Sudan University of Science and Technology

College of Graduate Studies

A Study of Some Mechanical Properties of Tyre Rubber Polymer

دراسة بعض الخواص الميكانيكية للبوليمر مطاط الإطارات

Submitted in partial fulfillment of the requirement for the degree of
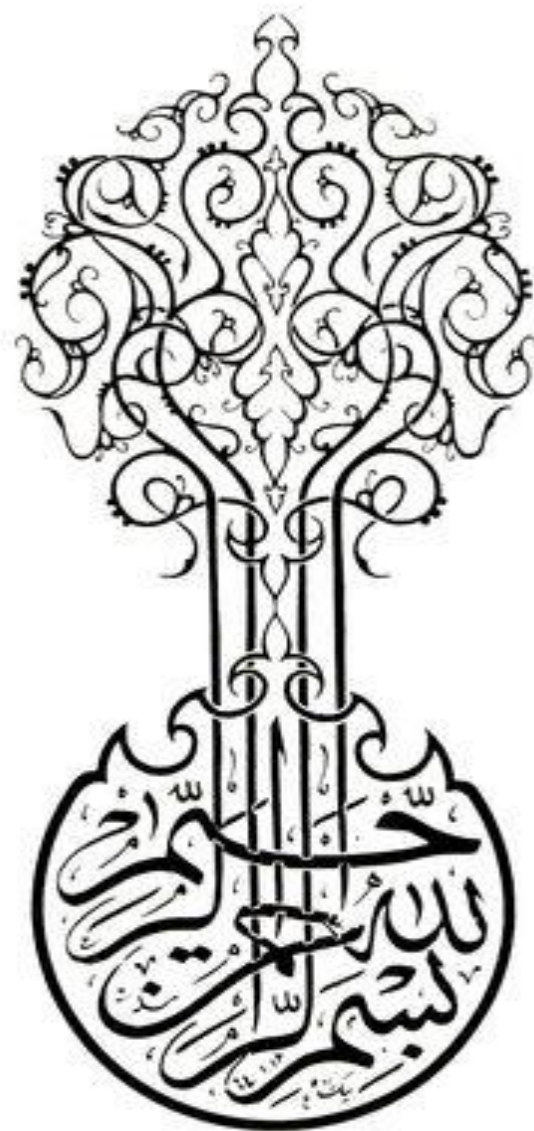
Master in physics

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I

الآيـــة

قَالَ تَعَالَى:

بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ

﴿ سَبِّحِ ٱسْمَ رَبِّكَ ٱلْأَعْلَى ۝١ ٱلَّذِى خَلَقَ فَسَوَّىٰ ۝٢ وَٱلَّذِى قَدَّرَ فَهَدَىٰ ۝٣ وَٱلَّذِىٓ أَخْرَجَ ٱلْمَرْعَىٰ ۝٤ فَجَعَلَهُۥ غُثَآءً أَحْوَىٰ ۝٥ ﴾

صدق الله العظيم

سورة الأعلي الآيات من(1–5)

II

Dedication

I dedicate this work to

My Father….

My Mother….

My Brothers and sisters….

My Colleague's comrades….

My professor ………

Acknowledgement

I would like to thank Allah for His grace to complete this work. I would also like to extend my thanks and gratitude to the supervisor of Dr. Ali Sulaiman, for his encouragement and supervision over the period of this study, for his kindness to follow me and for his indispensable help throughout this work.

Abstract

Some of the mechanical properties of polymer, such as tensile test, creep and swelling, were studied for two types of tire rubber at different concentrations of black carbon(70% ,30%) respectively. In the tensile test, the elasticity modulus was calculated and found that it was $7.836\,\mathrm{MN/m^2}$. Also in the study of creep, the time-dependent creep modulus and the creep compliance were calculated. Then the swelling behavior was introduced using three chemical solutions, namely methane, acetone and benzene, and found that the rubber, which contains 30% of carbon has been degraded by methane but it was not affected by the rest of the other solutions. While the other type of rubber has been swelled in benzene and its mass increased significantly.

المستخلص

في هذه الدراسة تم دراسة بعض الخواص الميكانيكية للبوليمر مثل اختبار الشد، الزحف والتشرب لنوعين من مطاط الاطارات بتراكيز مختلفة من الكربون الاسود (70%، 30%) على التوالي. في اختبار الشد تم حساب معامل المرونة ووجد انه يساوي $7.836 \ MN/m^2$. كما تم دراسة الزحف وحساب معامل الزحف المعتمد علي الزمن، واستجابة الزحف. ايضا تم التعرف علي سلوك التشرب باستخدام ثلاث محاليل كيميائية وهي الميثان، الاستون والبنزين ووجد ان المطاط الذي يحتوي علي نسبة (30%) من الكربون الاسود تحلل بواسطة الميثان ولم يتاثر ببقية المحاليل، النوع الاخر من البوليمر قد تشرب بواسطة البنزين وزادت كتلته بشكل ملحوظ.

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Chapter One

1.1 Introduction

Polymers are one of the most important organic materials. Due to their excellent properties, polymers are applied in various fields ranging from everyday life products, for example, containers, coating, shoes, tires, rubber bands, and tubes, to industrial products, for example, construction parts and automotive materials [1, 2]. Polymers are ideal materials because of resistance to corrosion, low coefficients of friction as glazing materials, low density and high toughness along with high transparency properties. The practical choice of polymeric materials is however not only determined by the mechanical properties, but also by the price, simplicity of production, processing and the practical limitations in the real application[3,4].The demand of polymers around the world was as high as 17 million tons in 2000, and this number increased to 28.7 million tons in 2014 [5] In order to support such high demands, the production of polymers must be efficient; thus, the speed and the reliability should be considered carefully during production. Furthermore, the measuring and monitoring methods for quality control must be implemented to aid production. The materials of modern pneumatic tires are synthetic rubber, natural rubber, fabric and wire, along with carbon black and other chemical compounds. They consist of a tread and a body. The tread provides traction while the body provides containment for a quantity of compressed air. Styrene-butadiene copolymer is the most popular material used in the production of rubber tires [6] Particulate fillers are used to modify the physical and mechanical properties of polymers in many ways. Polymeric materials are noted for their versatility, high resistance to chemicals, outstanding adhesion to a variety of substrates, toughness, high electrical resistance, durability at high and low temperatures, low shrinkage upon cure, flexibility, and the ease with which

they can be poured or cast without forming bubbles[7,8]. Rubber has the ability to undergo plastic deformation and still can return to its previous form. This ability gives the rubber advantages to be selected in many manufacturing product such as tire etc.

1.2 Problem Statement

Rubber is a special polymer with high tensile strength and low hardness. Rubber take a place in marketable as a good product such as tire, medical glove, slipper etc. Different type of products needs different type of tensile strength as well as hardness. Therefore, to reduce tensile strength and increase hardness, fillers are needed. Findik et al. [9] stated that fillers are reinforced into rubber mixture for better performance and reducing cost. The purpose of this research is to investigate from the mechanical properties of synthetic rubber .

1.3 The Aim of The Work

The main objectives of this research after considering the method and materials used is to study the mechanical properties of Synthetic rubber that uses in the car tires. The mechanical properties such as strength modulus, the creep of rubber and swelling behavior of rubber.

1.4 Scope of Study

The research is based on experimental lab research. The mechanical properties that being tests are tensile, creep and swelling test. The tensile test and creep was done in physical laboratory. Swelling test was done in chemical laboratory with three chemical test; methane solution, acetone solution and benzene.

1.5 Literature Review
1.5.1 Mechanical Properties

1.5.1.1 Tensile Strength

Many researches have been done in order to investigate the mechanical properties of rubber and natural fillers before. A.I. Khalf et al. [10] have investigated the effect of rice husk filler in styrene butadiene rubber with the presence of maleic anhydride. The tensile strength of rubber sample increase until 25 PHR of filler content, before it start to decrease at 30 PHR. This is because of the high content of filler that may cause the poor bonding in rubber matrix causing the tensile strength to drop.
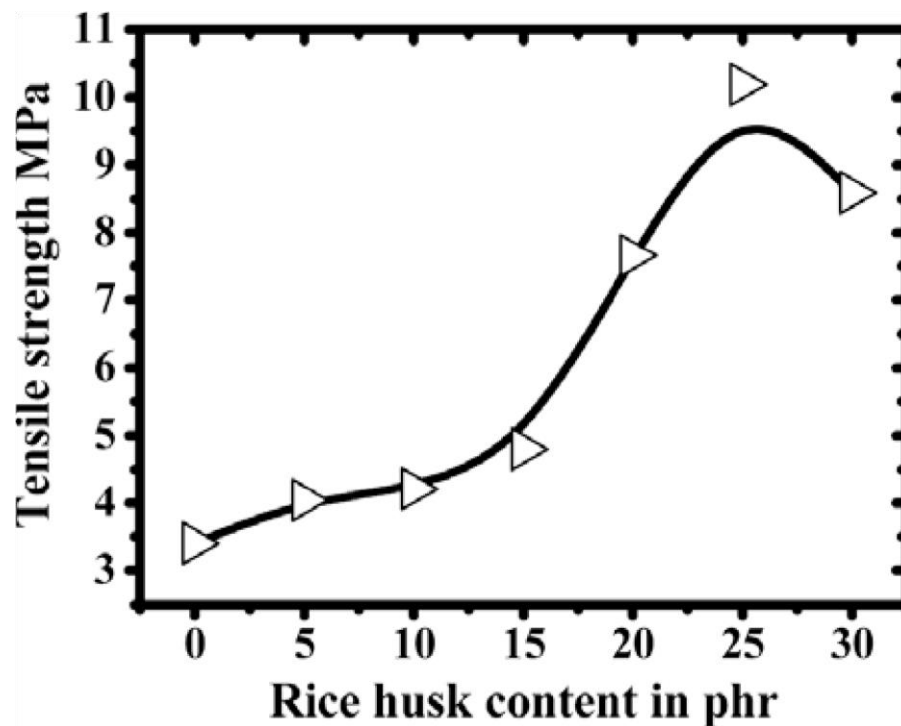
Figure (1.1): Tensile strength-rice husk content relationship

N. Rattanasom et al. [11] on the other hand have investigated the mechanical properties of natural rubber reinforced with various fillers. Gum is virgin rubber, C6 is addition of 6 PHR of clay, CB6 is addition of 6 PHR of carbon black, CB14 is addition of 14 PHR of carbon black, S6 is addition of 6 PHR of silica and S35 is addition of 35 PHR of silica. Clay in 6 PHR quantity show promising aspect in tensile strength than the other.
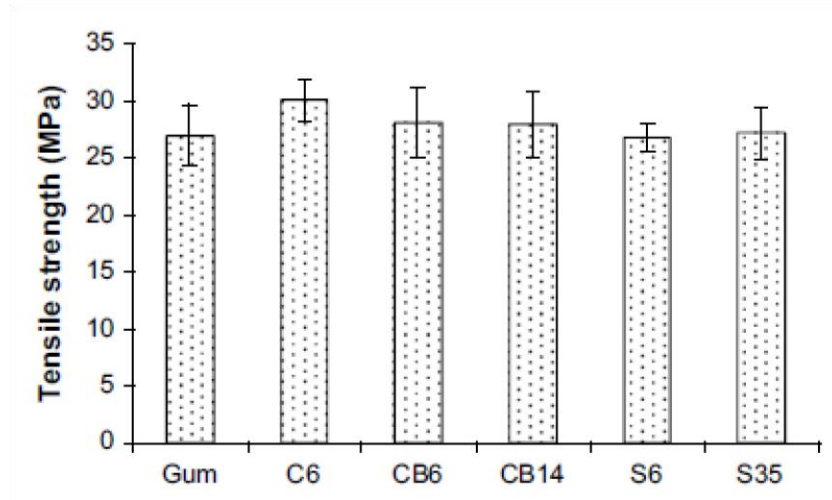
Figure (1.2): Tensile strength of natural rubber reinforced with various fillers.

1.5.1.2 Tensile Modulus

Many researches have been done to determine the tensile modulus of rubber compound. In order to check the compatibility of rubber composite, the modulus is defined in the stress-strain relationship. Hanafi Ismail et al. [12] have determined the tensile modulus of white rice husk ash loading in natural rubber. The additions of natural filler basically increase tensile modulus of the rubber compound.
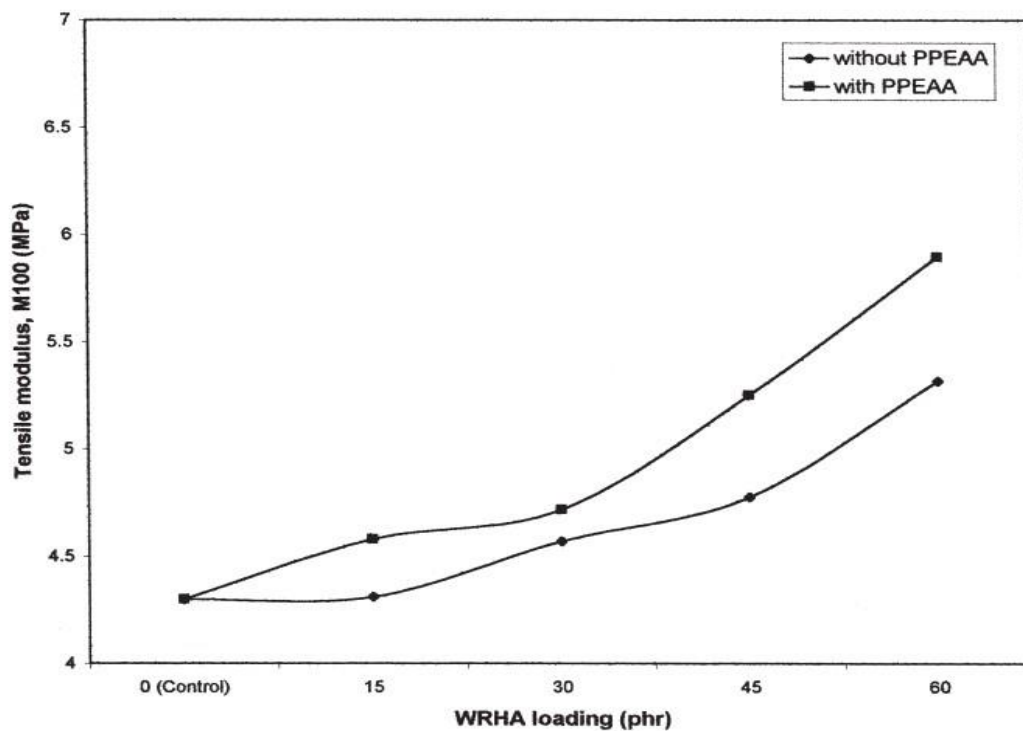
Figure (1.3): Tensile modulus of white rice husk ash loading in natural rubber/linear low density polyethylene blends

1.5.1.3 Swelling

Swelling behavior is the ability of the rubber product to absorb chemical. Swelling test was done in order to check chemical resistance in rubber sample. Many researches have been done according to swelling behavior. Hanafi Ismail et al. [12] have investigated the swelling behavior of recycled rubber powder filler on natural rubber. The more filler give more chemical resistance. As the natural rubber was filled, the rubber became more stable and increase chemical resistance ability and less chemical can be absorb.
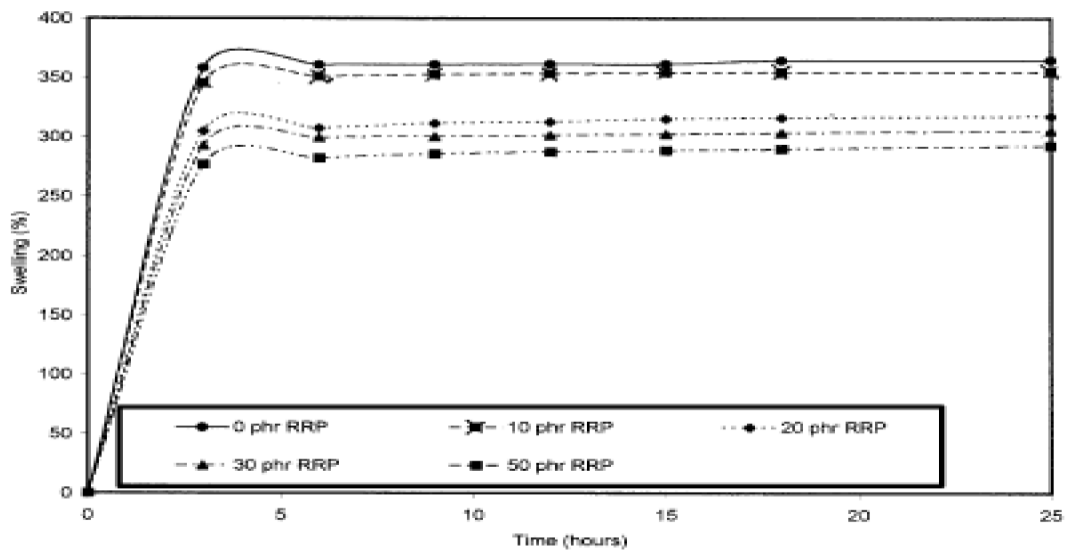
Figure (1.4): Swelling behavior of recycled rubber powder filler on natural rubber.

Chapter Two

Polymers

2.1 Introduction

The word polymer is derived from the classical Greek words poly meaning "many" and meres meaning "parts." Simply stated, a polymer is a long-chain molecule that is composed of a large number of repeating units of identical structure. Certain polymers, such as proteins, cellulose, and silk, are found in nature, while many others, including polystyrene, polyethylene, and nylon, are produced only by synthetic routes. In some cases, naturally occurring polymers can also be produced synthetically. An important example is natural (Hevea) rubber, known as polyisoprene in its synthetic form. Polymers that are capable of high extension under ambient conditions find important applications as elastomers. In addition to natural rubber, there are several important synthetic elastomers including nitrile and butyl rubber. Other polymers may have characteristics that enable their fabrication into long fibers suitable for textile applications. The synthetic fibers, principally nylon and polyester, are good substitutes for naturally occurring fibers such as cotton, wool, and silk. In contrast to the usage of the word polymer, those commercial materials other than elastomers and fibers that are derived from synthetic polymers are called plastics [13]. A typical commercial plastic resin may contain two or more polymers in addition to various additives and fillers. These are added to improve a particular property such as processability, thermal or environmental stability, or mechanical properties

2.2 Historical Development of Polymers

Starting in 1811, Henri Braconnot did pioneering work in derivative cellulose compounds, perhaps the earliest important work in polymer science. The development of vulcanization later in the nineteenth century improved the durability of the natural polymer rubber, signifying the first popularized semi-synthetic polymer. In 1907, Leo Baekeland created the first completely synthetic

polymer, Bakelite, by reacting phenol and formaldehyde at precisely controlled temperature and pressure. Bakelite was then publicly introduced in 1909.

Polymers have existed in natural form since life began and those such as DNA, RNA, proteins and polysaccharides play crucial roles in plant and animal life. From the earliest times, man has exploited naturally-occurring polymers as materials for providing clothing, decoration, shelter, tools, weapons, writing materials and other requirements. However, the origin of today's polymer industry is commonly accepted as being the nineteenth century when important discoveries were made concerning the modification of certain natural polymers. In eighteenth century, Thomas Hancock gave an idea of modification of natural rubber through blending with certain additives. Later on, Charles Goodyear improved the properties of natural rubber through vulcanization process with sulfur. The Bakelite was the first synthetic polymer produced and was soon followed by the synthetic fiber, rayon, which was developed in 1911. The systematic study of polymer science started only about a century back with the pioneering work of Herman Staudinger.

2.3 Polymer types

Polymer is a generic name given to a vast number of materials of high molecular weight. These materials exist in countless form and numbers because of very large number and type of atoms present in their molecule. Polymer can have different chemical structure, physical properties, mechanical behavior, thermal characteristics, etc., and on the basis of these properties polymer can be classified in different ways, which are summarized in Table 1.1, whereas, important and broad classification of polymers are described in the next section.

Table 1.1: Classification of Polymers

Basis of Classification	Polymer Type
Origin	Natural, Semi synthetic, Synthetic
Thermal Response	Thermoplastic, Thermosetting
Mode of formation	Addition, Condensation
Line structure	Linear, Branched, Cross-linked
Application and Physical Properties	Rubber, Plastic, Fibers
Tacticity	Isotactic, Syndiotactic, Atactic
Crystallinity	Non crystalline(amorphous), Semi-crystalline, Crystalline
Polarity	Polar, Non polar
Chain	Hetro, Homo-chain

2.3.1 Origin

On the basis of their occurrence in nature, polymers have been classified in three types [14]:-

A. **Natural polymer: -** The polymers, which occur in nature are called natural polymer also known as biopolymers. Examples of such polymers are natural rubber, natural silk, cellulose, starch, proteins, etc.

B. **Semi synthetic polymer: -** They are the chemically modified natural polymers such as hydrogenated, natural rubber, cellulosic, cellulose nitrate, methyl cellulose, etc.

C. **Synthetic polymer: -** The polymer which has been synthesized in the laboratory is known as synthetic polymer. These are also known as manmade polymers. Examples of such polymers are polyvinyl alcohol, polyethylene, polystyrene, polysulfone, etc.

2.3.2 Thermal Response

On the basis of thermal response, polymers can be classified into two groups [15]:-

A. **Thermoplastic polymers:-** They can be softened or plasticized repeatedly on application of thermal energy, without much change in properties if treated with certain precautions. Example of such polymers are Polyolefins, nylons, linear polyesters and polyethers, PVC, sealing wax etc.

B. **Thermosetting polymers:** - Some polymers undergo certain chemical changes on heating and convert themselves into an infusible mass. The curing or setting process involves chemical reaction leading to further growth and cross linking of the polymer chain molecules and producing giant molecules. For example, Phenolic, resins, urea, epoxy resins, diene rubbers, etc.

2.3.3 Mode of Formation

On the basis of mode of formation, polymers can be classified as:-

A. **Addition polymers: -** They are formed from olefinic, diolefnic, vinyl and related monomers. They are formed from simple addition of monomer

molecules to each other in a quick succession by a chain mechanism. This process is called addition polymerization. Examples of such polymers are polyethylene, polypropylene, polystyrene.

B. **Condensation polymer:-** They are formed from intermolecular reactions between bifunctional or polyfunctional monomer molecules having reactive functional groups such as –OH, -COOH, -NH$_2$, -NCO, etc..

2.3.4 Line Structure
On the basis of structure, polymers are of three types.

A. **Linear polymer:-** If the monomer units are joined in a linear fashion, polymer is said to be linear polymer.
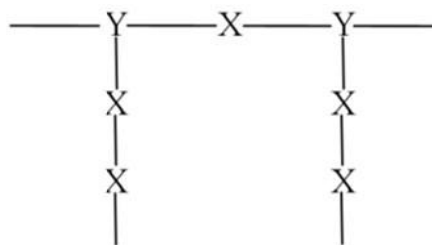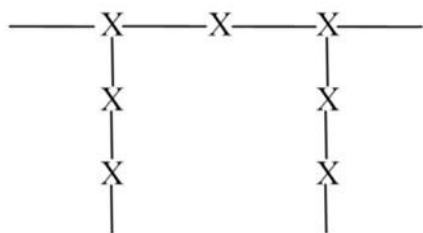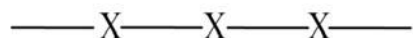
Linear Homopolymer   Linear Copolymer

Figure (2.1) shows the linear polymer

B. **Branched polymer:-** When monomer units are joined in branched manner, it is called branched polymer.

C. **Cross linked polymer:-** A polymer is said to be a cross linked polymer, if the monomer units are joined together in a chain fashion.
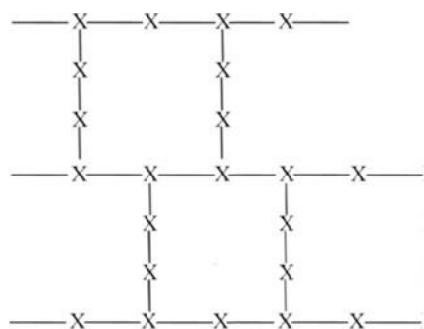
Cross linked Homopolymer   Cross linked Copolymer
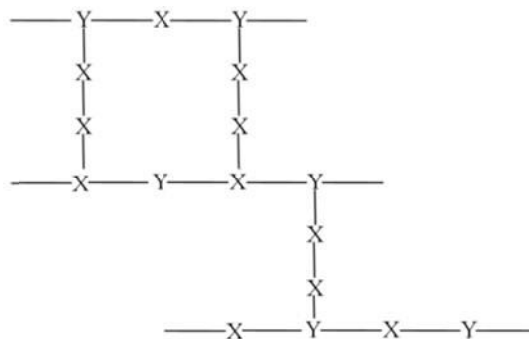
Figure (2.2) shows the type of cross linked polymer

2.3.5 Application and Physical Properties

Depending on its ultimate form and use a polymer can be classified as:-

A. **Rubber (Elastomers):-** Rubber is high molecular weight polymer with long flexible chains and weak intermolecular forces. They exhibits tensile strength in the range of 300-3000 psi and elongation at break ranging between 300-1000%. Examples are natural and synthetic rubber.

B. **Plastics: -** Plastics are relatively tough substances with high molecular weight that can be molded with (or without) the application of heat. These are usually much stronger than rubbers. They exhibit tensile strength ranging

between 4000-15000 psi and elongation at break ranging usually from 20 to 200% or even higher. The examples of plastics are, polyethylene, polypropylene, PVC, polystyrene, etc.

C. **Fibers: -** Fibers are long- chain polymers characterized by highly crystalline regions resulting mainly from secondary forces. They have a much lower elasticity than plastics and elastomers. They also have high tensile strength ranging between 20,000- 150,000 psi, are light weight and possess moisture absorption properties.

2.3.6 Tacticity:-

It may be defined as the geometric arrangement (orientation) of the characteristic group of monomer unit with respect to the main chain (backbone) of the polymers. On the basis of structure, polymer may be classified into three groups:-

A. **sotactic polymer:-** It is the type of polymer in which the characteristic group are arranged on the same side of the main chain.
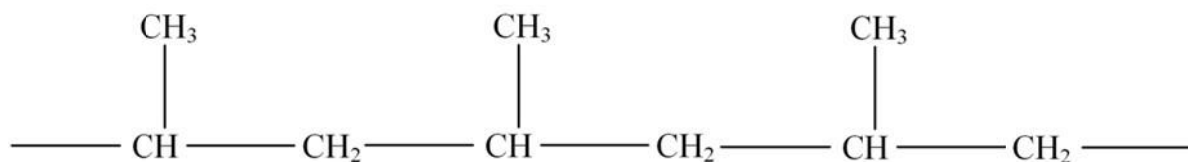
Figure (2.3) shows Isotactic polypropene

B. Syndiotactic polymer:- A polymer is said to be syndiotactic if the side group (characteristic group) are arranged in an alternate fashion.

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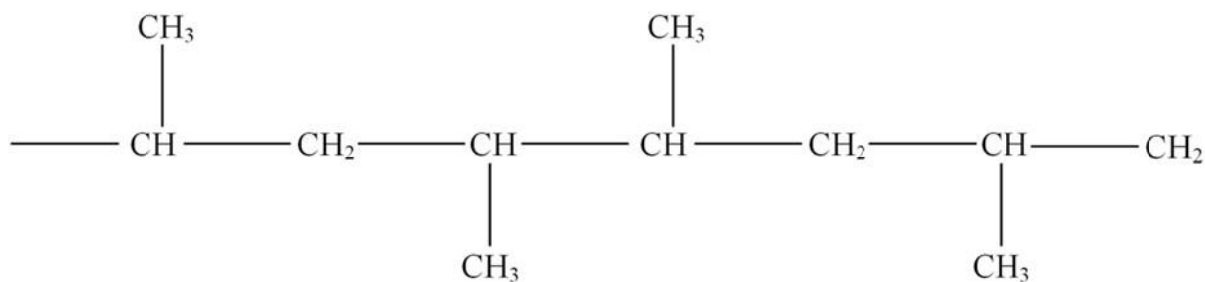
Figure (2.4) shows the Syndiotatic polypropene

C. **Atactic polymer:-** A polymer is said to be atactic, if the characteristic groups (side group) are arranged in irregular fashion (randomness) around the main chain. It has proper strength and more elasticity.
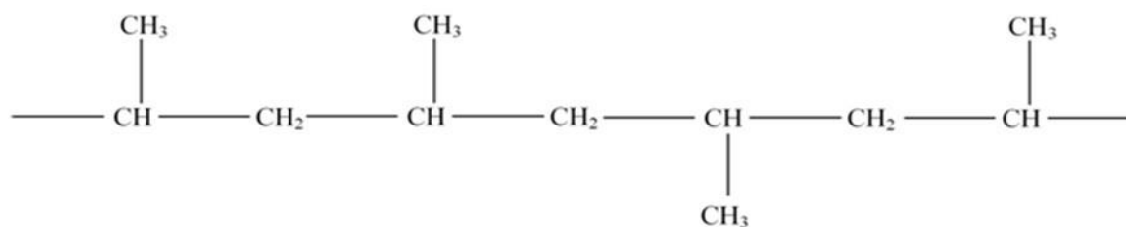
Figure (2.5) shows atactic polypropene

2.4 Polymer synthesis & processing

Processing of polymers mainly involves preparing a particular polymer by synthesis of available raw materials, followed by forming into various shapes. Raw materials for polymerization are usually derived from coal and petroleum products. The large molecules of many commercially useful polymers must be synthesized from substances having smaller molecules. The synthesis of the large molecule polymers is known as polymerization in which monomer units are joined

over and over to become a large molecule. More upon, properties of a polymer can be enhanced or modified with the addition of special materials. This is followed by forming operation. Addition polymerization and condensation polymerization are the two main ways of polymerization.

2.4.1 Addition polymerization

Also known as chain reaction polymerization, is a process in which multi-functional monomer units are attached one at a time in chainlike fashion to form linear/3-D macro-molecules. The composition of the macro-molecule is an exact multiple of for that of the original reactant monomer. This kind of polymerization involves three distinct stages – initiation, propagation and termination. To initiate the process, an initiator is added to the monomer. This forms free radicals with a reactive site that attracts one of the carbon atoms of the monomer [16].When this occurs, the reactive site is transferred to the other carbon atom in the monomer and a chain begins to form in propagation stage. A common initiator is benzoyl peroxide. When polymerization is nearly complete, remaining monomers must diffuse a long distance to reach reactive site, thus the growth rate decreases. The process for polyethylene is as follows

$$R\cdot + \begin{array}{c} H \\ | \\ C \\ | \\ H \end{array} = \begin{array}{c} H \\ | \\ C \\ | \\ H \end{array} \longrightarrow R - \begin{array}{c} H \\ | \\ C \\ | \\ H \end{array} - \begin{array}{c} H \\ | \\ C \cdot \\ | \\ H \end{array}$$
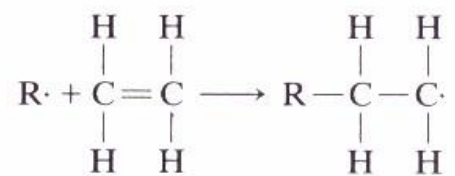
Here R: represents the active initiator. Propagation involves the linear growth of the molecule as monomer units become attached to one another in succession to

produce the chain molecule, which is represented, again for polyethylene, as follows

$$R-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}\cdot + \underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}=\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}} \longrightarrow R-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}\cdot$$
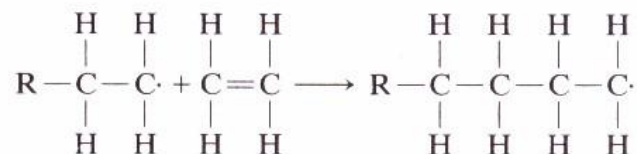
As we need polymers with controlled molecular weight, polymerization needs to be terminated at some stage. Propagation may end or terminate in different ways. First, the active ends of two propagating chains may react or link together to form a non-reactive molecule, as follows:

$$R\cdots\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}\cdot + \cdot\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}\cdots R \longrightarrow$$

$$R\cdots\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}\cdots R$$
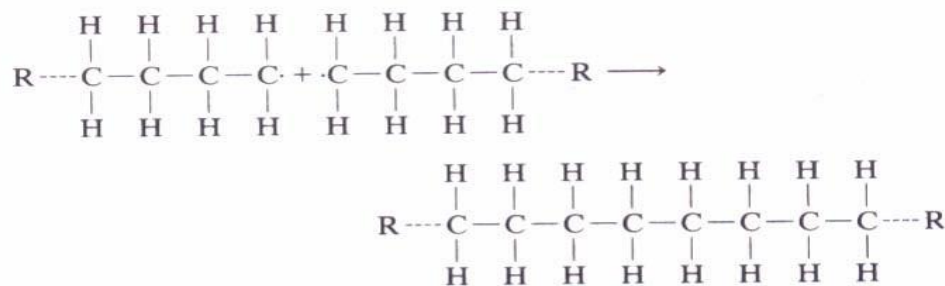
Thus terminating the growth of each chain or an active chain end may react with an initiator or other chemical species having a single active bond, as follows:

$$-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}\cdot + \cdot R \longrightarrow -\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-R$$
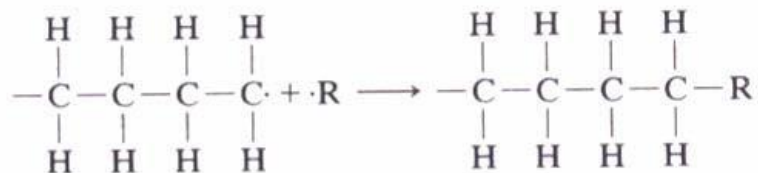
With the resultant cessation of chain growth. Polyethylene, polypropylene, PVC, and polystyrene are synthesized using addition polymerization.

2.4.2 Condensation polymerization

Also known as step growth polymerization, involves more than one monomer species; and there is usually a small molecular weight by-product such as water, which is eliminated. The repeat unit here forms from original monomers, and no product has the chemical formula of mere one mer repeat unit. The polymerization of dimethyl terephthalate and ethylene glycol to produce polyester is an important example. The by-product, methyl alcohol, is condensed off and the two monomers combine to produce a larger molecule (mer repeat unit). Another example, consider the formation of a polyester from the reaction between ethylene glycol and adipic acid; the intermolecular reaction is as follows:
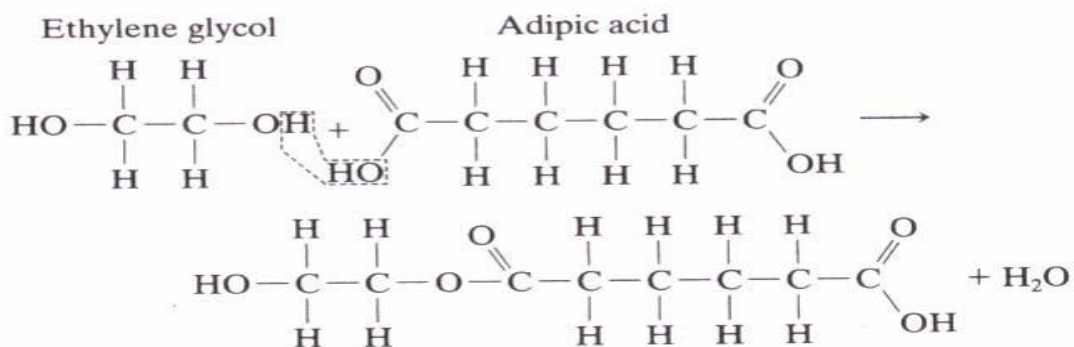
This stepwise process is successively repeated, producing, in this case, a linear molecule. The intermolecular reaction occurs every time a mer repeat unit is formed. Reaction times for condensation are generally longer than for addition polymerization. Polyesters, phenol-formaldehyde, nylons, polycarbonates etc are produced by condensation polymerization. Condensation polymerization reactions also occur in sol-gel processing of ceramic materials.

Chapter Three

Physical Properties of Polymer

3.1 Introduction

Physical properties of polymers include molecular weight, molar volume, density, degree of polymerization, crystallinity of material, and so on. Some of these are discussed herewith in the following sections.

3.2 Degree of Polymerization and Molecular Weight

The degree of polymerization (DP)-n in a polymer molecule is defined as the number of repeating units in the polymer chain. For example,

$$-(-CH_2 - CH_2-)-_n$$
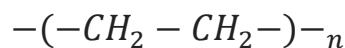
The molecular weight of a polymer molecule is the product of the degree of polymerization and the molecular weight of the repeating unit. The polymer molecules are not identical but are a mixture of many species with different degrees of polymerization, that is, with different molecular weights [17]. Therefore, in the case of polymers we talk about the average values of molecular weights.

3.2.1 Molecular Weight Averages

Suppose we have a set of values $\{x_1, x_1, \dots\dots\dots, x_n\}$ and the corresponding probability of occurrence is given by $\{P_1, P_2, \dots\dots\dots\dots, P_n\}$ then the average value is defined as follows:

$$\sum_{i=0}^{\infty} P_i X_i \tag{3.1}$$

3.2.2 Number-Average Molecular Weight.

If N_i is the number of polymer molecules having the molecular weight M_i, then the "number-average" probability of the given mass is given by:

$$P_i = \frac{N_i}{\sum_{j=0}^{\infty} N_j} \tag{3.2}$$

The number-average molecular weight is given by:

$$M_n = \left[\frac{N_i}{\sum_{j=0}^{\infty} N_j} \right] \quad , \quad M_i = \frac{\sum_{i=0}^{\infty} M_i N_i}{\sum_{j=0}^{\infty} N_j} \tag{3.3}$$

1. The physical properties (such as transition temperature, viscosity, etc.) and mechanical properties (such as strength, stiffness, and toughness) depend on the molecular weight of polymer. The lower the molecular weight, lower the transition temperature, viscosity, and the mechanical properties. Due to increased entanglement of chains with increased molecular weight, the polymer gets higher viscosity in molten state, which makes the processing of polymer difficult.

3.2.3 Weight-Average Molecular Weight.

The weight-average probability is given by:

$$P_i = \frac{N_i M_i}{\sum_{j=0}^{\infty} N_j M_j} \tag{3.4}$$

The weight-average molecular weight is given by:

$$M_w = \sum_{i=0}^{\infty} \left[\frac{N_i M_i}{\sum_{j=0}^{\infty} N_j M_j} \right] \ , \ M_i = \left[\frac{\sum_{i=0}^{\infty} N_i M_i^2}{\sum_{j=0}^{\infty} N_j M_j} \right] \tag{3.5}$$

A typical plot showing the number-average and weight-average molecular weight is shown in Fig.3.1). The number-average molecular weight is less than the weight-average molecular weight (see Fig.3.1). The degree of polymerization can be calculated using the number-average molecular weight.

$$\text{Degree of polymerization} = \frac{\text{Number average molecular weight}}{\text{Molecular weight of the repeat unit}} \tag{3.6}$$
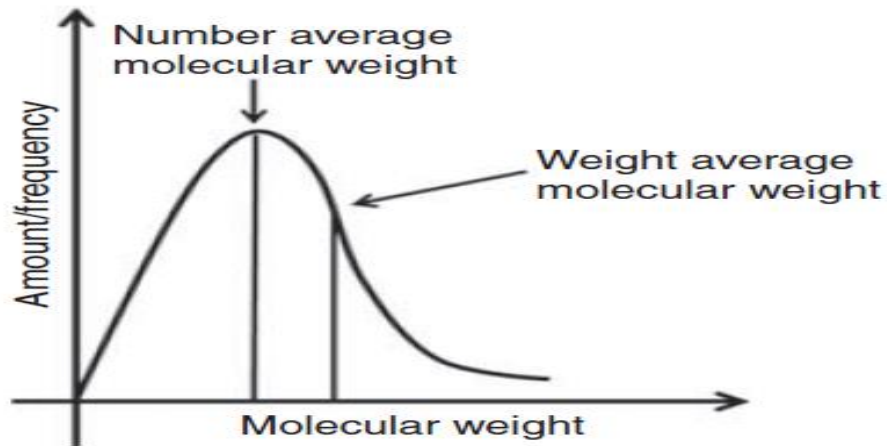

Figure (3.1). Average molecular weights of polymer

3.2.4 Polydispersity Index or Heterogeneity Index

Weight-average molecular weights to the number-average molecular weights is called polydispersity index (PDI) or heterogeneity index, which measures the polydispersity of the polymer mixture.

$$PDI = \frac{M_W}{M_N} \tag{3.7}$$

The dispersity measures heterogeneity of sizes of molecules or particles in the mixture. The mixture is called monodisperse if the molecules have the same size, shape, or mass. If the molecules in the mixture have an inconsistent size, shape and mass distribution, the mixture is called polydisperse.The natural polymers are generally monodisperse as all synthetic polymers are polydisperse with some exceptions. The PDI is equal to or greater than 1 whereas the polymer chains approach uniform chain length, the PDI tends to unity.

3.3 Polymer Crystallinity: Crystalline and Amorphous Polymers

The polymeric chains being very large are found in the polymer in two forms as follows: Lamellar crystalline form in which the chains fold and make lamellar structure arranged in the regular manner and amorphous form in which the chains are in the irregular manner. The lamellae are embedded in the amorphous part and can communicate with other lamellae via tie molecules (see Fig. 3.2). Polymer may be amorphous or semi-crystalline in nature.
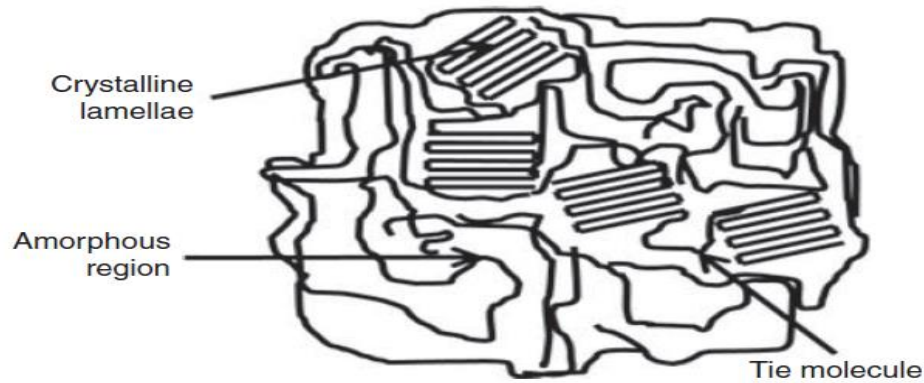
Figure (3.2) Semi-crystalline polymer.

The %crystallinity is given by:

$$\%\text{crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \tag{3.8}$$

Where ρ_c =density of the completely crystalline polymer, ρ_a =density of the completely amorphous polymer, ρ_s =density of the sample,

A typical range of crystallinity can be defined as amorphous (0%) to highly crystalline (>90%). The polymers having simple structural chains as linear chains and slow cooling rate will result in good crystallinity as expected. In slow cooling, sufficient time is available for crystallization to take place. Polymers having high degree of crystallinity are rigid and have high melting point, but their impact resistance is low. However, amorphous polymers are soft and have lower melting points. For a solvent, it is important to state that it can penetrate the amorphous part more easily than the crystalline part. Examples of amorphous polymers: polystyrene and poly(methyl methacrylate). Examples of crystalline polymers: polyethylene, and PET polyester.

Spherulites: if the molten polymer is cooled down, then the crystalline lamellae grow in radial direction from a nucleus along the three dimensions leading to a spherical structure called spherulite. The amorphous region is in between the crystalline lamellae (Fig. 3.3). Spherulite formation and its diameter depend on various parameters such as the number of nucleation sites, polymer molecule structure and rate of cooling [18]. Due to highly ordered lamellae in the spherulite, it shows higher density, hardness, tensile strength, and Young's modulus. The elasticity and impact resistance are shown, because the lamellae are connected to amorphous regions.
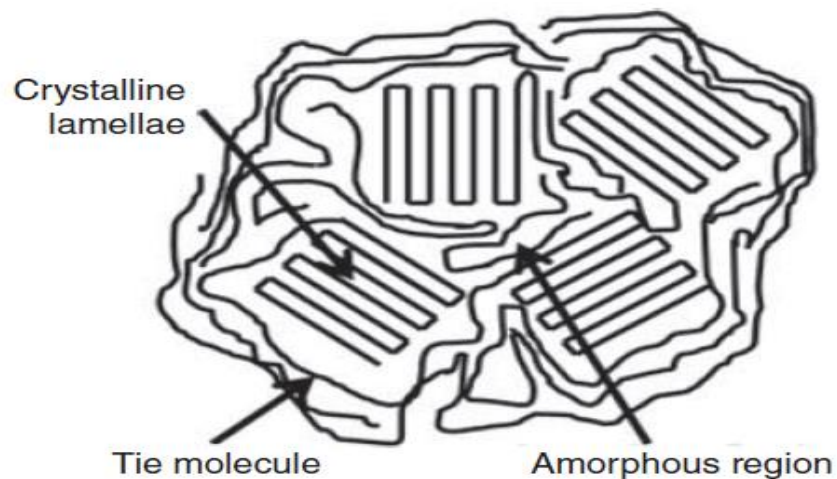

Figure (3.3) a typical structure of spherulite

Chapter Four

Mechanical Properties of Polymers

4.1 Introduction

Polymers vary from liquids and soft rubbers to hard and rigid solids. The unique properties of polymers coupled with their light weight make them preferable alternatives to metallic and ceramic materials in many applications. In the selection of a polymer for a specific end use, careful consideration must be given to its mechanical properties. This consideration is important not only in those applications where the mechanical properties play a primary role, but also in other applications where other characteristics of the polymer such as electrical, optical, or thermal properties are of crucial importance. In the latter cases, mechanical stability and durability of the polymer may be required for the part to perform its function satisfactorily.

The mechanical behavior of a polymer is a function of its microstructure or morphology. Polymer morphology itself depends on many structural and environmental factors. Compared with those of metals and ceramics, polymer properties show a much stronger dependence on temperature and time. This strong time and temperature sensitivity of polymer properties is a consequence of the viscoelastic nature of polymers [19].This implies that polymers exhibit combined viscous and elastic behavior. It is of great importance to be familiar with some basic mechanical properties of the material before its application in any field, such as how much it can be stretched, how much it can be bent, how hard or soft it is, how it behaves on the application of repeated load and so on.

4.2 Strength

In simple words, the strength is the stress required to break the sample. There are several types of the strength, namely tensile (stretching of the polymer), compressional (compressing the polymer), flexural (bending of the polymer), torsional (twisting of the polymer), impact (hammering) and so on. The polymers follow the following order of increasing strength: linear < branched < cross-linked < network.

4.2.1 Factors Affecting the Strength of Polymers

I.   Molecular Weight

The tensile strength of the polymer rises with increase in molecular weight and reaches the saturation level at some value of the molecular weight (Fig. 4.1) the tensile strength is related to molecular weight by the following equation.
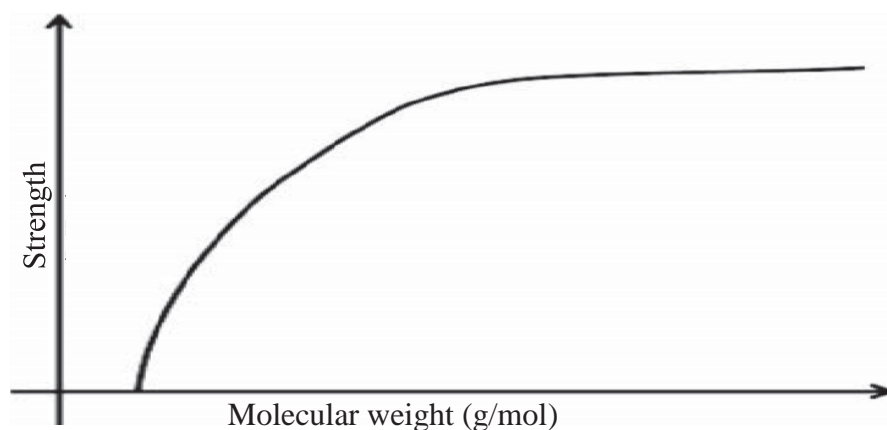

Figure (4.1). Variation of tensile strength with molecular weight of the polymer.

$$\sigma = \sigma_\infty - \frac{A}{M} \tag{4.1}$$

Where σ_∞ Is the tensile strength of the polymer with molecular weight of infinity, A is some constant, M is the molecular weight.

At lower molecular weight, the polymer chains are loosely bonded by weak van der Waals forces and the chains can move easily, responsible for low strength, although crystallinity is present. In case of large molecular weight polymer, the chains become large and hence are entangled, giving strength to the polymer.

II. Cross-linking

The cross-linking restricts the motion of the chains and increases the strength of the polymer

III. Crystallinity

The crystallinity of the polymer increases strength, because in the crystalline phase, the intermolecular bonding is more significant. Hence, the polymer deformation can result in the higher strength leading to oriented chains.

4.3 Percent Elongation to Break (Ultimate Elongation)

It is the strain in the material on its breakage, as shown in Fig. 4.2. It measures the percentage change in the length of the material before fracture. It is a measure of ductility. Ceramics have very low ($<1\%$), metals have moderate ($1–50\%$) and thermoplastic ($>100\%$), thermosets ($<5\%$) value of elongation to break.

4.4 Young's Modulus (Modulus of Elasticity or Tensile Modulus)

Young's Modulus is the ratio of stress to the strain in the linearly elastic region (Fig. 4.3). Elastic modulus is a measure of the stiffness of the material.

$$E = \frac{\text{Tensile Stress}(\sigma)}{\text{Tensile Strain}(\varepsilon)} \qquad (4.2)$$
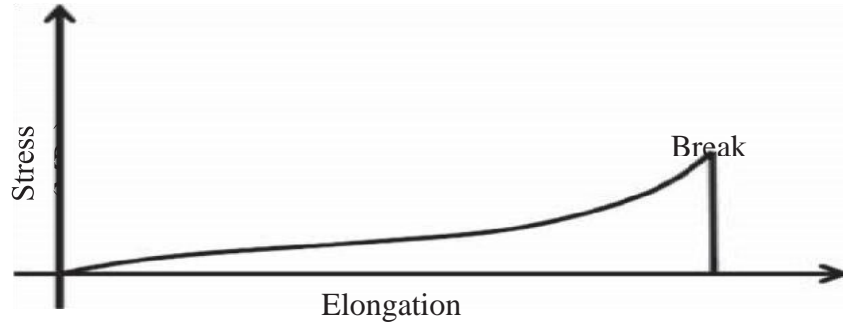

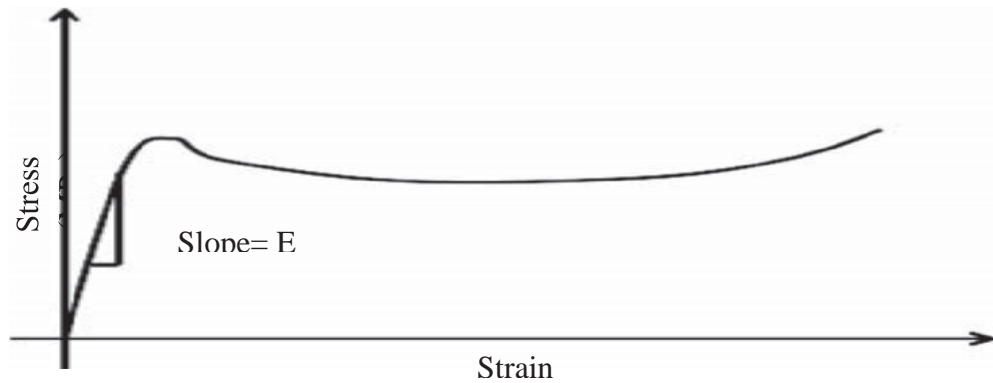Figure (4.2) Elongation to break of the polymer.

Figure (4.3). Young's modulus of the polymer

4.5 Toughness

The toughness of a material is given by the area under a stress–strain curve (Fig.4.4).

$$\text{toughness} = \int \sigma \, d\varepsilon \qquad (4.3)$$
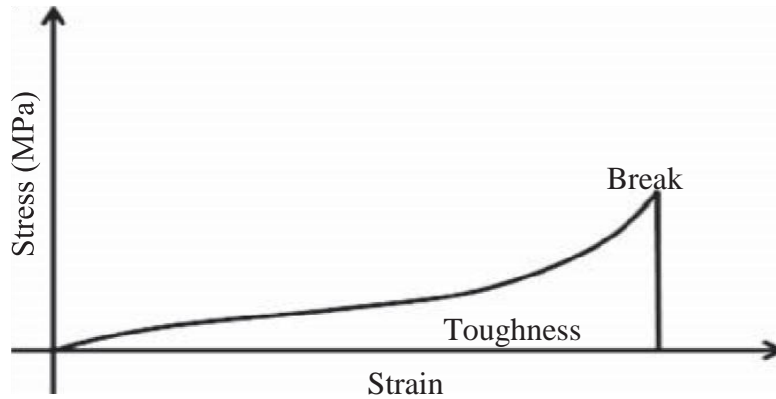
Figure 4.4 .The toughness of polymer material
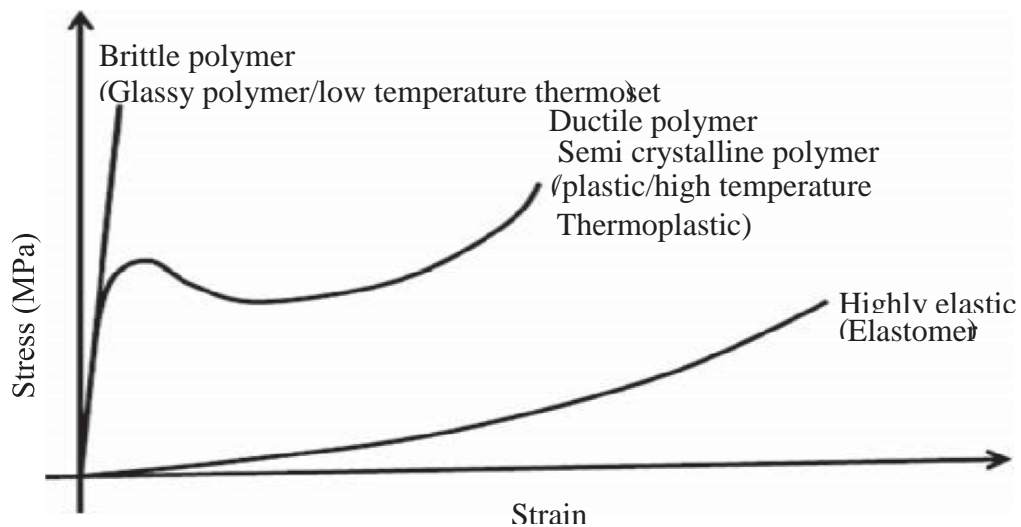
Figure (4.5). Stress–strain behavior of different types of materials.

The toughness measures the energy absorbed by the material before it breaks. A typical stress–strain curve is shown in Fig. 4.5, which compares the stress–strain behavior of different types of materials. The rigid materials possess high Young's modulus (such as brittle polymers), and ductile polymers also possess similar elastic modulus, but with higher fracture toughness. However, elastomers have low values of Young's modulus and are rubbery in nature. The yield strength of

the plastic polymer is the corresponding stress where the elastic region (linear portion of the curve) ends (Fig. 4.6). the tensile strength is the stress corresponding to the fracture of the polymer. The tensile strength may be higher or lower than the yield strength (Fig. 4.6). the mechanical properties of the polymer are strongly affected by the temperature. A typical plot of stress versus strain is shown in Fig. 4.7. From the plot, it is clear that with increase in the temperature, the elastic modulus and tensile strength are decreased, but the ductility is enhanced.

4.6   Viscoelasticity:

There are two types of deformations: elastic and viscous. Consider the constant stress level applied to a material as shown in the Fig. 4.8. In the elastic deformation (Fig. 4.9), the strain is generated at the moment the constant load (or stress) is applied, and this strain is maintained until the stress is not released
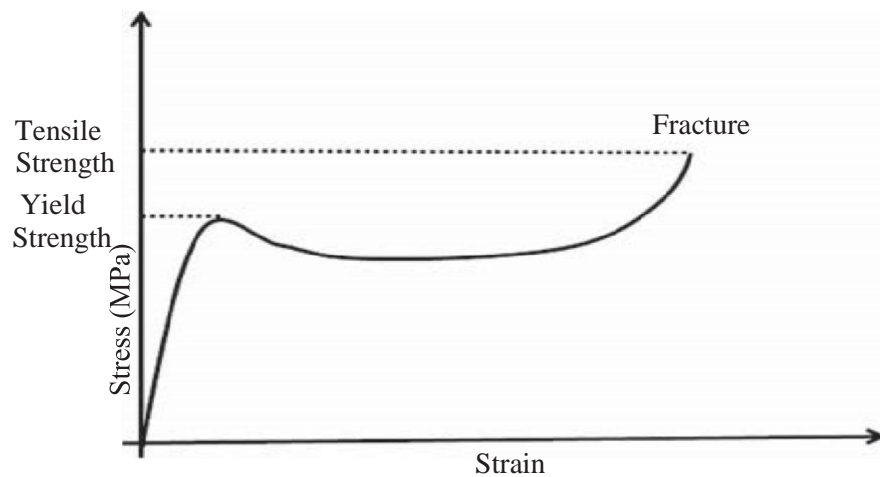

Figure 4.6. Yield strength and tensile strength of polymer.
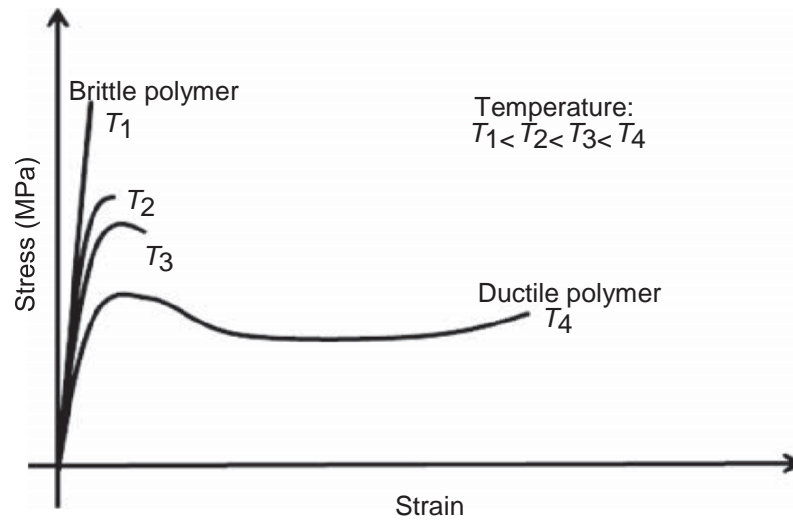
Figure (4.7) Effect of temperature on the mechanical properties of polymer.
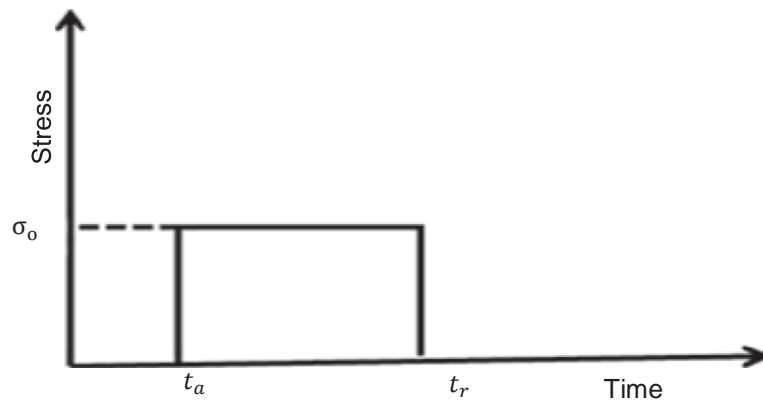
Figure (4.8). Constant stress applied to a polymer.
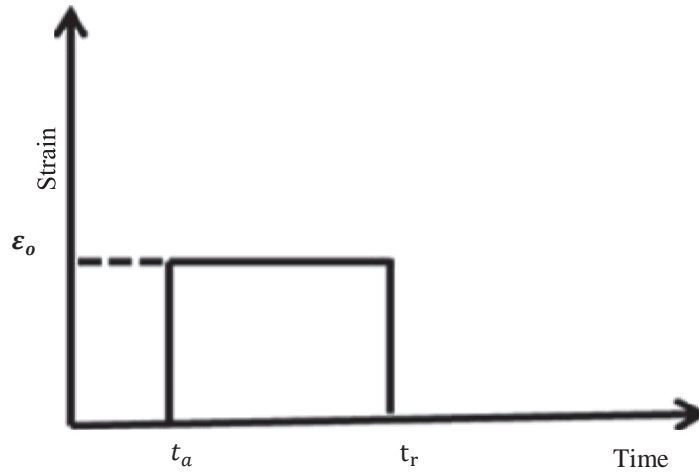
Figure (4.9) Elastic deformation

On removal of the stress, the material recovers its original dimensions completely, that is the deformation is reversible (Fig. A1.17), that is:

$$\sigma = E\varepsilon \qquad (4.4)$$

Where E is the elastic modulus, σ is applied stress, and ϵ is the strain developed.

However, in viscous deformation (Fig. 4.10), the strain generated is not instantaneous and it is time dependent. The strain keeps on increasing with time on application of the constant load, that is, the recovery process is delayed. When the load is removed, the material does not return to its original dimensions completely, that is, this deformation is irreversible (Fig. 4.10).

$$\sigma = \gamma \frac{d\varepsilon}{dt} \qquad (4.5)$$

Where γ =viscosity, and   dϵ /dt =strain rate

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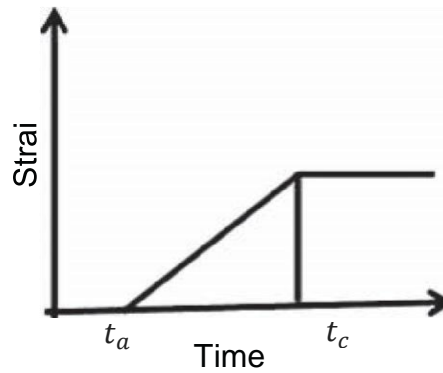
Figure (4.10) viscous deformation.
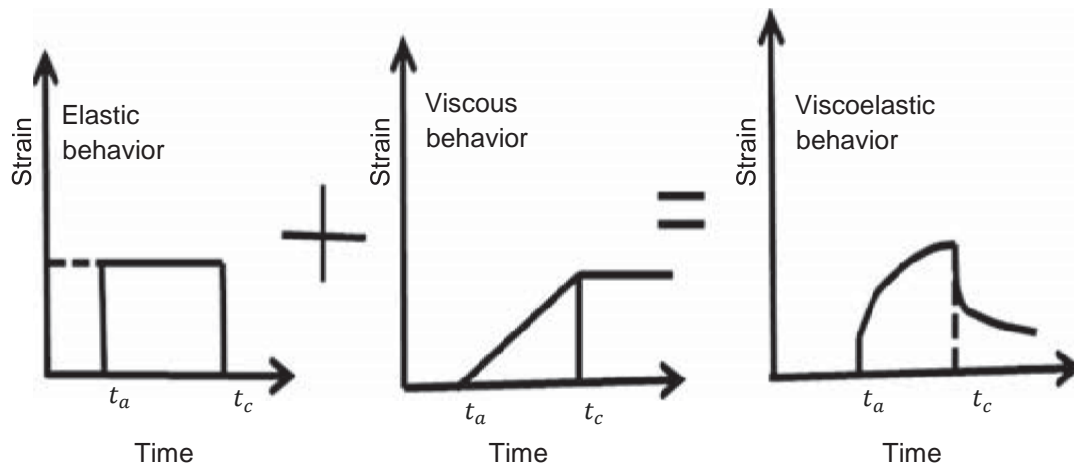
Figure (4.11) Viscoelastic deformation: the combined behavior of viscosity and elasticity.

Usually, polymers show a combined behavior of elastic and plastic deformation (Fig. 4.11) depending on the temperature and strain rate. At low temperature and high strain rate, elastic behavior is observed, and at high temperature but low strain rate, the viscous behavior is observed. The combined behavior of viscosity and elasticity is observed at intermediate temperature and strain rate values. This behavior is termed as viscoelasticity, and the polymer is termed as viscoelastic.

4.6.1 Viscoelastic Relaxation Modulus

At a given temperature, when the polymer is strained to a given value, then the stress required to maintain this strain is found to decrease with time. This is called stress relaxation (Fig. 4.12). The stress required to maintain the constant strain value is decreased with time, because the molecules of polymer get relaxed with time, and to maintain the level of strain, somewhat lower value of stress is sufficient (Fig. 4.12).

$$E_{rel}(t) = \frac{\sigma(t)}{\varepsilon_o} \tag{4.6}$$
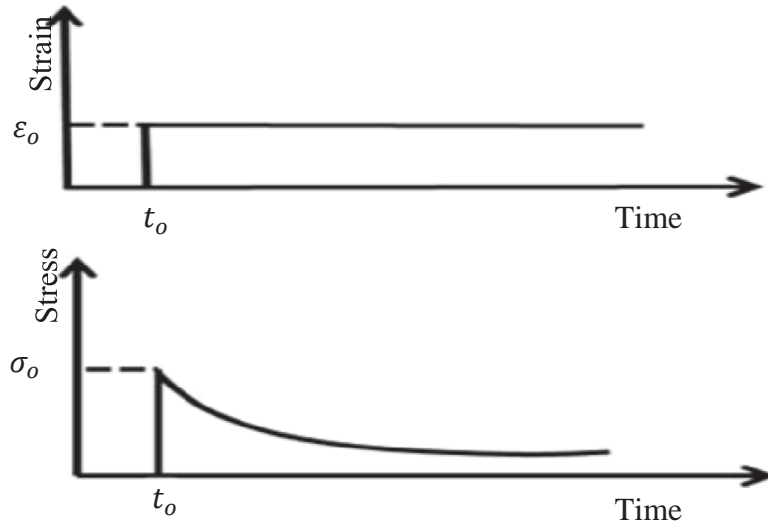
Figure (4.12). Stress relaxation in polymer.
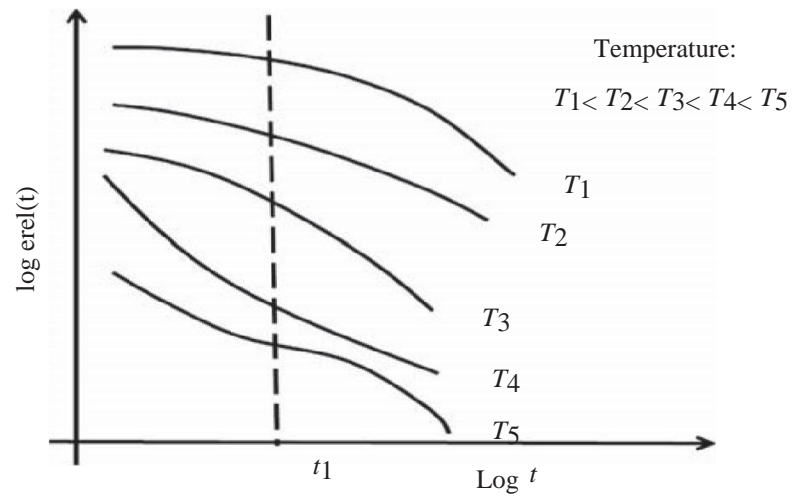
Figure (4.13) Variation of relaxation modulus with temperature and time.
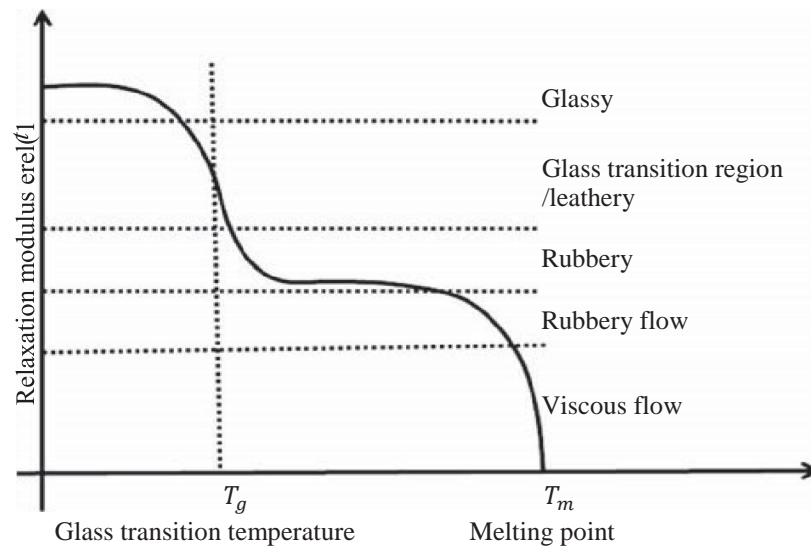
Figure (4.14) Variation of relaxation modulus with temperature after a given time t.

The decrease in stress follows the exponential decay:

$$\sigma = \sigma_o e^{-t/\tau} \tag{4.7}$$

Where σ =stress at time t, σo =peak stress level, and τ =relaxation time constant
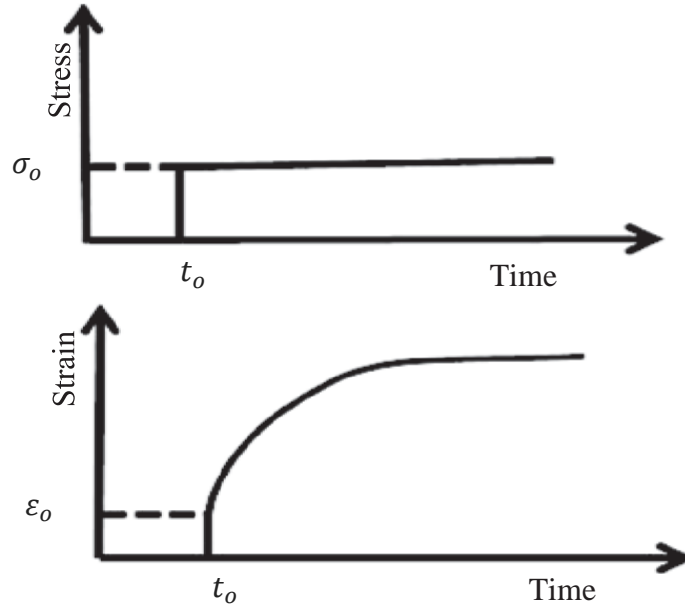
Figure (4.15) Viscoelastic creep.

The relaxation modulus is found to decrease with increase in temperature and time as shown in Fig. 4.13.Now, consider the time t1. Measure the values of relaxation modulus at time t1 at different temperatures, say T1, T2, T3 … for the viscoelastic polymer and plot the relaxation modulus versus temperature. A typical plot is shown in Fig. 4.14. The glass transition temperature lies near the upper temperature extremity.

4.6.2 Viscoelastic Creep

Creep can be considered as the opposite of stress relaxation (lowering of the stress with time maintaining the constant strain level) where the polymer suffers time-dependent deformation (increasing strain with time) at constant stress level. At a given temperature, when a constant load is applied to the material, there is a time-dependent increase of strain in the material (Fig. 4.15). This behavior of the material is called viscoelastic creep. The increase in molecular weight and stiffness of the chains results in better creep resistance of the material.

We can define the time-dependent creep modulus as follows:

$$E_{creep}(t) = \frac{\sigma_o}{\varepsilon(t)} \tag{4.8}$$

Or we can define the creep compliance as follows:

$$J_{creep}(t) = \frac{\varepsilon(t)}{\sigma_o} \tag{4.9}$$

Where σ_o =constant applied stress, (t) =strain at time t.

4.7   Mechanical Tests

Polymer components, like other materials, may fail to perform their intended functions in specific applications as a result of

1. Excessive elastic deformation

2. Yielding or excessive plastic deformation

3. Fracture

Polymers show excessive elastic deformation, particularly in structural, load-bearing applications, due to inadequate rigidity or stiffness. For such failure, the controlling material mechanical property is the elastic modulus. The elastic moduli of some polymers are subject to some measure of control through appropriate structural modification. Failure of polymers in certain applications to carry design loads or occasional accidental overloads may be due to excessive plastic deformation resulting from the inadequate strength properties of the polymer. For the quantification of such failures, the mechanical property of primary interest is the yield strength and the corresponding strain. The ultimate strength, along with the associated strain, also provides useful information.

Cracks constitute regions of material discontinuity and frequently precipitate failure through fracture. Fracture may occur in a sudden, brittle manner or through fatigue (progressive fracture). Brittle fracture occurs in materials where the absence of local yielding results in a build-up of localized stresses, whereas fatigue failure occurs when parts are subjected to alternating or repeated loads

[20]. Fatigue fractures occur without visible signs of yielding since they occur at strengths well below the tensile strength of the material.

Polymers will continue to be used in a variety of end-use situations. Therefore, to ensure their successful performance in these applications, it is necessary to clearly understand their mechanical behavior under a variety of stress conditions. Particular cognizance must be taken of the relatively high sensitivity of polymer failure modes to temperature, time, and loading history. For good design, it is important to be able to relate design load and component dimensions to some appropriate material property that defines the limits of the load-bearing capability of the polymer material. A variety of test methods exist for predicting mechanical performance limits under a variety of loading conditions. These range from simple tension, compression, and shear tests to those designed to test complex stress states and polymer time temperature response. Our discussion emphasizes problems of a one-dimensional nature, and cases of nonlinear deformation will be treated in an elementary fashion.

A. Stress-strain Experiments

Stress–strain experiments have traditionally been the most widely used mechanical test but probably the least understood in terms of interpretation. In stress–strain tests the specimen is deformed (pulled) at a constant rate, and the stress required for this deformation is measured simultaneously (4.16)

As we shall see in subsequent discussions, polymers exhibit a wide variation of behavior in stress–strain tests, ranging from hard and brittle to ductile, including yield and cold drawing. The utility of stress–strain tests for design with polymeric

materials can be greatly enhanced if tests are carried out over a wide range of temperatures and strain rates.
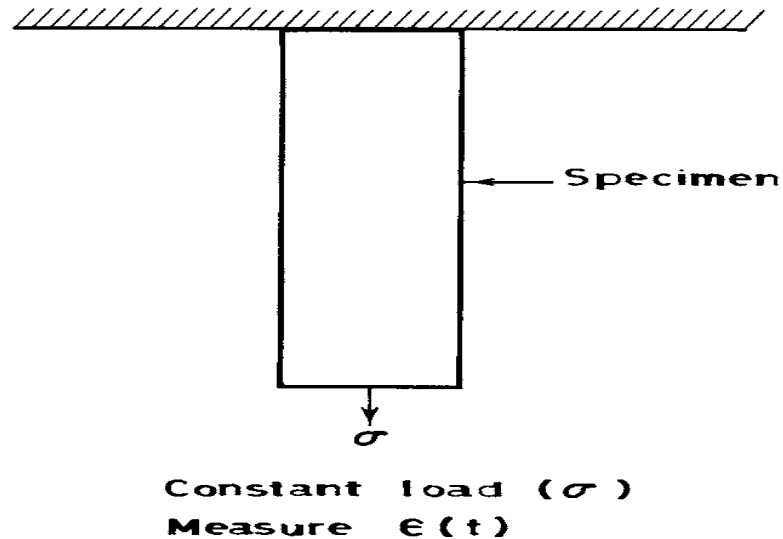
Figure (4.16) Schematic of stress–strain test.

B. Creep Experiments

In creep tests, a specimen is subjected to a constant load, and the strain is measured as a function of time. The test specimen in a laboratory setup can be a plastic film or bar clamped at one end to a rigid support while the load is applied suddenly at the other end (Figure 4.17). The elongation may be measured at time intervals using a cathetometer or a traveling microscope. Measurements may be conducted in an environmental chamber.
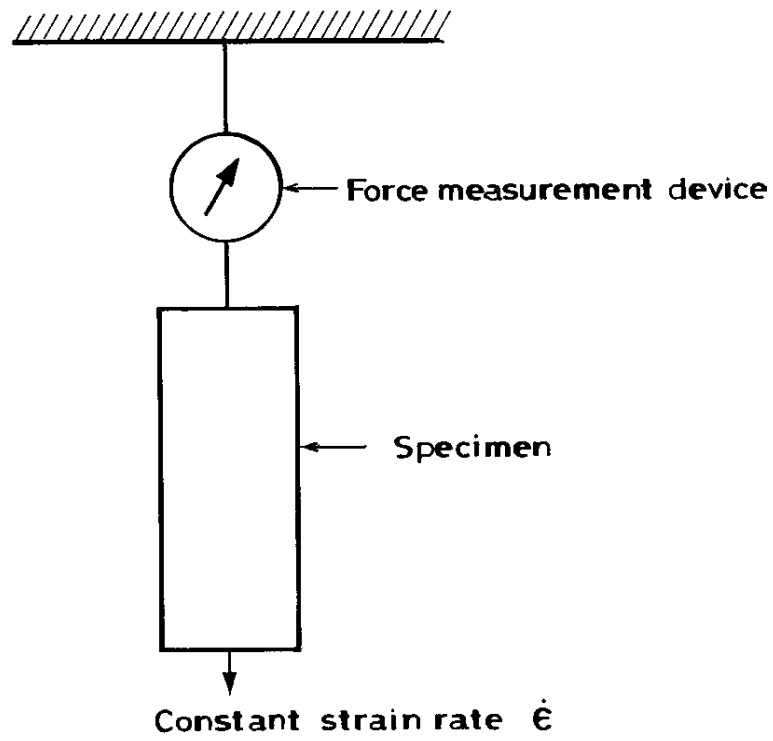
Figure (4.17) Schematic representation of creep experiment.
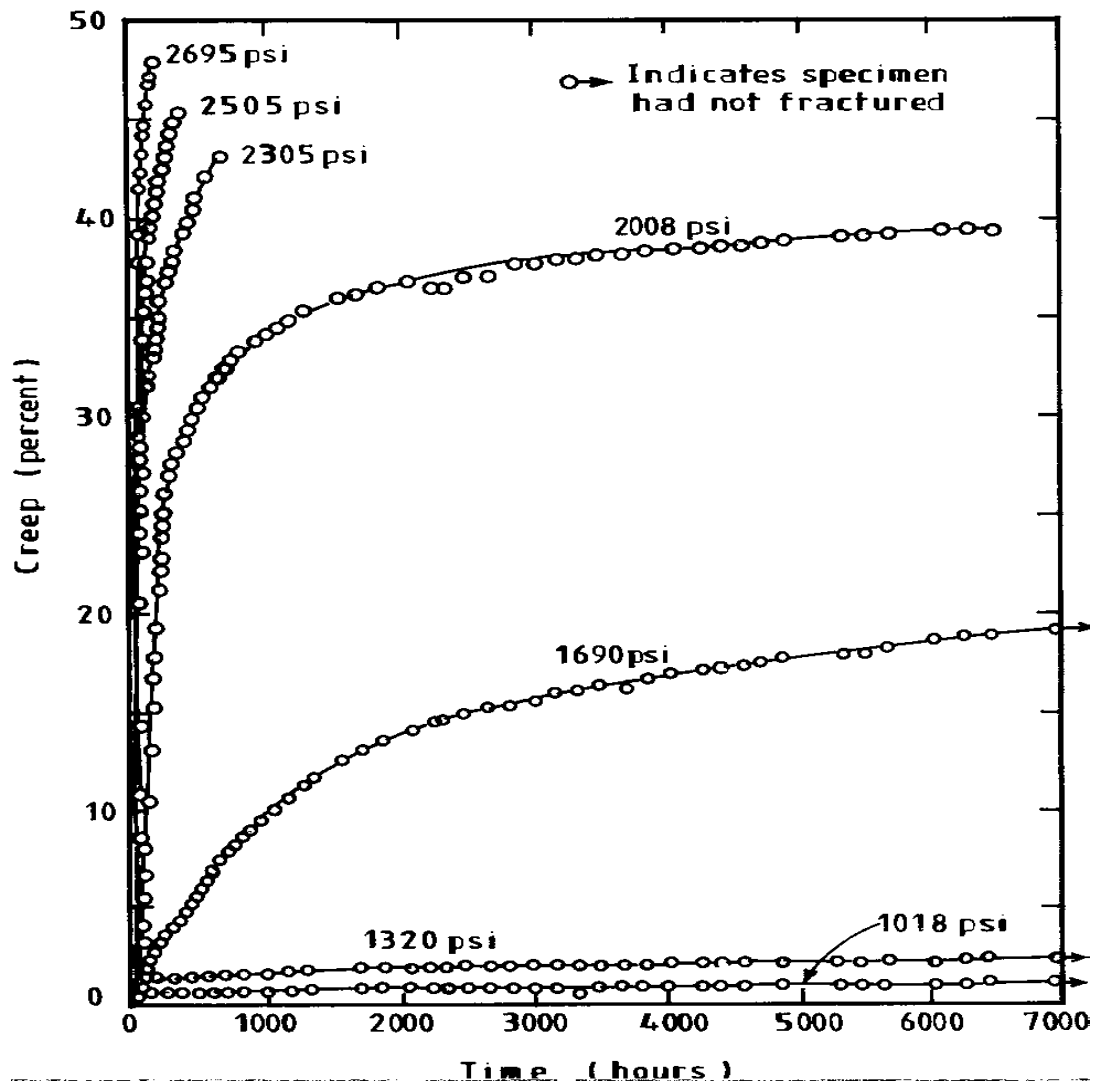
Figure (4.18) Creep of cellulose acetate at 45°C. [21]

Creep tests are made mostly in tension, but creep experiments can also be done in shear, torsion, flexure, or compression. Creep data provide important information for selecting a polymer that must sustain dead loads for long periods. The parameter of interest to the engineer is compliance (J), which is a time-dependent reciprocal of modulus. It is the ratio of the time-dependent strain to the applied constant stress [$J(t) = \varepsilon(t)/\sigma_o$]. Figure 4.18 shows creep curves for a typical polymeric material.

Chapter Five

Material and Method

5.1 Introduction

The industrial development and technological depends largely on progress in the material field as a result of this great industrial development that the world has witnessed in all areas need to study the characteristics of industrial uses multiple materials appeared to be of high quality specifications in terms of cost, weight and properties in general and physics in particular characteristics For adoption in industrial applications. Polymers are one of the most important materials used in industrial applications such as the manufacture of tires and some shoes are used in wire insulators and other applications. In this chapter we will study some properties of polymers mechanics. To study the necessary set of valuable properties, polymers differing from one another by their chemical structure and properties are usually mixed together, either homogeneously or heterogeneously. The mechanical properties of inhomogeneous mixture are worse than those of individual polymers, while the mechanical properties of homogeneous mixture are good. Polymers can exhibit the features of glassy, brittle solid or an elastic rubber, or that of a viscous liquid, depending on the temperature and time scale of measurement. The studies on mechanical properties of polymer can, therefore, be carried out by subjecting them to some form of mechanical stress either continuous or in a periodic manner at different rate. Some of the important properties of polymers with regard to their use as engineering material are tensile strength, compressive and flexural strength, hardness, creep, fatigue resistance and impact resistance. Toughness of a polymer is the ability to absorb mechanical energy without fracturing. The property such as tensile strength is the maximum

amount of tensile load per unit area a material can withstand, while the tensile elongation gives the measure of increase in length in response to a tensile load expressed as a percent of the original length. Elongation at break is the maximum elongation the plastic can undergo.

Engineering applications of polymers are governed to a great extent by strain hardening considerations. The designer using polymeric materials must, therefore, understand their mechanical behavior with respect to the maximum permissible strains to avoid failure. As for most materials, a simple tensile stress-strain curve provides a good start towards understanding the mechanical behavior of a particular polymer. This curve is usually established by continuously measuring the force developed as the sample is elongated at constant rate of extension until it breaks.

5.2 Material

5.2.1 Specimens

In this research two types of rubber polymer used in the manufacture of car tires ,internal and external ,the first type contains the percentage of carbon 30% other type contains the percentage of carbon 70% At room temperature. And also used some chemical solutions Such as acetone is the organic compound with the formula $((CH)_3)_2CO$ it is a colorless, volatile, flammable liquid, and is the simplest ketone. Acetone is miscible with water and serves as an important solvent in its own right, typically for cleaning purposes in laboratories. The molecular weight of acetone is 58.08 g/mole and its density is 784 kg/m^3 [22]. Also the methane solution use, it is a chemical compound with the chemical formula CH_4 it is a group-14 hydride and the simplest alkane, and is the main constituent of

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natural gas the molecular weight of methane is 16.04 g/mole and its density is 0.656 kg/m^3 [23].Benzene was also used is an important organic chemical compound with the chemical formula C_6H_6 As it contains only carbon and hydrogen atoms, benzene is classed as a hydrocarbon, the molecular weight of benzene is 78.114 g/mol and its density is 876 kg/m^3[24]. This chemical solutions was used to studies of some mechanical properties of rubber, and that by knowing the impact on the m ass of rubber and its interaction with it.

5.3 Method

5.3.1 Stress, Strain and Young's Modulus

An experiment was carried out by taking a Specimen of synthetic rubber which contains 30% carbon and its original length was measured. The Specimen was placed on a holder and loads were placed. The change in length was measured and thus the stress and strain curves were obtained by the graph.

5.3.2 Swelling measurement

The experiment was carried out by taking a specimen of synthetic rubber containing the ratio of carbon 30% with a specific mass, and was placed in the solution and the mass was measured after different times passage. The values of the change in mass versus the time of change were recorded. This experiment was applied in two types of solutions, Methane and Acetone solution. Also the specimen of the synthetic rubber containing of 70% carbon was placed in the benzene solution. And the change in the mass were recorded in the different times. Results were obtained from the graph.

5.3.3 Creep measurement

This experiment was conducted by taking the tow type of a specimens of synthetic rubber the length of the original specimens was measured both. The sample was installed and a heavy load was placed at the bottom of the specimen and the change in length was measured in centimeters against the time of change. The graph was drawn and calculations were made.

5.4 Results

Table (5.1) shows the values of the strain and stress

$\sigma = \frac{mg}{A}$ MN/m^2	$\varepsilon = \Delta L / L_o$ m
0	0
24.525	0.0025
49.05	0.0075
73.575	0.0327
98.1	0.0453
122.625	0.0579
147.15	0.0831
171.675	0.1083
196.2	0.1209
220.725	0.146

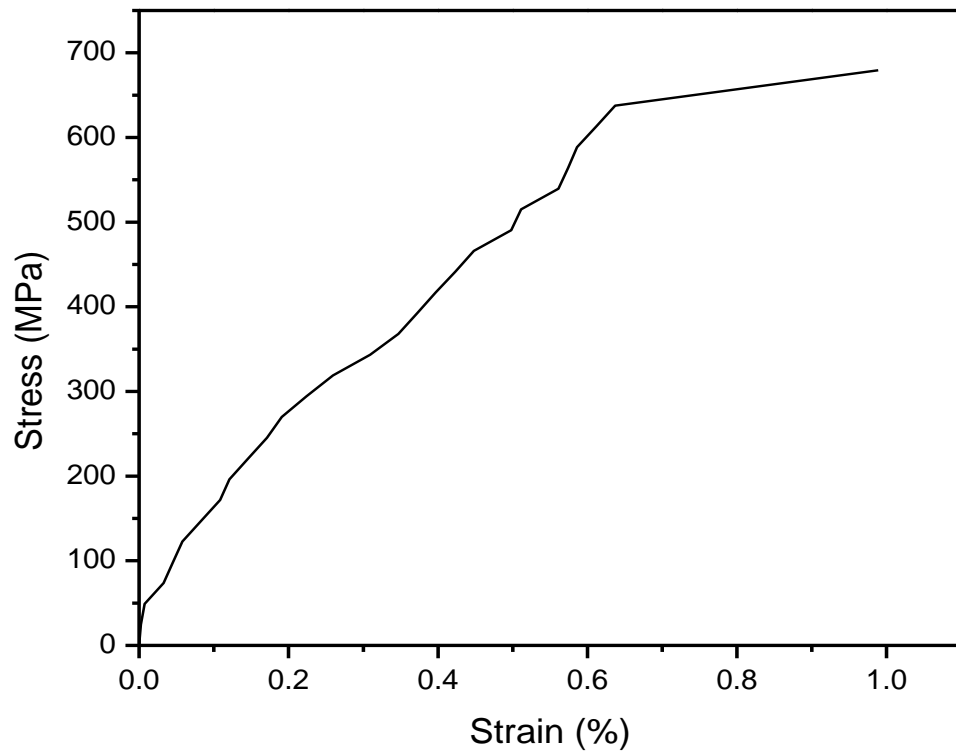|	
245.25	0.171
269.775	0.191
294.3	0.224
318.825	0.2594
343.35	0.309
367.875	0.347
392.4	0.372
416.925	0.397
441.45	0.423
465.975	0.448
490.5	0.498
515.025	0.511
539.55	0.561
564.075	0.574
588.6	0.586
613.125	0.612
637.65	0.637
679.465	0.989

Figure (5.1) illustrate the relation between the stress and strain

From the curve above it was found that the Elastic region modulus (young's modulus) (E)

$$E = \text{slop} \times \frac{L}{A}$$

$$789 \times \frac{0.397}{40 \times 10^{-6}}$$

$$7.836 \times 10^{6} \ N/m^{2}$$

$$= 7.836 \ MN/m^{2}$$

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$$\text{Lower yield strength} = \frac{\text{maximum load}}{\text{cross-section area}}$$

$$= \frac{319.134}{40 \times 10^{-6}} = 7.978 \ MN/m^2$$

$$\text{Yield strength at 0.2 \%} = \frac{360.48}{40 \times 10^{-6}} = 9.012 MN/m^2$$

$$\text{Upper yield strength} = \frac{545.674}{40 \times 10^{-6}} = 13.641 MN/m^2$$

Table (5.2) illustrate the values of the change in the mass against the time for the methane solution

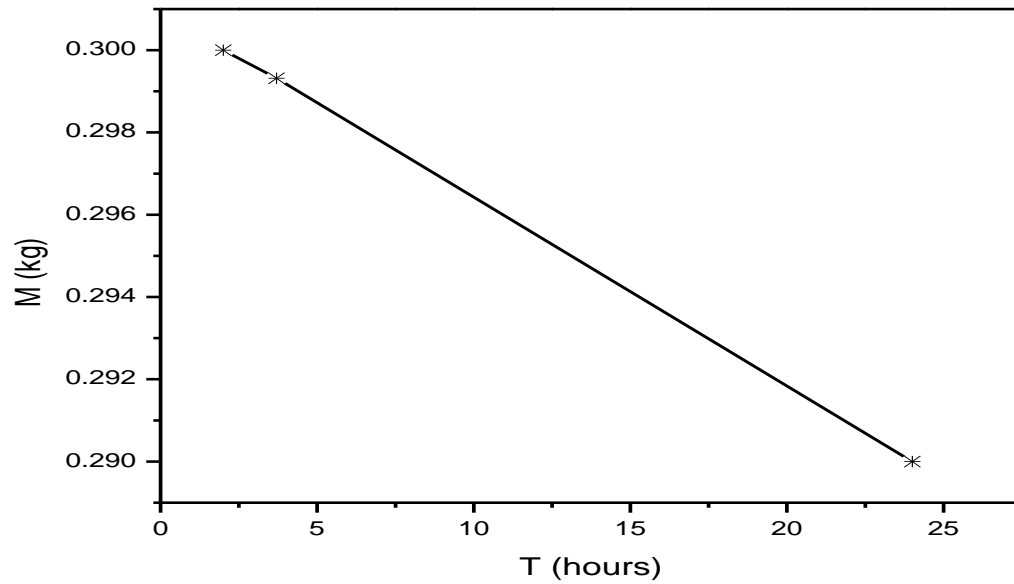| M0/g	T/hours	m/g
0.30	2	0.30
0.30	4	0.30
0.30	24	0.29

Figure (5.2) illustrate the relation between the load and times

Table (5.3) shows the values of the change in the mass with time for the acetone solution

M0/g	T/hours	m/g
0.30	2	0.30
0.30	4	0.30
0.30	24	0.30
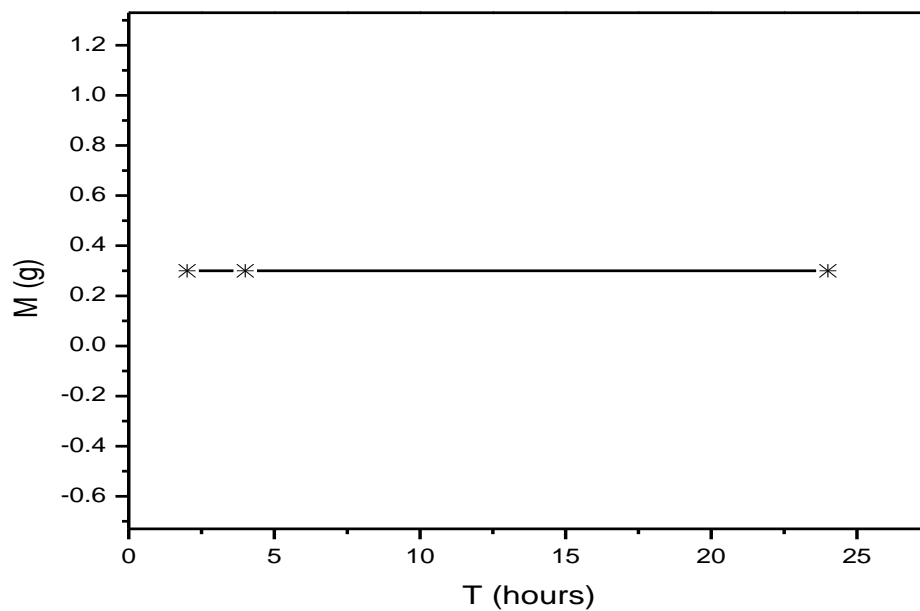
Figure (5.3) illustrate the relation between the load and times

Table (5.4) shows the values of the change in mass with times for the benzene solution

M0/g	T/hours	M/g
2.00	2	2.52
2.00	4	2.86
2.00	24	3.06
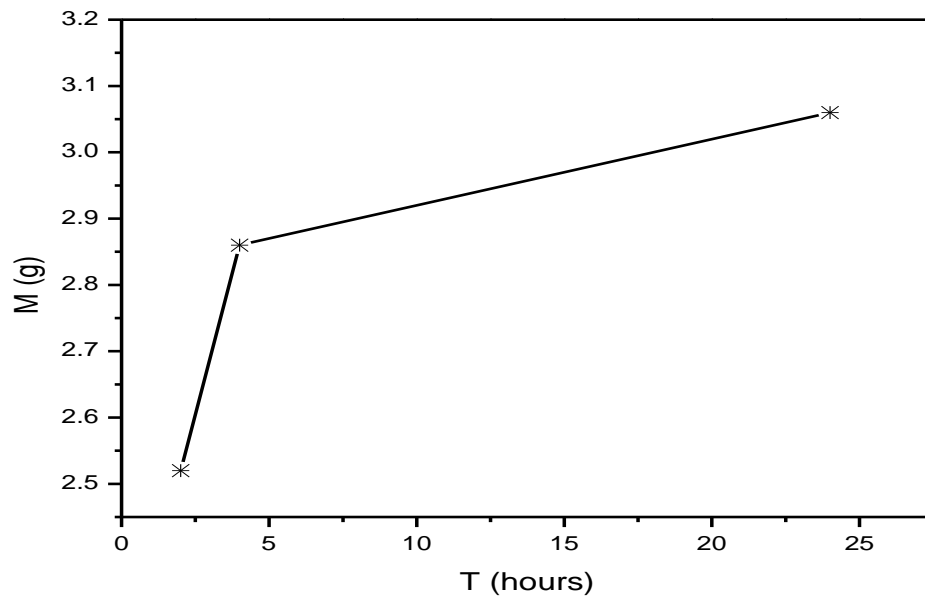
Figure (5.4) illustrate the relation between load and times

Table (5.5) shows the values of the increasing of length with times

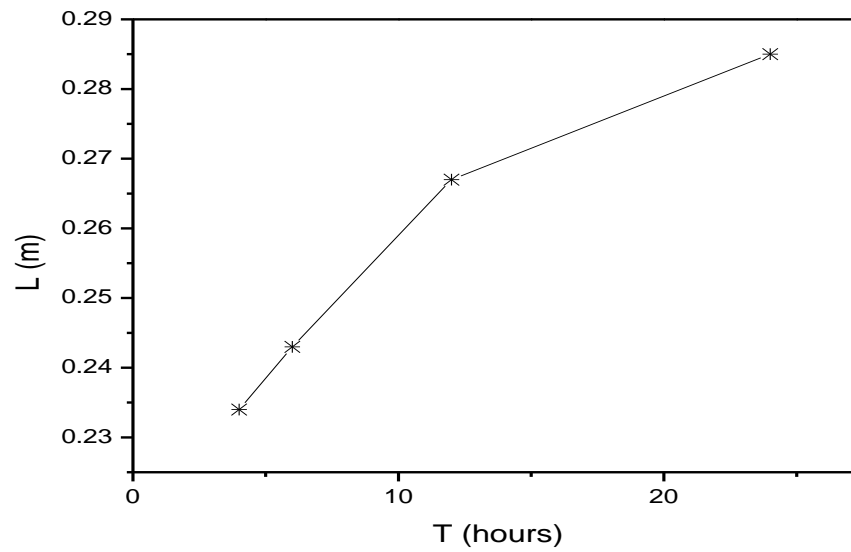| L/cm	T/hours
23.4	4
24.3	6
26.7	12
28.5	24

Figure (5.5) illustrate the relation between the length and times

Table (5.6) shows the values of the length changed with times

T/h	L/m
4	0.241
6	0.243
12	0.248
24	0.255

52
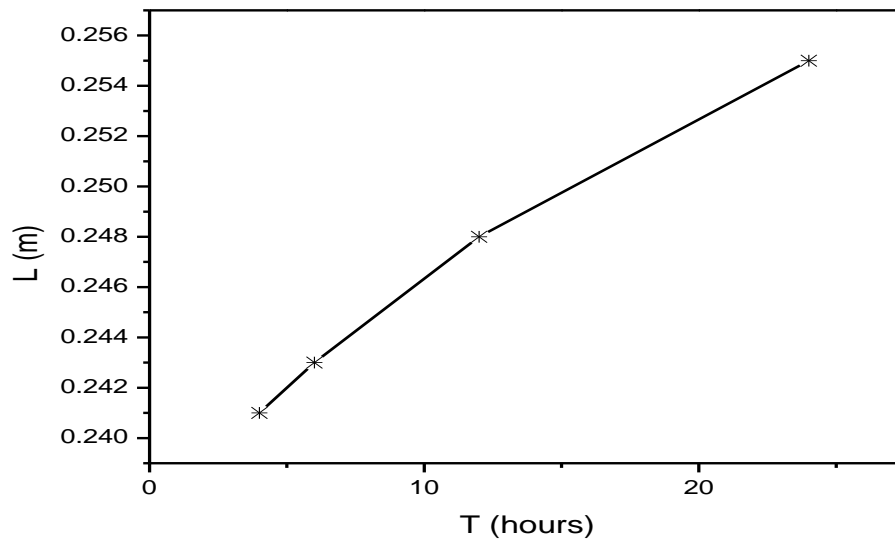
Figure (5.6) illustrate the relation between the length and times

Table (5.7) shows the values of the time-dependent creep modulus and the creep compliance in strain at time t of the rubber that containing 30% of the black carbon.

L/m	L_0 =0.23m	T/hours	$\varepsilon(t)$	E_{creep}	J_{creep}	σ_o
0.234		4	0.01739	33.775	0.0296	0.5874
0.243		6	0.05652	10.392	0.0962	
0.267		12	0.16086	3.6516	0.2738	
0.285		24	0.23913	2.156	0.40709	

Figure (5.7) illustrate the relation between the strain and the time-dependent creep modulus.
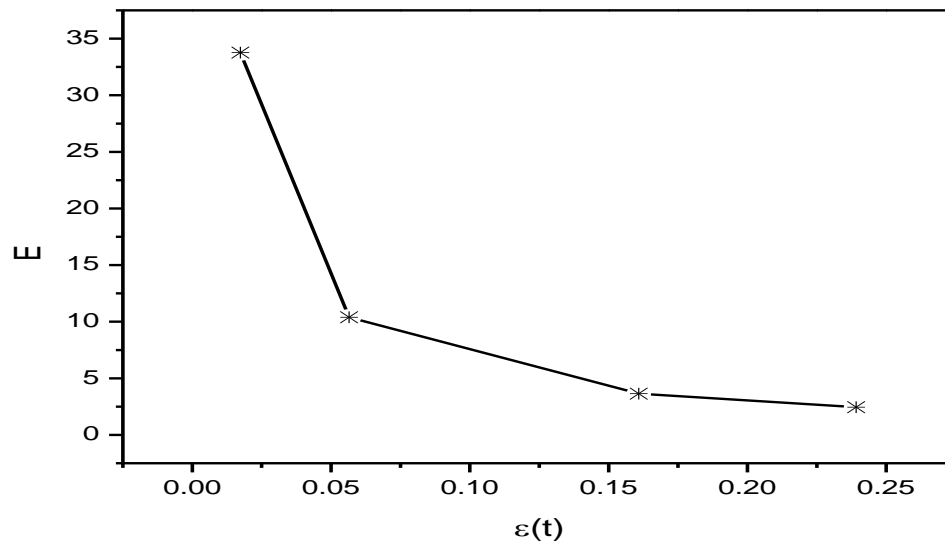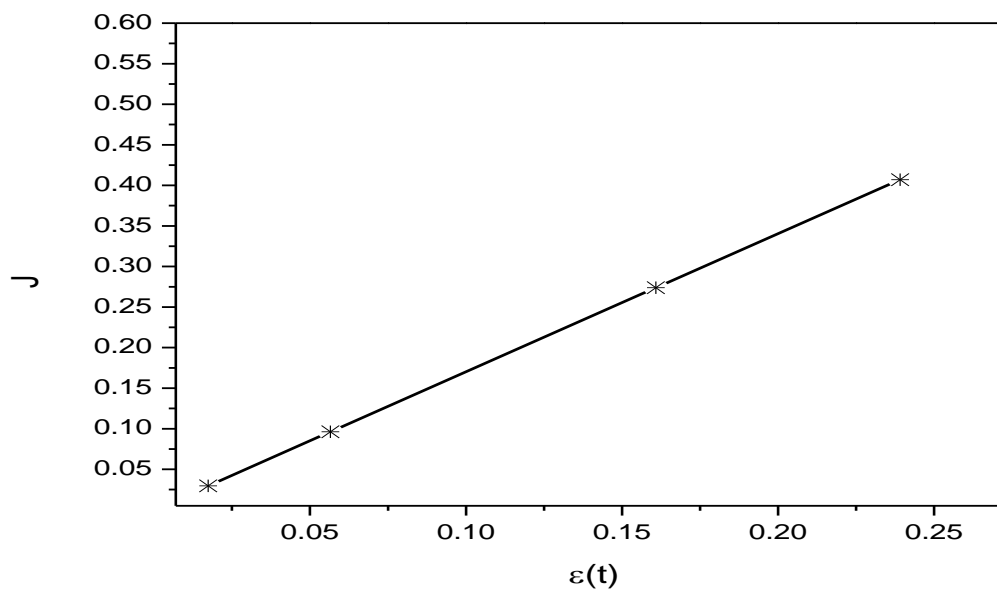

Figure (5.8) illustrate the relation between the strain and the creep compliance

Table (5.8) shows the values of the time-dependent creep modulus and the creep compliance in the strain at time t of the rubber tire containing 70% of the black carbon.

L/m	$L_0=0.24$ m	T/hours	$\varepsilon(t)$	E_{creep}	J_{creep}	σ_o
0.241		4	0.00416	1084.59	0.000832	5
0.243		6	0.0125	400	0.0025	
0.248		12	0.0333	150.150	0.00666	
0.255		24	0.0625	80	0.0125	

Figure (5.9) illustrate the relation between the strain at time (t) and the time-dependent creep modulus.

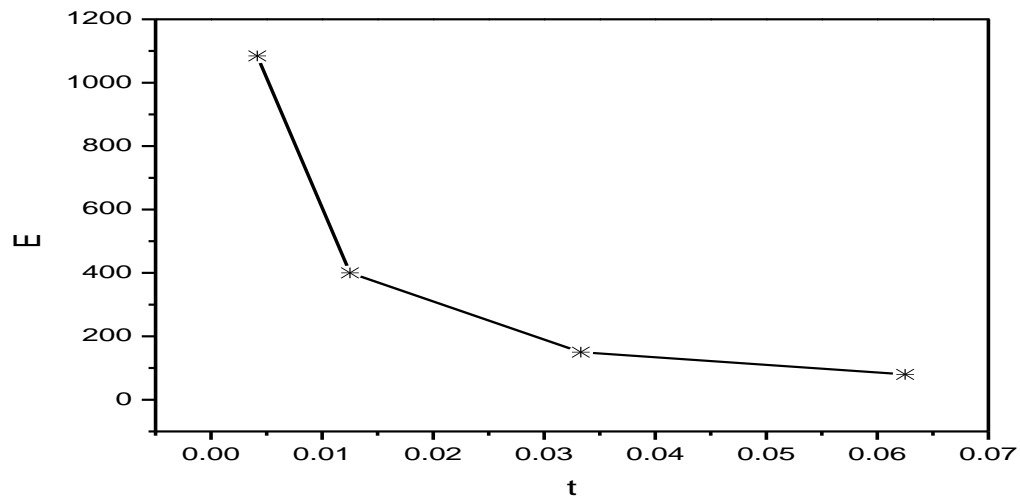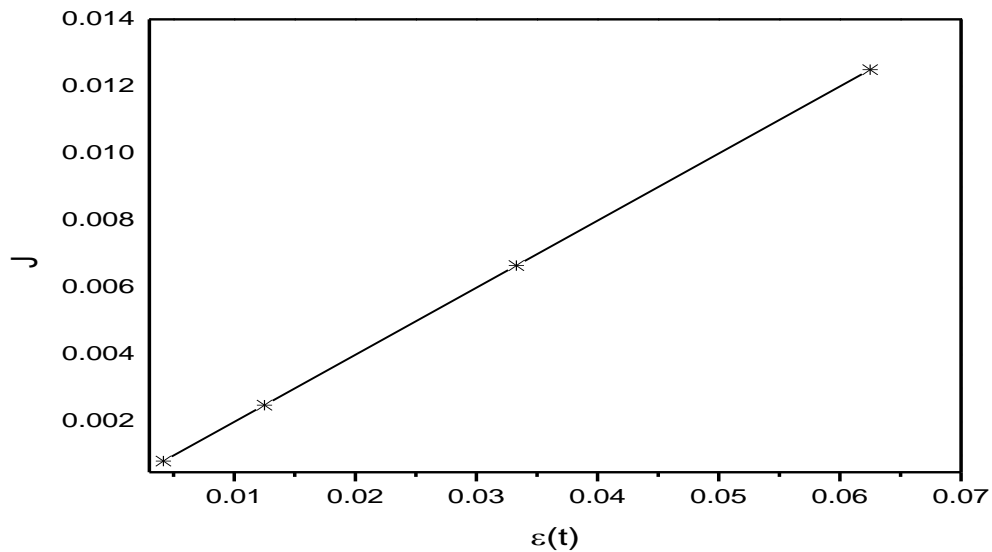Figure (5.10) illustrate the relation between the strain at time (t) and the creep compliance.

5.5 Discussion

In this work the main product of a tensile test is a load versus elongation curve which is then have been converted into a stress versus strain curve. The strain and stress test results showed in table 5.1 by using equations (4.10),(4.11) respectively and the relation between them is illustrated in figure (5.1) the true stress, based on the actual cross-sectional area of the specimen, had been investigated, it is found that the stress-strain curve increases continuously up to fracture, in agreement with theoretical consideration.

As can be seen in the figure, the stress and strain initially increase with a linear relationship. This is the linear-elastic portion of the curve and it indicates that no plastic deformation has occurred. In this region of the curve, when the stress is reduced, the material will return to its original shape. In this linear region, the line

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obeys the relationship defined as Hooke's Law where the ratio of stress to strain is a constant [25]. From the curve in figure (5.1) the elasticity modulus of rubber and yield point have been determined, of rubber. The yield strength is defined as the stress required to produce a small amount of plastic deformation.

Table 5.2 showed the results of the Swelling of the rubber that containing 30% from carbon black, it is clear from the results the rubber was affected by the methane solution, and rubber started to degradation, The relationship between mass and time was expressed in figure (5.2). Table (5.3) showed the results of the swelling of the rubber that containing 30% from carbon black, the results shown in the table indicate that the rubber was not affected by the Acetone solution. Table (5.4) shows the results of the swelling of synthetic rubber, which contains 70% of the black carbon. The results indicate that the rubber mass has increased gradually, due to the fact that synthetic rubber used in the manufacture of tires is made by adding many fillers to improve the mechanical properties For rubber, When designing, some materials are also placed

Table (5.5) shows the results of the creep for the car tires, which contains 30% carbon. The results indicate that the rubber is deformed over time under the effect of the applied load below its yield strength. The relationship between time and elongation is linear, as in Figure 5.5, however, the deformation of rubber Increases with increase the time. Also the Table (5.7) shows the values of the time-dependent creep modulus and the creep compliance in strain at time t for the rubber tire, Obtained by using the equations (4.8), (4.9) respectively. The relation between the strain and the time-dependent creep modulus has been found it's a decreasing relationship as in figure (5.7), as that the relationship between the strain and the creep compliance has been found it is a linear relationship.

Table (5.6) shows the results of creep for the rubber tire containing 70% of the black carbon, the results indicate that the rubber tire is deformed over time under the effect of the applied load below its yield strength. The relation between the elongation and the time has been found it is linear relation as in figure (5.6), Table (5.8) shows the values of the time-dependent creep modulus and the creep compliance in the strain at time t of the rubber tire containing 70% of the black carbon, obtained by using the equations (4.8),(4.9) respectively. Where the relation between the strain at time (t) and the time-dependent creep modulus has been found it is a decreasing relationship as in figure (5.9), while the relation between the strain at time (t) and the creep compliance was found a linear relation. where it was found that the creep for the rubber tire containing 70% of the black carbon is very small than the rubber tire containing 30% of the black carbon, This is due to the latter contains a low percentage of carbon and fillers materials.

5.6 Conclusion

The mechanical properties of rubber tire have been investigated, such as Tensile test it is used to determine the modulus of elasticity (Young's modulus), it was found that the (E) for the rubber tire equal $7.836 \, \text{MN/m}^2$, It was found that this rubber tire with methane solution significantly reduces its mass with increased time while it is not affected by the acetone solution. But the rubber tire containing 70% of black carbon it was swelled in by benzene and there is a remarkable increase in its mass.

The creep of rubber tire also studied the time-dependent creep modulus and the creep compliance have been computed for both rubber tire (30% and 70%) carbon black concentration.

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