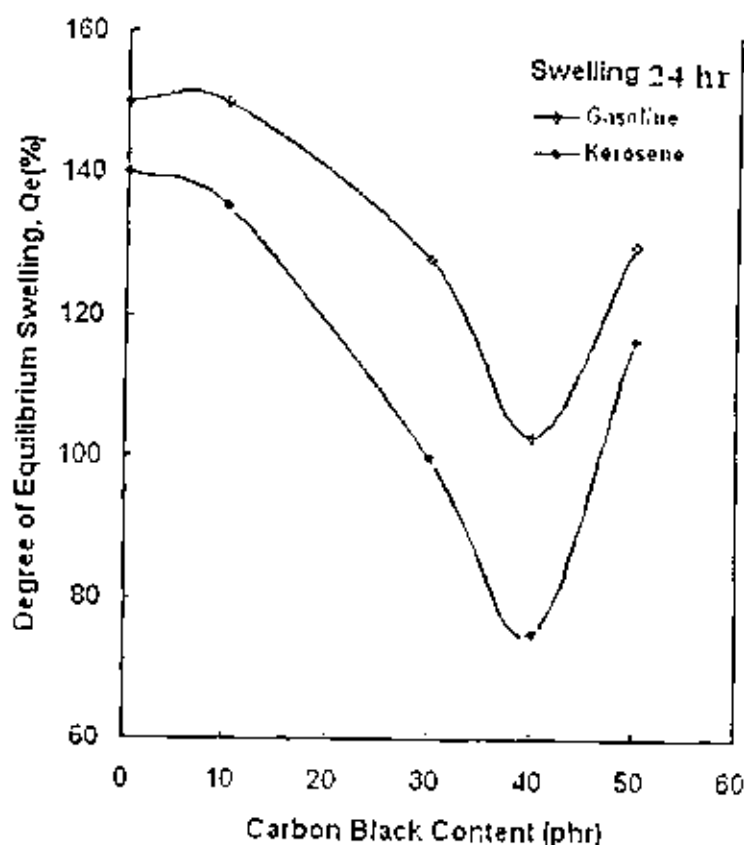


Fig. (3.12): Dependence of the degree of equilibrium swelling, Q_e , in both of gasoline and kerosene on HAF black content.

It is clear that Q_e decreases with increasing the carbon black concentration. The tendency of HAF black to form aggregates impedes the solvent penetration into the matrix. Besides, the incorporation of 40phr of HAF black gives lower values of Q_e , i.e. minimum free volume inside the matrix (better dispersion of the filler within the matrix). However the incorporation of carbon black more than 40 phr increases Q_e , i.e. increases the free volume inside the matrix. As explained before this phenomenon is due to the agglomeration of the carbon black particles to form a domain that acts like a foreign body within the matrix which is responsible for the deterioration of the physical properties of the vulcanizate.

Moreover, the values of Q_e in gasoline are higher than those in kerosene. The relatively smaller molecular size of gasoline and/or the presence of rich-oxygenated compounds, capable of forming secondary bonds with the polymeric chain, enhance gasoline penetration into the matrix and in turns the degree of swelling more than kerosene.

(ii) *Relaxation Time τ* :

The time dependence of the degree of swelling in both of gasoline and kerosene for the (NBR/EPDM) blends loaded with different concentrations of HAF black are shown in figures (3.13 and 3.14).

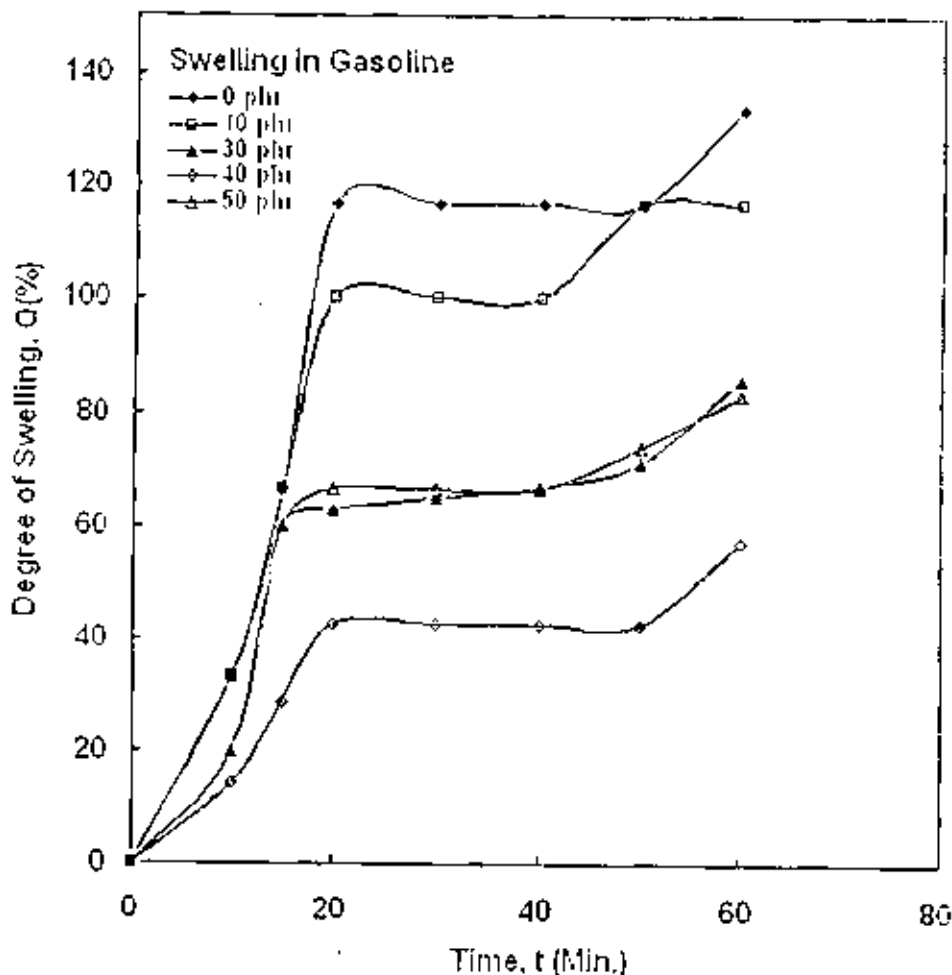


Fig. (3.13): The time dependence of degree of swelling in gasoline for (NBR/EPDM) blends loaded with different concentrations of HAF black.

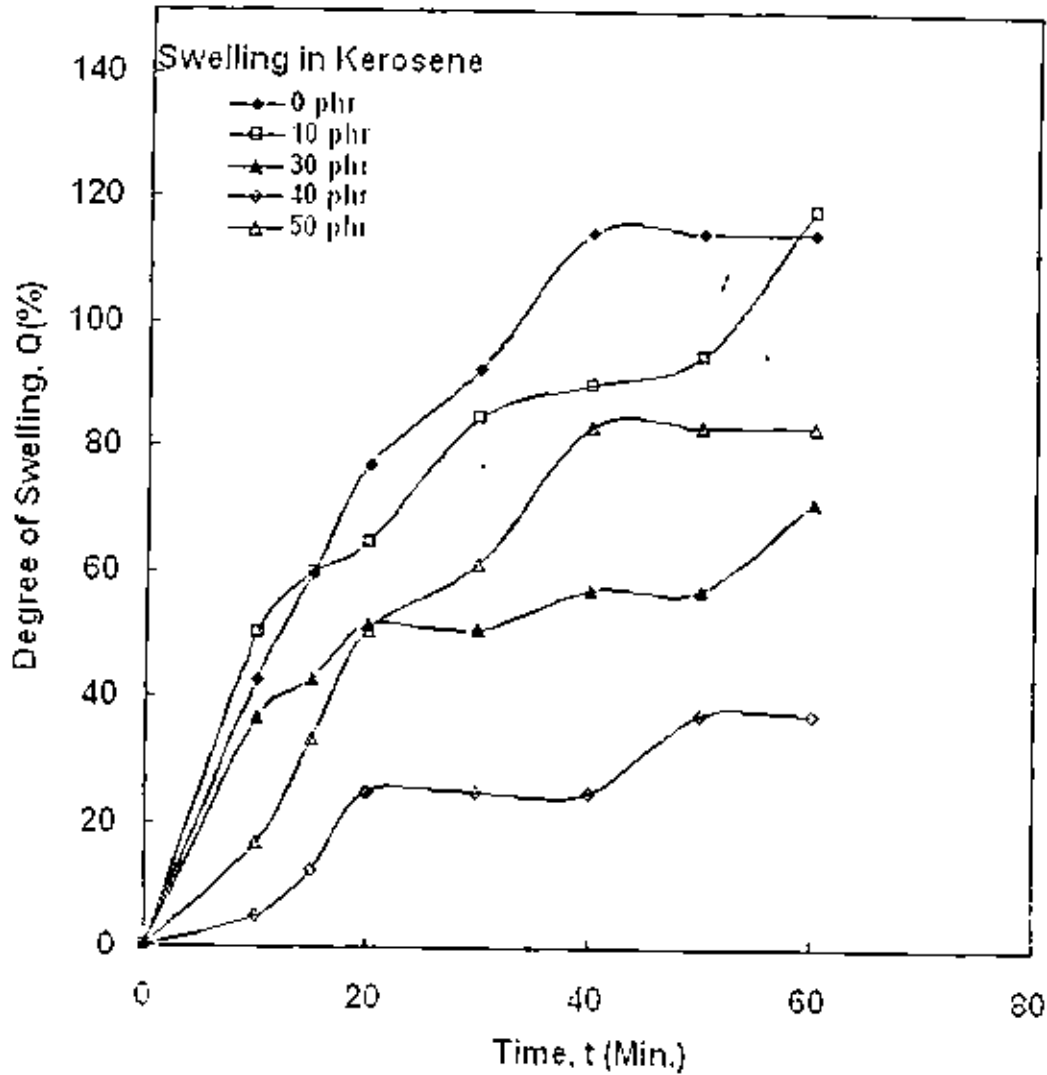


Fig. (3.14): The time dependence of degree of swelling in kerosene for (NBR/EPDM) blends loaded with different concentrations of HAF black.

The general behavior may be approximated by an exponential growth function for all samples showing positive swelling mechanism of the form.

$$Q_t = Q_\infty [1 - \exp(-t/\tau)] \quad (3.7)$$

where, Q_t is the degree of swelling as a function of time and τ is a characteristic time which depends on both the polymer matrix and the crosslink density as is observed from Table (3.7).

Table (3.7) The values of Relaxation Time τ (min).

Carbon Black Content (phr)	τ (min.) Gasoline	τ (min.) Kerosene
0	26.24	32.25
10	40.16	35.2
30	70.42	62.11
40	89.28	83.33
50	67.56	41.66

From table (3.7), It is noticed that τ , for the tested samples those swelled in both gasoline and kerosene, increases with increasing the carbon black concentration except for S_{50} . This might be the result of the physical crosslinking action induced by carbon black aggregates which in turns, increases the required time for the swelling process.

Besides, sample S_{40} has the higher value of τ , which as mentioned before, may be due to the compact structure of the matrix at this HAF concentration.

(iii) Penetration and Diffusion of Solvent:

The variation of the increase in weight due to swelling in both of gasoline and kerosene with the square root of time, in minutes for (NBR/EPDM) blends loaded with different concentrations of HAF black are shown in figures (3.15 and 3.16). The first increase in M_t with time is due to the liquid adsorption inside the sample till to reach steady state value, while the second rise in M_t at higher times is due to the broken of the crosslinked chains as a result of high internal pressure of the liquid on the cross-links. The slopes of the straight lines obtained at the early stage of the process ($M_t/t^{1/2}$) were calculated. Using equations [(1.22) & (1.23)], the penetration rate (P) and the diffusion coefficient (D) were calculated, see Table (3.8).

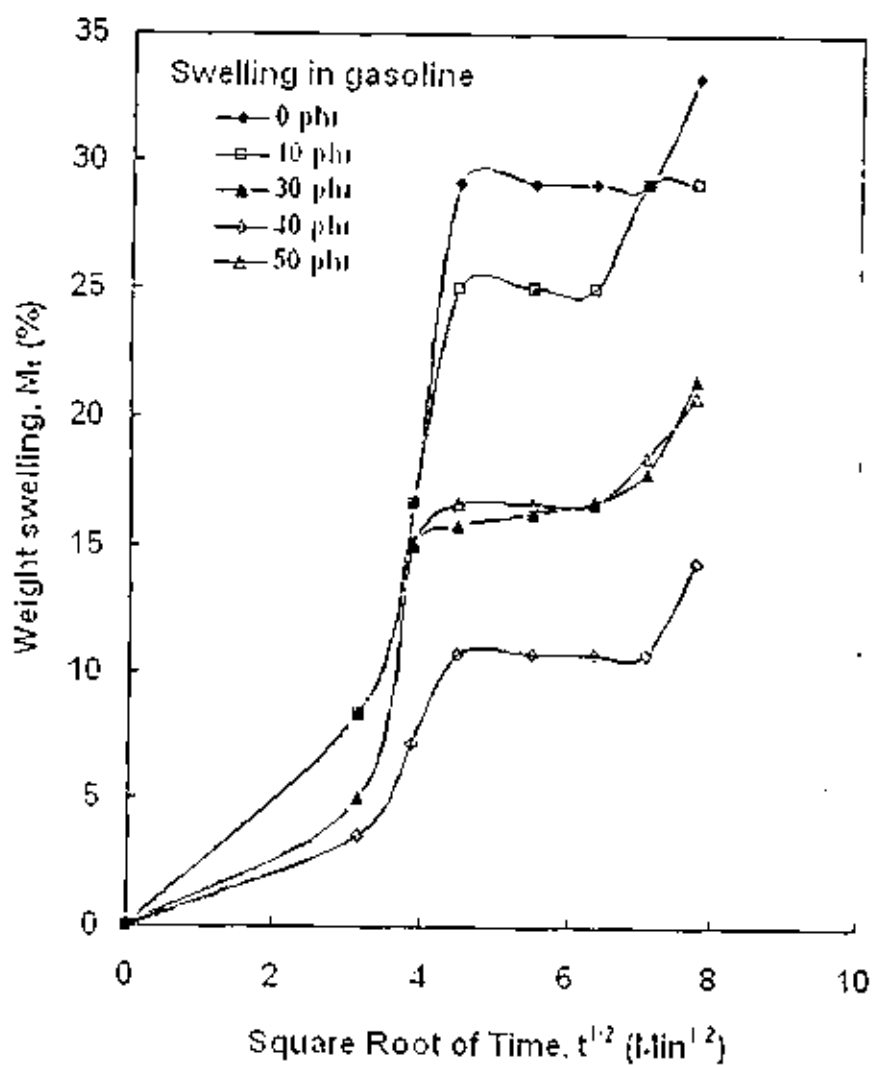


Fig. (3.15): Weight swelling in gasoline, M_t versus square root of time for (NBR/EPDM) blends loaded with different concentrations of HAF black.

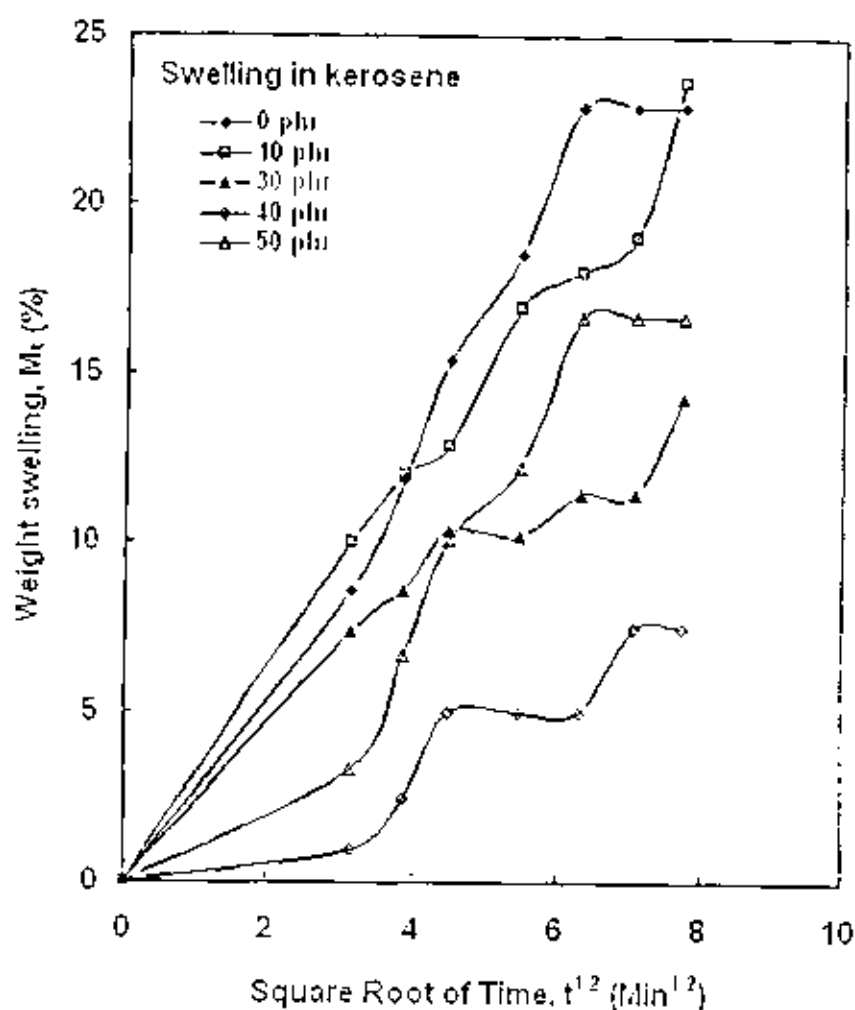


Fig. (3.16): Weight swelling in kerosene, M_t versus square root of time for (NBR/EPDM) blends loaded with different concentrations of HAF black.

Table (3.8) The values of P and D for (NBR/EPDM) blends loaded with different concentrations of HAF black swelled in gasoline & kerosene.

Carbon Black Content (phr)	$P \times 10^4$ (cm/min ^{1/2}) Gasoline	$P \times 10^4$ (cm/min ^{1/2}) Kerosene	$D \times 10^8$ (cm ² /min.) Gasoline	$D \times 10^8$ (cm ² /min.) Kerosene
0	1.51	1.21	1.79	1.15
10	1.31	1.11	1.34	0.96
30	1.02	1.00	0.82	0.79
40	0.82	0.64	0.52	0.33
50	1.03	0.96	0.83	0.72

From table (3.8), It is noticed that P and D for both of gasoline and kerosene, decrease with increasing the carbon black concentration. This might be the result of the physical crosslinking action, as mentioned before, induced by carbon black aggregates. These aggregates which exist at different plate lamellae and act as screens, reduce the penetration rate of the solvent ⁽⁷²⁾ molecules into the bulk of the rubber mix. Again, the minimum value of both P and D for the sample S_{30} can be attributed to the compact structure as mentioned before.

Conclusion

A variety of experimental techniques is employed to draw a consistent picture of the physicochemical and physicomechanical properties of NBR/EPDM blends loaded with different concentrations of carbon black. Stress-strain, creep and swelling behavior of such materials were investigated with special reference to the effect of adding carbon black. The main outcome of this study may be summarized as:

Incorporation of HAF/black increases the stiffness, young's modulus (E), rupture stress, (σ_R) and the degree of crosslinking, ν , of NBR/EPDM blend. Each of these parameters shows a maximum around 40 phr of HAF/black (sample S_{40}), followed by a decrease with further increase of HAF/black concentration. While, the rupture strain (ϵ_R) behaves an opposite behavior.

From the forward creep, we concluded that the increase in carbon black concentration results in an increase in the conventional elastic modulus, E_1 , high elasticity modulus, E_2 , and the viscosity for steady creep, η_2 , up to 40 phr of HAF/black, beyond which they decrease. The addition of the carbon black lowers the activation volume q , into which the macromolecular chain may be translated or slipped through it during the creep process.

On increasing filler loading, both the retardation time, τ , and the relaxation strength, Δ , increase and attain maximum values for sample S_{40} . Meanwhile, the memory function, $\beta(t)$, decreases with increasing filler concentration and shows a minimum for sample S_{40} .

The degree of swelling Q_G , the penetration rate P and consequently diffusion coefficient for the tested samples those swelled in both of gasoline and kerosene, were found to decrease with the HAF- content. Besides,

a minimum values for these parameters appear at 40 phr of HAF/black. In contrast, the characteristic time (τ), was found to increase with increasing the carbon black concentration and sample S₄₀ has the higher value of τ , which confirm our mechanical measurements.

A compact structure was believed to be attained at 40 phr of HAF/black (sample S₄₀) which is responsible of the maxima and minima in all the above measurements.

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الخلاصة

الطريقة الحديثة المستخدمة في الحصول على مواد مطاطية لها خواص جيدة هي طريقة الخلط وهذه الطريقة أقل تكلفة من عملية تخليق بوليميرات جديدة، ومن الناحية التكنولوجية فإن هذه الخلطات تجمع بين خواص المكونات.

ومن المعروف أن مطاط النيتريل (NBR) يتميز بمقاومه عالية للإنتفاخ عند اتصاله بالزيوت أو المذيبات، إلا أن مقاومته للأوزون والحرارة ضعيفة جدا. وعلى العكس من ذلك فإن مطاط الإيثيلين بروبيلين داين (EPDM) يقاوم الأوزون والحرارة ولكن مقاومته للإنتفاخ بالزيوت أو المذيبات ضعيفة. وعلى ذلك فإن الخلائط المولفة من (NBR) و (EPDM) تحمل صفات كلا النوعين من حيث مقاومة الإنتفاخ بالمذيبات ومقاومة الأوزون والحرارة وهذه الصفات الجيدة لا تتوافر مجتمعة في أي من هذين النوعين. وقد اهتمت الدراسة بتحضير خلائط من مطاط (EPDM) مع مطاط النيتريل (NBR) وتم تحميل الخليط بنسب مختلفة من أسود الكربون (HAF)

وتم اعداد عينات القياس تحت نفس الظروف وحسب الطرق القياسية وكان الهدف الرئيسي هو دراسة تأثير أسود الكربون (HAF) على كل من الخواص الفيزيوكيميائية والفيزوميكانيكية لهذه الخلائط

وكانت النتائج المستحصلة على النحو التالي :

أولاً: من منحنيات الإجهاد - الإنفعال تم استخلاص كلا من إجهاد وانفعال القطع وكذلك معامل بنج وكثافة الربط العرضي واعتمادهم على نسب أسود الكربون في العينة.

ثانياً: تم دراسة تأثير نسب أسود الكربون على منحنيات الزحف الأمامي والزحف العكسي تحت تأثير إجهادات مختلفة. ومن هذه المنحنيات تم حساب كل من معامل المرونة التقليدي و معامل المرونة العالية والزوجة للزحف الثابت ولزوجة الزحف العكسي وحجم التنشيط وزمن الإعاقة وقوة الإسترخاء.

ثالثاً: تم حساب اعتماد درجة الانتفاخ على زمن غمر المخلوط في كل من الجازولين والكيروسين وعليه أمكن حساب كل من معدل نفاذ ومعامل انتشار السائل داخل المخلوط .



التاريخ :
الموافق : 16-7-2007
الرقم الاشاري : 1063/1/2007

كلية العلوم

قسم الكيمياء

عنوان البحث

((دراسة الخواص الفيزيوكيميائية و الفيزوميكانيكية لخلائط

المطاط المحمل بتركيزات مختلفة من أسود الكربون))

مقدمة من الطالب

فؤاد عبد الله جهان

* * لجنة المناقشة :

.....

الدكتور / مدحت محمود المبيض
(مشرف الرسالة)

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الدكتور / زيدان جاسم خلف
(متنحن داخلي)

.....

الدكتور / علي عبد السلام العجمي
(متنحن خارجي)

.....
أمين اللجنة الشعبية لطلبة العلوم

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

﴿دَعْوَاهُمْ فِيهَا سُبْحَانَكَ اللَّهُمَّ وَتَحِيَّتُهُمْ فِيهَا سَلَامٌ وَأٰخِرُ دَعْوَاهُمْ

أَنْ الْحَمْدُ لِلَّهِ رَبِّ الْعَالَمِينَ﴾ ﴿يونس 10

صدق الله العظيم



جامعة التحدي
كلية العلوم
قسم الكيمياء

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رسالة مقدمه لاستكمال متطلبات درجة الماجستير في الكيمياء
من قبل

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سرت - ليبيا
2007 - 2006