

## **Effect of Temperature and UV on Some Mechanical Properties of PVC Pipes**

For water and sewer pipes, PVC competes with other materials due to its good properties.

This work was conducted to study some mechanical properties of two PVC pipe materials under different conditions. The samples were prepared by cutting PVC pipes to rings which were softened by using an oven to obtain flat specimens. The samples of tensile, impact and fatigue tests were prepared from the flat specimens according to standard specifications. The effect of strain rate (crosshead speed), temperature and UV radiation on tensile properties of PVC pipes material were investigated. Furthermore, influence of temperature and UV radiation on impact strength and fatigue behavior of PVC pipe materials were examined.

In tensile tests, the results showed that the yield stress and modulus of elasticity improved with increasing strain rate while they decreased with increasing temperature. Moreover, the fracture strain enhanced with temperature and decreased with strain rate. The yield stress and modulus of elasticity were 38.34 MPa and 2916.66 MPa at 28°C while they were 13.62 MPa and 2258.06 MPa at 70°C, respectively. The yield stress and modulus of elasticity increased and then decreased with increasing time of UV.

Results of impact test demonstrated that the impact strength increased with temperature and decreased with notch depth and UV radiation. The impact strength was 34.21 kJ/m<sup>2</sup> at 26°C whilst it was 65.38 kJ/m<sup>2</sup> at 48°C. The impact strength was 34.21 kJ/m<sup>2</sup> for unexposed sample to UV while it was 29.18 kJ/m<sup>2</sup> for the sample that was exposed to UV for 17 days.

Results of fatigue test illustrated that the cycles to failure dropped with increasing of stress. Additionally, it was observed that the fatigue life decreased with the increase of temperature; the cycles to failure were 334218 at 6°C while they were 4671 at 50°C. Besides, the results displayed that the cycles to failure increased remarkably when the samples exposed 17 days to UV. Nevertheless, after this period, the cycles to failure decreased significantly. The cycles to failure were 392022, 18224 and 48818 for the specimens exposing to UV for 17 days, 45 days and for original specimen at the same stress (5.58 MPa ), respectively.

# Chapter Two

## Theoretical part

### 2-1 Introduction

Polymer is a large molecule built up by the repetition of small, simple chemical units. In some cases the repetition is linear , much as a chain is built up from its links. In other cases chains are branched or interconnected to form three dimensional networks. The repeat unit of polymer is usually equivalent or nearly equivalent to the monomer, or starting material from which the polymer is formed. The repeat unit of poly (vinyl chloride) is-CHCHCl-; its monomer is vinyl chloride, CH=CHCl.

The length of the polymer chain is specified by the number of repeat units in the chain. This is called the degree of polymerization (DP). The DP is also defined as the number of repetitions of mers in a polymer chain.

Mathematically ,

$$DP = \frac{\text{Molecular weight of polymer}}{\text{Molecular weight of a single monomer}} \dots\dots\dots (2-1)$$

The molecular weight of the polymer is the product of the molecular weight of the repeat unit and the DP. As an example, poly (vinyl chloride). A polymer of DP 1000 has a molecular weight of  $63 \times 1000 = 63,000$ . Most high polymers useful for plastics, rubber, or fibers have

molecular weight between 10,000 and 1,000,000. The molecular weight increases with the size of the molecule. The molecules having low DP are called oligomers, the oligo meaning few. Usually, the term polymer is used for macromolecule, i.e. a large size molecule <sup>[32]</sup>.

The first polymers used were natural products, especially cotton, starch, proteins, and wool. Beginning early in the twentieth century, synthetic polymers were made. The first polymers of importance, Bakelite and nylon, showed the tremendous possibilities of the new materials<sup>[33]</sup>.

Polymers can be made that contain more than one type of repeat unit. Such polymers are called copolymers. The presence of more than one type of repeat unit opens up many possibilities for variation in the structure of the polymer, or chain architecture as it is sometimes called. If the two monomers of a bi-component copolymer are perfectly alternating, an alternating copolymer results, as shown in Figure (2-1a). If the monomer units alternate in a random fashion, a random copolymer results, as in Figure (2-1b). Figure (2-1c) shows a block copolymer, in which the different monomers prefer to add to each other, resulting in large segments of one type of monomer, followed by large segments of the other type of monomer. Finally, a second type of monomer can be added as a branch to a polymer backbone, as shown in Figure (2-1d), resulting in a graft copolymer. These different types of copolymers can have markedly different physical properties and are the basis for many important materials in the healthcare and consumer products industries <sup>[34]</sup>.

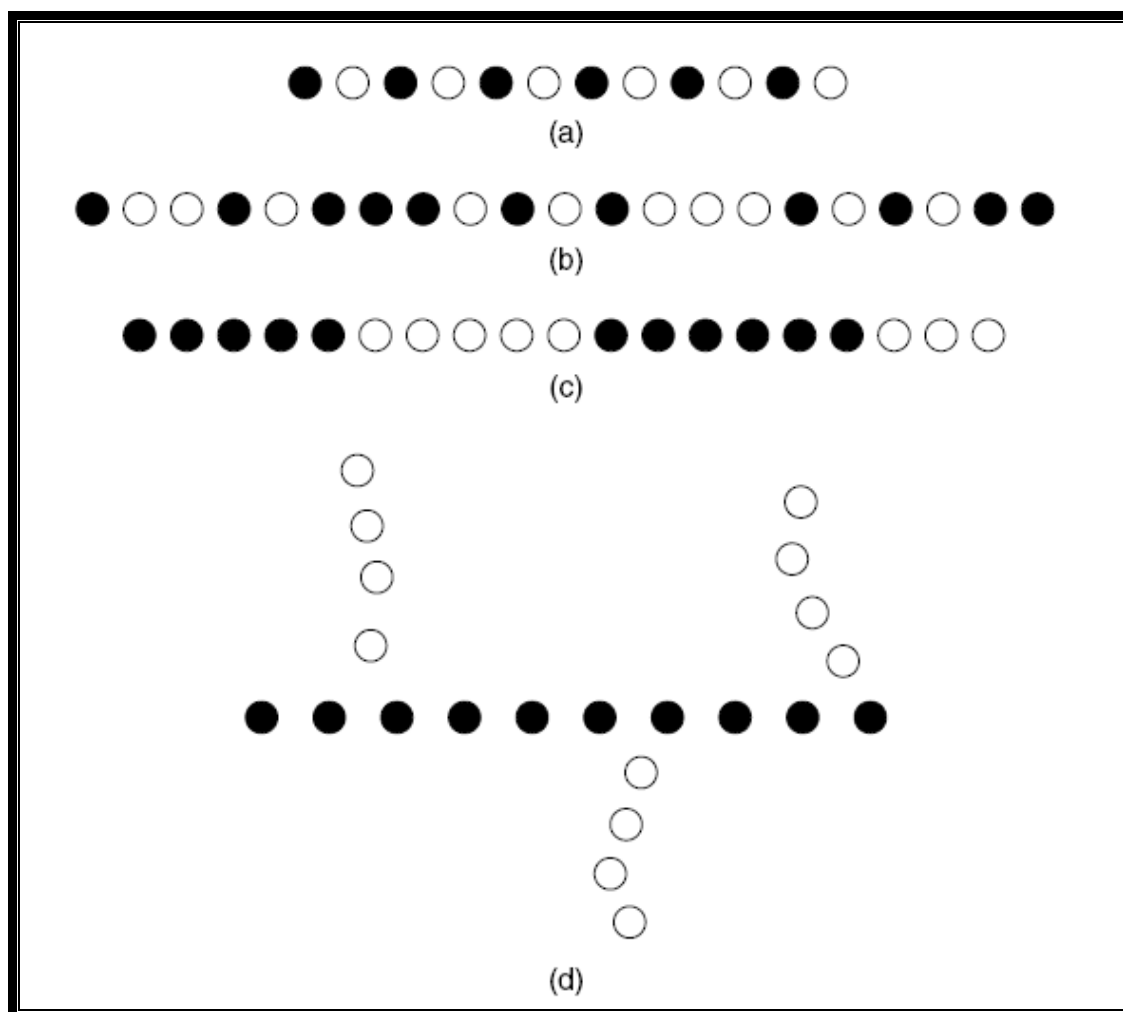


Fig. (2-1): Summary of copolymer classifications: (a) alternating, (b) random, (c) block, and (d) graft <sup>[34]</sup>.

## 2-2 Classification of polymers

There are many possible classifications of polymers. One is classifications based on structure: linear, branched or network polymers. Figure (2-2) shows these types of polymer schematically. It should be noted that the real structures are three-dimensional, which is particularly important for networks <sup>[35]</sup>.

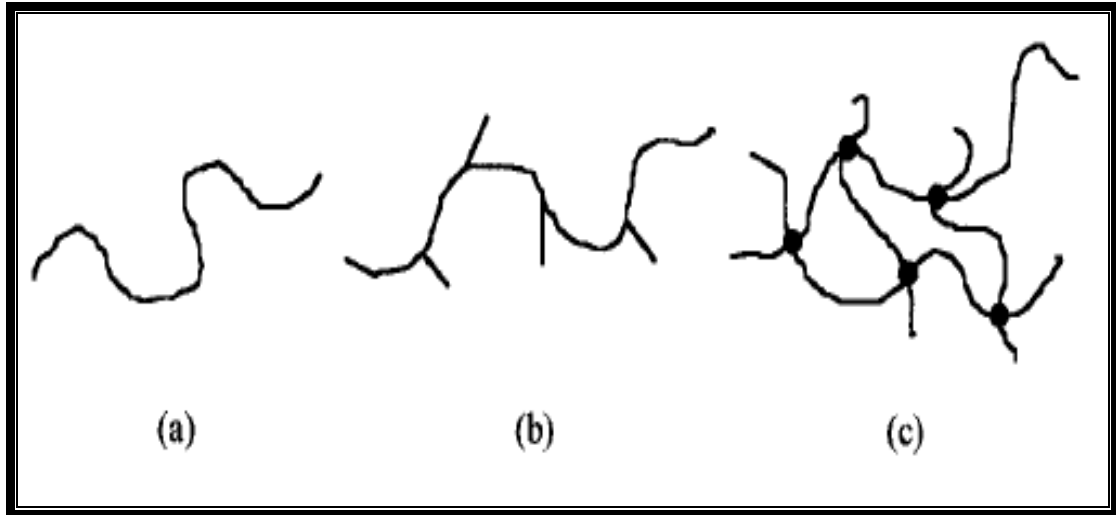


Fig. (2-2): Schematic representations of (a) a linear polymer, (b) a branched polymer and (c) a network polymer<sup>[35]</sup>.

Polymers are broadly classified in three categories<sup>[32]</sup>:

- i) Plastics
- ii) Elastomers
- iii) Fibers

### ***2-2-1 Plastics***

These are the organic material that can easily shaped or moulded by mechanical or chemical action, with or without the application of heat.

Plastic materials may further be classified as thermoplastic or thermosetting<sup>[36]</sup>.

#### ***2-2-1-1 Thermoplastics***

The plastics which soften on heating and harden on cooling in a reversible fashion are called thermoplastics. No chemical reaction occurs during the heating cycle. Thus heating and cooling cycles can be repeated any number of times to obtain a desired shape. The transformation can be represented by:

Thermoplastic  $\xrightarrow{\text{Heat}}$  softens  $\xrightarrow{\text{cool}}$  Hard

This characteristic of the thermoplastics is attributed to their linear chain structure and absence of cross-bonding between the molecules. The linear chain molecules are held together by weak secondary bonding. In the soft or molten state, linear polymers behave as rubber-like liquids with distinct viscoelastic properties. They display features of elastic materials as well as liquids. The above characteristic has made it possible to recycle the waste thermoplastic products. In the solid state they may exist as glassy material such as polymethyl methacrylate (PMMA) or partially crystalline material such as nylon.

The most common commodity thermoplastics are polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS) <sup>[34,36]</sup>.

### ***2-2-1-2 Thermosets***

Thermosets are network polymers that are heavily cross-linked to give a dense three-dimensional network. They are normally rigid. They cannot melt on heating and they decompose if the temperature is high enough.

The most common types of thermosets are the phenolformaldehydes (PF), urea-formaldehydes (UF), melamine-formaldehydes (MF), epoxies (EP), and polyurethanes (PU) <sup>[34,36]</sup>.

### ***2-2-2 Elastomers***

ASTM D1566 defines elastomers as “macromolecular materials that return rapidly to approximately the initial dimensions and shape after substantial deformation by a weak stress and release of the stress.

Elastomers, when compared with other engineering materials, are characterized by large deformability, lack of rigidity, large energy storage

capacity, nonlinear stress-strain curves, high hysteresis, large variations in the stiffness, temperature, and rate of loading, and compressibility of the same order of magnitude as most liquids. Certain of the elastomeric materials possess additional useful characteristics to a relative degree, such as corrosive chemical resistance, oil resistance, ozone resistance, temperature resistance, and resistance to other environmental conditions. The common elastomers are natural rubber, styrene butadiene rubber, acrylonitrile butadiene rubber, chloroprene <sup>[32,37]</sup>.

### ***2-2-3 Fibers***

These consists of long molecular chains and all the chains are aligned in the direction of length of the fiber. The directional properties are improved by alignment, i.e. the strength of fibers are greatly enhanced in the direction parallel to the fiber length. These provide strength to the molecular units.

The fiber polymer are quite capable of being drawn into long filaments having at least a 100:1 length to diameter ratio. Some polymers used as fibers, such as nylon and cellulose acetate, serve equally well as plastics<sup>[32]</sup>.

### **2-3 Polyvinyl chloride (PVC)**

Polyvinyl chloride (PVC) is one of the most widely used plastics in the vinyl family. Poly(vinyl chloride) (PVC) has been, for more than 70 year, one of the most important polymers, and it is the second most produced thermoplastic resin, placing after polyolefins and before styrene polymers, with a worldwide capacity of more than 31 million tons (i.e.,ca.20% of the total plastic production) <sup>[38]</sup>.



Sodium chloride (salt) and natural gas or oil are the resources necessary to make polyvinyl chloride (Figure 2-3). Electricity is passed through a salt solution to produce chlorine, while the oil or gas undergoes a cracking process to produce ethylene. The next step involves causing a reaction between the two gases to produce ethylene dichloride, which then undergoes another cracking process to produce vinyl chloride monomer. This is then polymerized- the molecules joined together – to produce a sludge which is centrifuged and dried to achieve polyvinyl chloride in the form of a white powder<sup>[39]</sup>.

PVC is prepared by the polymerization of vinyl chloride in a free radical-addition polymerization reaction. The polymer can be made by suspension, emulsion, solution, or bulk polymerization methods. The polymer is essentially linear, but a low number of short chain branches may exist. The structure of the PVC repeating unit is represented as  $(\text{CH}_2\text{CHCl})_n$ .

PVC is self-extinguishing and, therefore, has applications in the field of flame resistant wire and cable. PVC's good flame resistance results from removal of HCl from the chain, releasing HCl gas. Air is restricted from reaching the flame because HCl gas is denser than air. PVC also has excellent resistance to acids, bases, alcohol, oils, and many other hydrocarbons. It thus finds applications in parts for the chemical processing industries.

There are two basic forms of PVC: rigid and plasticized. Rigid PVC is an unmodified polymer and exhibits high rigidity. It is stronger and stiffer than polyethylene (PE) and polypropylene (PP). Plasticized PVC is modified by the addition of low-molecular-weight plasticizers to flexibilize the polymer.

Plasticized PVC can be formulated to give products a rubbery behavior. PVC resins are generally heavily compounded with additives to

improve properties. A wide variety of applications for PVC exist because one can tailor the properties by the selection of additives.

Rigid PVC can be processed using most conventional processing equipment. Because HCl is given off in small amounts during processing, corrosion of metal parts is a concern. PVC joints can be solvent- or heatwelded.

Plasticized PVC can be processed by methods such as extrusion and calendaring into a variety of products.

Rigid PVC is used in products including house siding, extruded pipe, and thermoformed and injection-molded parts. Rigid PVC is calendared into credit cards.

Plasticized PVC is used in applications such as flexible tubing, floor mats, garden hose, shrink wrap, and bottles<sup>[37]</sup>.

Table (2-1) shows the general physical, mechanical and thermal properties of PVC <sup>[1]</sup>.

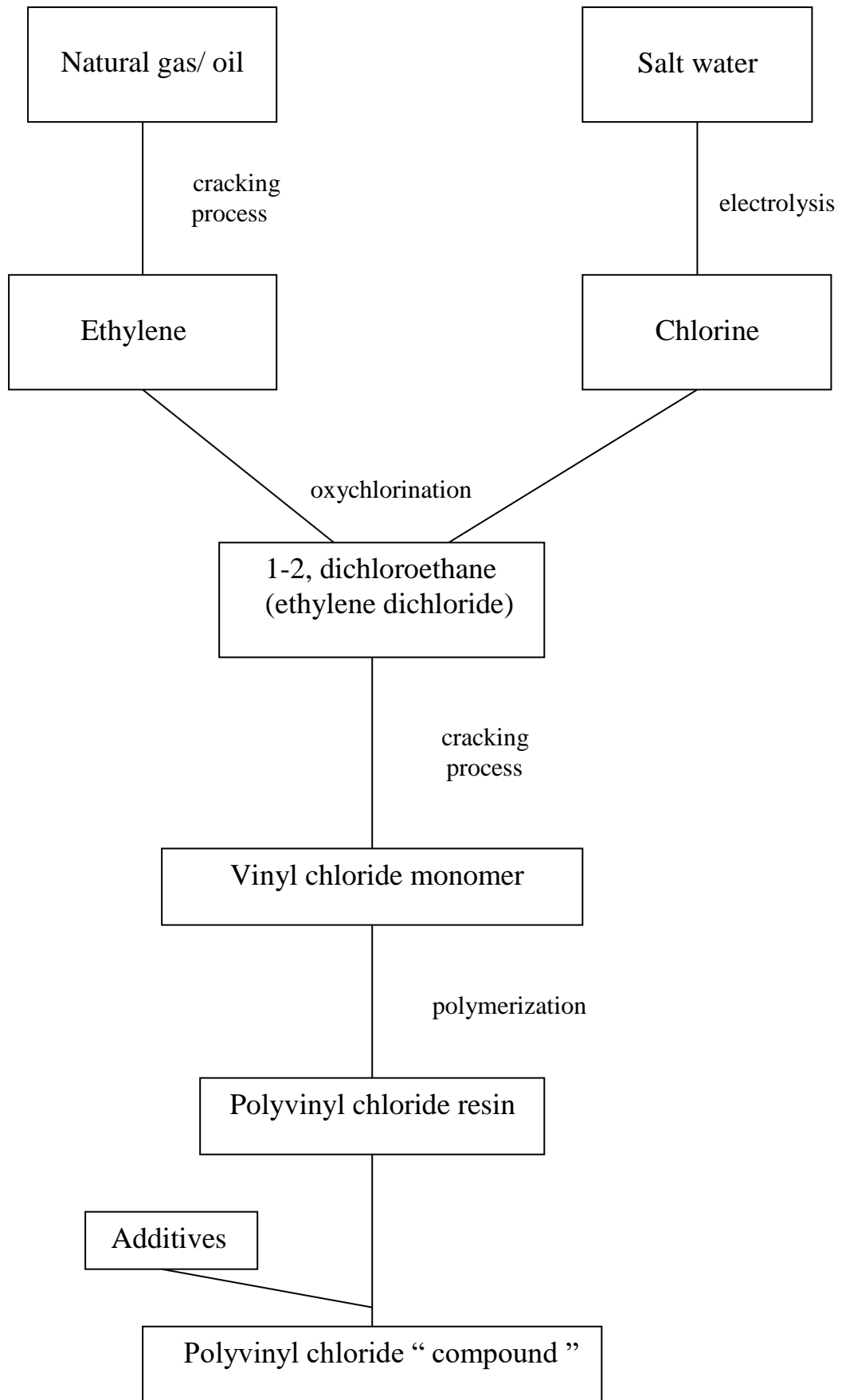


Fig. (2-3): The PVC production process [39].

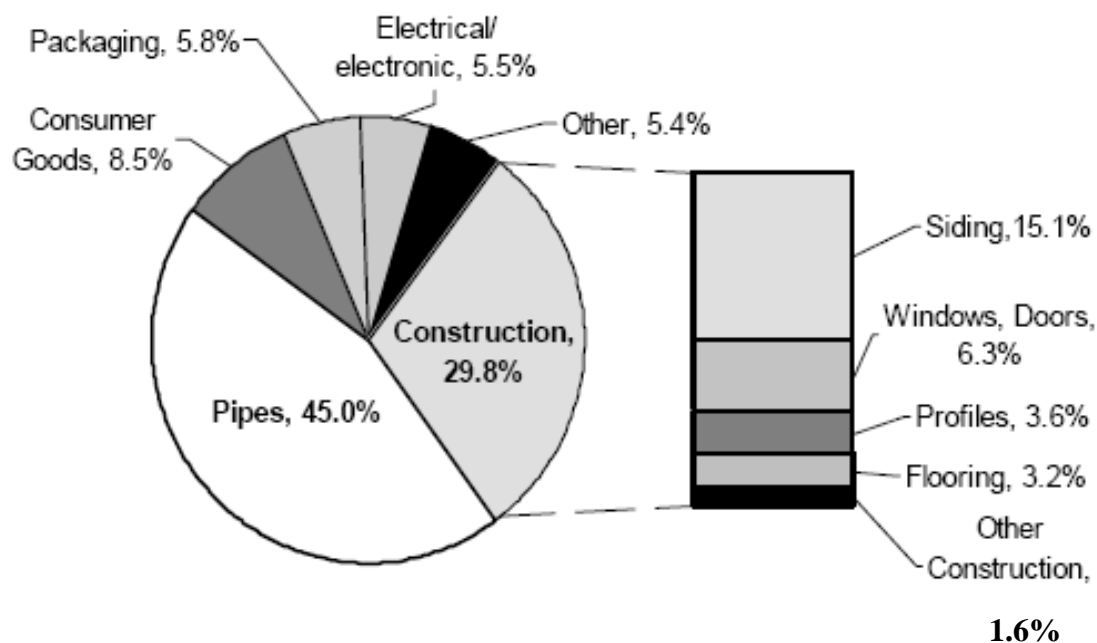
**Table ( 2-1):** Properties of PVC [1].

<b>Property</b>	<b>Unit</b>	<b>Value</b>
<b>Physical properties</b>		
<i>Molecular weight</i>		14000
<i>Relative density</i>		1.42
<i>Water absorption</i>	%	0.12
<b>Mechanical properties</b>		
<i>Ultimate tensile strength</i>	MPa	52
<i>Elongation at break</i>	%	50-80
<i>Short term creep rupture</i>	MPa	44
<i>Long term creep rupture</i>	MPa	28
<i>Elastic tensile modulus</i>	GPa	3.0-3.3
<i>Elastic flexural modulus</i>	GPa	2.7-3.0
<i>Long term creep modulus</i>	GPa	0.9-1.2
<i>Shear modulus</i>	GPa	1.0
<i>Bulk modulus</i>	GPa	4.7
<i>Impact strength: 20 °C</i>	kJ/m <sup>2</sup>	20
<i>Impact strength: 0 °C</i>	kJ/m <sup>2</sup>	8
<i>Coefficient of friction</i>		0.4
<i>Poisson's ratio</i>		0.4
<b>Thermal properties</b>		
<i>Softening point</i>	°C	80-84
<i>Max continuous service temperature</i>	°C	60
<i>Coefficient of thermal expansion</i>	/k	7x10 <sup>-5</sup>
<i>Thermal conductivity</i>	W/[m.k]	0.16
<i>Specific heat</i>	J/[kg.k]	1000
<i>Thermal diffusivity</i>	m <sup>2</sup> /s	1.1x10 <sup>-7</sup>

### **2-3-1 Applications of PVC**

Window frames, drainage pipe, water service pipe, medical devices, blood storage bags, cable and wire insulation, resilient flooring, roofing membranes, stationary, automotive interiors and seat coverings, fashion

and footwear, packaging, cling film, credit cards, synthetic leather and other coated fabrics<sup>[40]</sup>.



**Fig. (2-4):** Uses of PVC in US and Canada, 2002<sup>[41]</sup>.

### **2-3-2 PVC Additives**

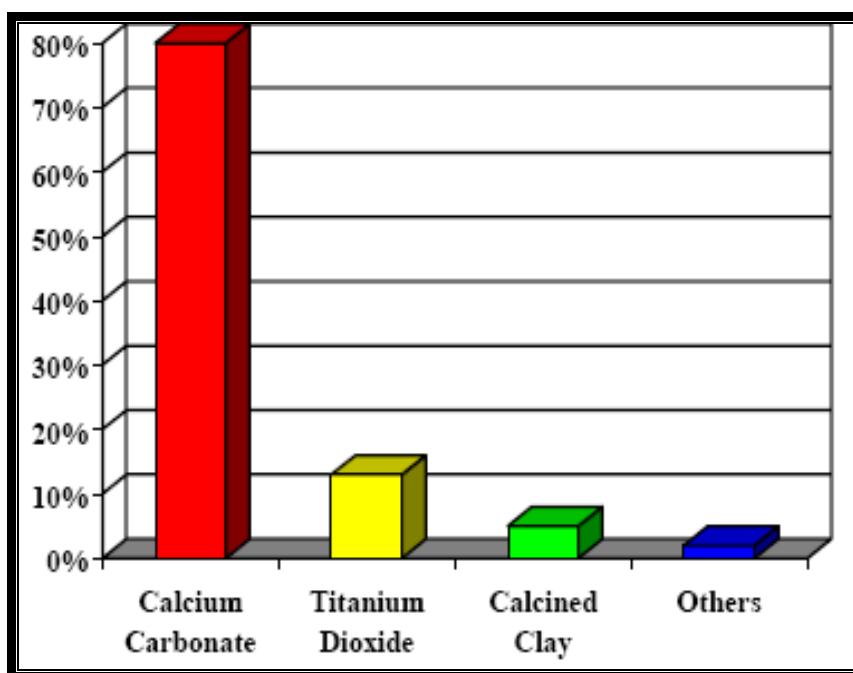
Polymers are rarely used in their virgin form, that is, the form obtained from the manufacturing plants after isolation and purification. With some exceptions (such as PS, PE and PP), pure virgin polymers are not suitable for processing straightaway<sup>[36]</sup>.

#### **2-3-2-1 Fillers**

Fillers are commonly employed in opaque PVC compounds to improve strength: to reduce cost and to improve dimensional stability, to improve electrical insulation properties, and to control the gloss. Various calcium carbonates are most commonly used fillers for PVC. Calcium carbonates ( $\text{CaCO}_3$ ) are mineral fillers. They are supplied in five

particulate forms: water-ground, dry-ground, ultra fine ground, precipitated, and surface treated <sup>[42]</sup>. The advantages of CaCO<sub>3</sub> over other mineral fillers for use in PVC include: lower cost, non-toxicity, transparency, low moisture content, easy coating ability and the acid-acceptance capability providing a degree of secondary stabilization for PVC during processing.

Approximately 80% of all the filler used in PVC is calcium carbonate. Titanium dioxide is second at around 12%, followed by calcined clay at about 5%. The remaining few percent is taken up by other materials, including glass and talc<sup>[43,44]</sup>.



**Fig. (2-5):** Fillers are used with PVC <sup>[44]</sup>.

### ***2-3-2-2 Heat stabilizers***

Heat stabilizers are used primarily to inhibit thermal degradation of PVC during processing. At elevated processing temperatures, PVC is subject to dehydrochlorination which will lead to an "unzipping" effect and results in degradation. To make the problem more complicated, the HCl given off during dehydrochlorination is a catalyst to further dehydrochlorination. Heat stabilizers for PVC must essentially perform two functions. First, they are added to prevent the dehydrochlorination from occurring initially. Secondly, the stabilizers are intended to react with the HCl given off, thus to slow the autocatalytic effect.

Some stabilizers perform both functions with a single product while some other stabilization systems require two or more additives to fulfill the entire task.

The development of effective heat stabilizers is one of the major breakthroughs which allows PVC to be commercialized in such a wide variety of applications.

The types of heat stabilizers available for PVC include organotin compounds, mixed metal systems consisting of barium-cadmium (Ba-Cd), barium-zinc (Ba-Zn) or calcium-zinc (Ca-Zn), as well as lead-based systems. The type of heat stabilizer used depends on the applications. Organotin stabilizers are the common compounds used for PVC products. The tin content varies depending on the end-use<sup>[45]</sup>.

Lead, despite all the discussions about its toxicity, is still the most used PVC stabilizer (Table 2-2)<sup>[38]</sup>.

Table (2-2) consumption of PVC stabilizers on Europe in 1988 (in tons)<sup>[38]</sup>.

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Lead	120,000
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Organotin	15,000
Mixed metal	15,000
Cadmium	0,05
Light stabilizers	6, 000

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### ***2-3-2-3 Plasticizer***

Plasticizers may be defined as non-volatile solvents added to polymeric material to soften and render them plastic or flowable for easy processing.

They also reduce hardness, rigidity and brittleness of the polymers. The action of a plasticizer is considered to be the weakening of the intermolecular forces between macromolecules thereby enabling molecular chains to slide freely past one another. This results in greater flexibility and plasticity of the material but at the same time reduction in its tensile strength and chemical resistance. Because of the poor compatibility of plasticizers with highly crystalline polymers, their use is confined to amorphous polymers or polymers with low degree of crystallinity <sup>[36]</sup>.

The addition of plasticizer to PVC changes its mechanical properties. It was demonstrated that the addition of small amounts of plasticizer could cause changes of all mechanical properties. For example, as depicted in Figure (2-6), after adding some certain amount of di-ethyl hexyl phthalate (DOP), it was observed that impact strength went down until 17% were added; then it started to go back up. Tensile strength increased until 8% were added and then decreased <sup>[46]</sup>.

Phthalates prepared from alcohols with about eight carbon atoms are by far the most important class and constitute more than 70% of plasticizers used. For economic reasons, di-isooctyl phthalate (DIOP), DOP, and the phthalate esters, often known as di-alkyl phthalate



(DAP) are used. Di-butyl phthalate and di- isobutyl phthalate are also efficient plasticizers [45].

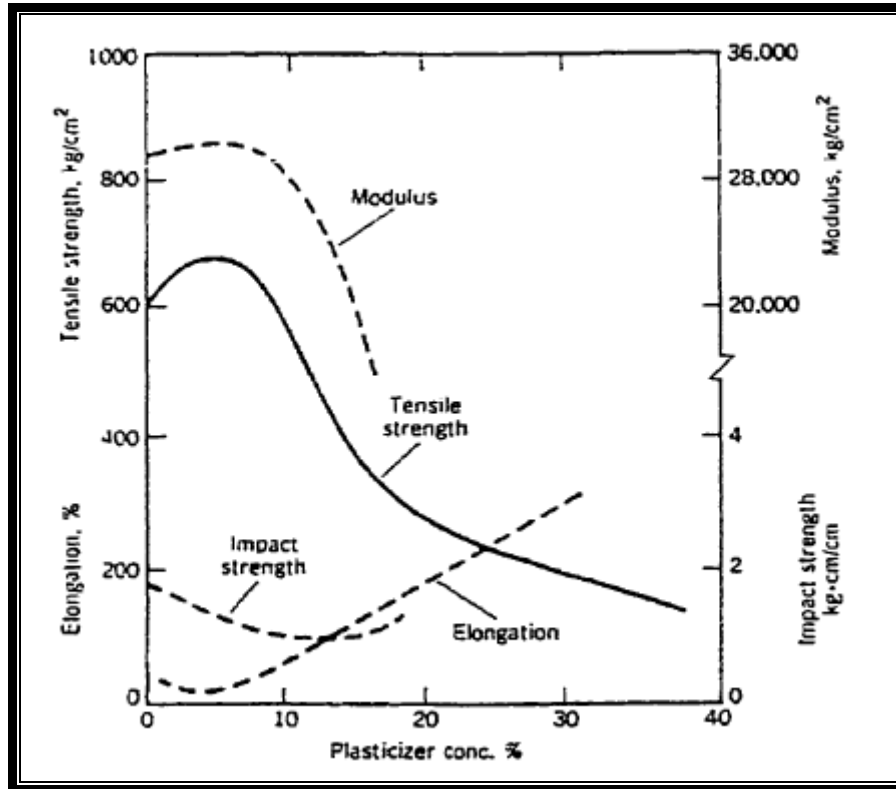


Fig. (2-6): Mechanical properties of PVC plasticized with various concentrations of DOP [45].

The stress–strain curves in tension of PVC/DOP blends prepared at 30 rpm are shown in Fig. (2-7). These results are typical for hard and brittle materials for blends with 10 phr of DOP, soft and tough for mixtures with 50 and 90 phr [47].

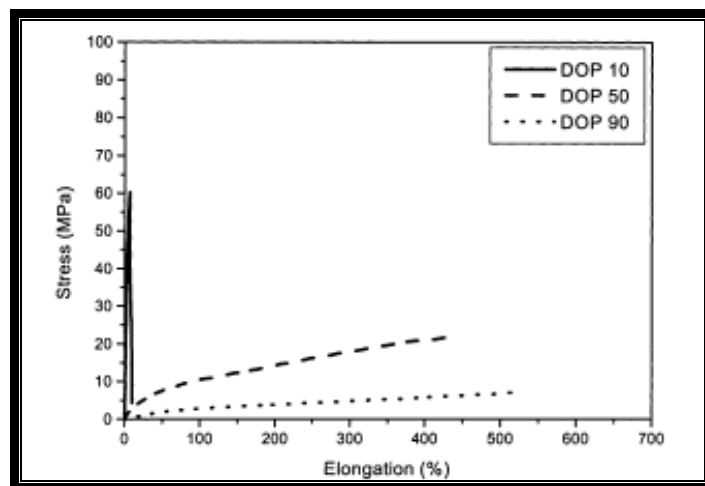


Fig. (2-7): Stress–strain curves of PVC/DOP extruded at 30 rpm<sup>[47]</sup>.

#### 2-3-2-4 UV Absorbers

UV (ultraviolet) radiation of wavelength 310nm is often considered the most damage to PVC. This range of wavelength excites the macromolecules of PVC in the sense of imparting excess energy sufficient to break bonds in the molecular chains. As a result, the free radicals formed initiate and participate in the degradation process which is accelerated by the presence of oxygen.

A variety of additives are available for the protection of plastics from degradation by ultraviolet (UV) light. The choice of UV stabilizer depends on such factors as the application, the polymer's characteristics (particularly its absorption spectrum), the stabilizer's effect on color, and the product's expected life. Another factor that should be considered is toxicity, because most organic UV stabilizers tend to migrate to the surface.

The UV-protective additives which are frequently included in PVC for outdoor use afford additional and complementary protection. They absorb and dissipate the incident UV radiation, essentially before it can initiate degradation.

Carbon black and  $\text{TiO}_2$  widely used as pigments for plastics, have a light stabilizing effect on many polymers including PVC. They are often

referred to as "light screens". Each compound functions as a physical barrier to both UV and visible radiation<sup>[48]</sup>.

### ***2-3-2-5 Lubricants***

While the addition of a lubricant in PVC-P is beneficial, for PVC-U it is essential.

The main function of the lubricants is to prevent sticking of the compound made of PVC and additives to processing equipment. Therefore, lubricant control the frictional and adhesive properties of plastics during processing and in service. Furthermore lubricants improve the dispersion of fillers and pigments in plastics and better dispersion could improve flow limits that which means better processing as well as material properties. Examples of these lubricants include stearic acid or other carboxylic acids, paraffin oils, and certain alcohols and ketones for PVC.

Lubricants are often classified as external or internal. The external lubricants have limited compatibility such that they will sweat out during processing to form a film between the bulk of the compound and the metal surfaces of die processing equipment.

They are considered to retard fusion or to promote metal release. Calcium stearate and lead stearate are often used as external lubricants.

Internal lubricants are mainly intended to improve the flow of the melt, or to reduce the melt viscosity. Unlike external lubricants they are reasonably soluble in PVC and have limited effect on fusion. Lubricants are more like plasticizers in their behavior at processing temperatures, whereas at room temperature, this effect is negligible. Wax derivatives, and long-chain esters are used as internal lubricants<sup>[48,49]</sup>.

### ***2-3-2-6 Pigments***

Many pigments are available commercially for use with PVC. Pigment selection should be based on the pigments ability to withstand process conditions, its effect on stabilizer and lubricant, and its effect on end-use properties.

Most often used pigments are carbon black and titanium dioxide ( $\text{TiO}_2$ )<sup>[48]</sup>.

### ***2-3-2-7 Flame Retardants***

The flammability is a major concern for polymeric materials, especially in the manufacturing of textile goods and children's toys. The inherent flame retardence in PVC means you can use less of an expensive flame retardency additive. Tritolyl phosphate and trixylyl phosphate are often used in PVC. Halogenated compounds such as chlorinated paraffins may also be used<sup>[32,50]</sup>.

### ***2-3-3 Processing of PVC***

PVC raw materials are available as resins, lattices, organosols, plastisols, and molding compounds. Fabrication methods include injection, compression, blow or slush molding, extruding, calendering, coating, laminating, rotational and solution casting, and vacuum forming<sup>[37]</sup>.

The word "extrusion" has its origin in the Greek root that means "push out". In the process of extrusion, the plastic material is continuously pushed or pumped through a die to produce a variety of continuous forms having constant cross-section.

The principle of extrusion is based on ability of thermoplastic to be formed into various shaped by the application of heat and pressure.

The machine is a mixing device cum pressure vessel and basically consists of two components: an extruder and a die. The extruder is mainly composed of a barrel with a screw rotating in it. The extruder barrel is further divided into three zones namely feed, compression and melting (metering) zones. The feed zone starts at the hopper end. Its function is to take the raw material (composed of granules and additives) from the hopper and transport (pump) them forward into the compression zone. In the compression zone, as the granules move along the screw, they are plasticized by contact with the heated wall of the cylinder barrel and by the generation of heat due to friction and shear between the layers of plastic. At the end of the melt zone, a breaker plate having perforations is often provided to perform various useful functions which include:

- (1) increasing back pressure,
- (2) converting rotational flow of the melt into flow parallel to the screw axis,
- (3) holding back impurities, and
- (4) holding back unplasticised material.

After coming out from the die, the extrudate is cooled immediately below its  $T_g$  to ensure dimensional stability.

This process can be used to produce any material that has a uniform cross-section, such as pipe, rods, and sheets <sup>[32,36]</sup>.

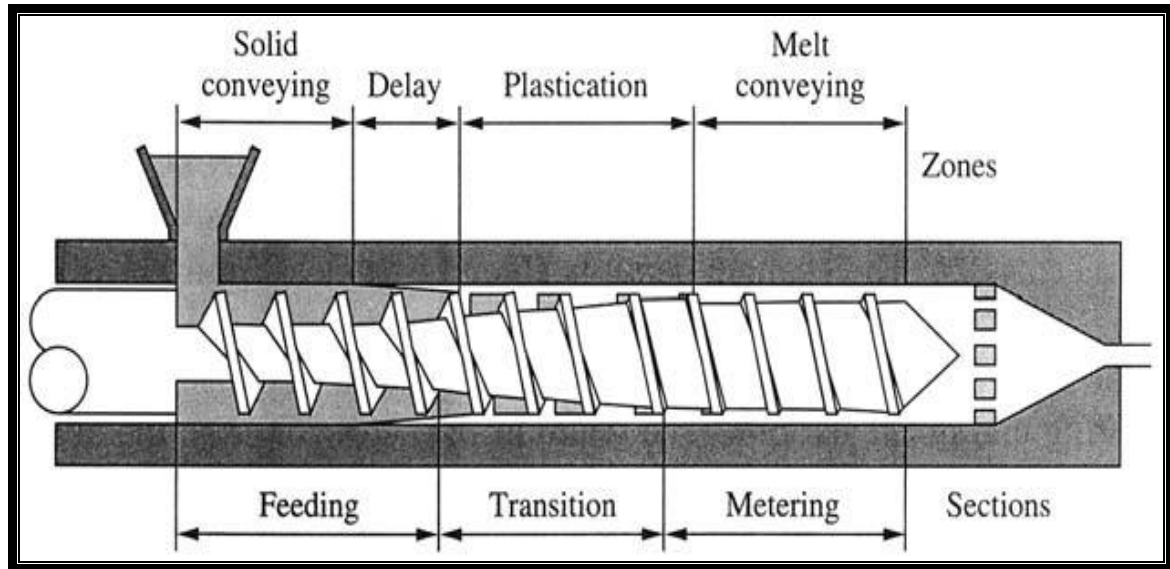


Fig. (2-8): Schematic representation of a single-screw extruder <sup>[51]</sup>.

## **2-4 Polymer Degradation**

Degradation of polymers may be considered as any type of undesired modification of a polymer chain backbone, side groups, or both. These modifications are usually chemical in nature; that is, they involve the breaking of primary bonds, leading to reduced molecular weight and altered physical properties. The causes of degradation may be environmental (such as heat, light, or atmospheric pollutants), induced, (as in rubber mastication), or a result of processing due to heat and/or air<sup>[52]</sup>.

### ***2-4-1 Radiative Degradation***

Radiative degradation in polymers can give rise to both low-molecular-weight species, as in thermal degradation, or crosslinked structures, which are insoluble and infusible. Though crosslinking actually leads to an increase in the molecular weight of the sample, it is still considered a degradative process since the resulting product has unfavorably altered physical properties. There are generally two types of radiative degradation processes in polymers, grouped according to the

amount of radiant energy involved and which result in different types of degradation.

Photolysis occurs when ultraviolet light (wavelength  $\lambda = 10^2-10^4 \text{ \AA}$ ) imparts energy on the sample of the order  $10^2-10^3 \text{ kJ/mol}$ . Radiolysis occurs when higher radiant waves ( $\lambda = 10^3-10^2 \text{ \AA}$ ) impart energy of the order  $10^5-10^{10} \text{ kJ/mol}$  to the sample. Each of these types attacks the polymer chain in a different fashion.

Ultraviolet (UV) light is light that comprises only the shorter wavelengths of invisible radiation. It is a zone of invisible radiations beyond the violet end of the spectrum of visible radiations. Because the wavelengths are shorter than visible radiations, their photons have more energy. This energy is enough to initiate some chemical reactions and degrade many plastics. Thus UV light is more damaging than visible light to most plastics <sup>[37,52]</sup>.

#### ***2-4-2 Thermal degradation***

Thermal degradation is deterioration by heat. In plastics thermal degradation is usually oxidation or pyrolysis. Oxidation is the general reduction in properties by reactions taking place with oxygen and accelerated by the presence of high temperatures. Pyrolysis is reaction of the polymer purely with heat.

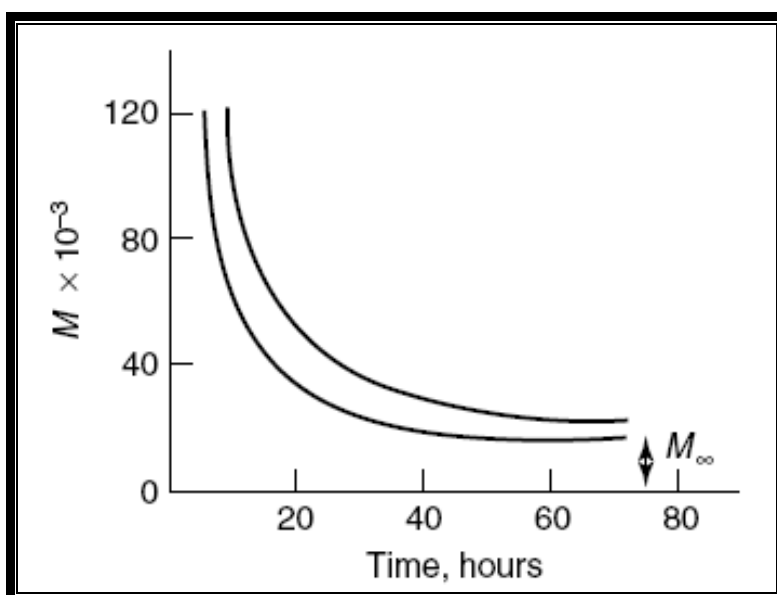
With pyrolysis, degradation occurs by breakage of the polymer chain called chain scission and resulting reduction in molecular weight <sup>[37]</sup>.

#### ***2-4-3 Mechanochemical Degradation.***

Mechanochemical degradation occurs in polymers as the result of an applied mechanical force. This type of degradation is quite common in machining processes such as grinding, ball milling, and mastication. In

general, the degradation processes are similar to the other types of degradation, in that radicals are formed and cause subsequent reactions, such as oxidation and chain transfer, that can lead to either crosslinking or a reduction in molecular weight, though molecular weight reduction is the most common result. There are some unique aspects of mechanochemical degradation, however. In contrast to thermal degradation, radical formation is nonrandom, and the location of chain scission depends on the manner in which the forces are applied to the polymer. Also, the molecular weight decreases rapidly from an initial degree of polymerization for polymers under mechanical shear, then level off to a limiting degree of polymerization (Figure 2-9).

In addition to a reduction in molecular weight, mechanical forces generally lead to an increase in solubility, a narrowing of the molecular weight distribution, decreased tensile strength, decreased crystallinity, and increased plasticity. These effects are highly dependent upon the machining conditions [52].



**Fig.(2-9):** Effect of machining time on molecular weight of polymer [52].



#### ***2-4-4 Chemical Degradation.***

For most applications in the chemical process industry, chemical degradation is the most important type of polymer degradation. It is also the largest class overall, encompassing degradation due to both gaseous and liquid species on all polymer classes. Even within a polymer class, such as polyolefins, slight changes in the chain chemistry can lead to enormous changes in chemical compatibility.

In addition to oxygen, the most important gaseous agents that lead to polymer chemical degradation are nitrogen dioxide (NO<sub>2</sub>) , sulfur dioxide (SO<sub>2</sub>), and ozone (O<sub>3</sub>) [52].

#### ***2-4-5 Biodegradation:***

Biodegradation or biological degradation of polymers consists of those processes which are resulted from an attack on the material by living organisms, e.g., bacteria, fungi, insects, and rodents. Biodegradation is fundamentally a chemical process involving enzymes produced by microorganisms. High humidity, moderately increased temperature, and darkness are usually favorable for proper functioning of microorganisms [ 53,54 ].

### **2-5 Tensile properties of polymers**

#### ***2-5-1 Stress–Strain Behavior of Polymers***

Three important types of stress–strain curves are illustrated in Figure (2-10). The brittle plastic stress–strain curve is linear up to fracture at about 1% to 2% elongation. Typical stresses at break are of the order of 10,000 psi, or about  $6 \times 10^7$  Pa. Ordinary polystyrene behaves this way.

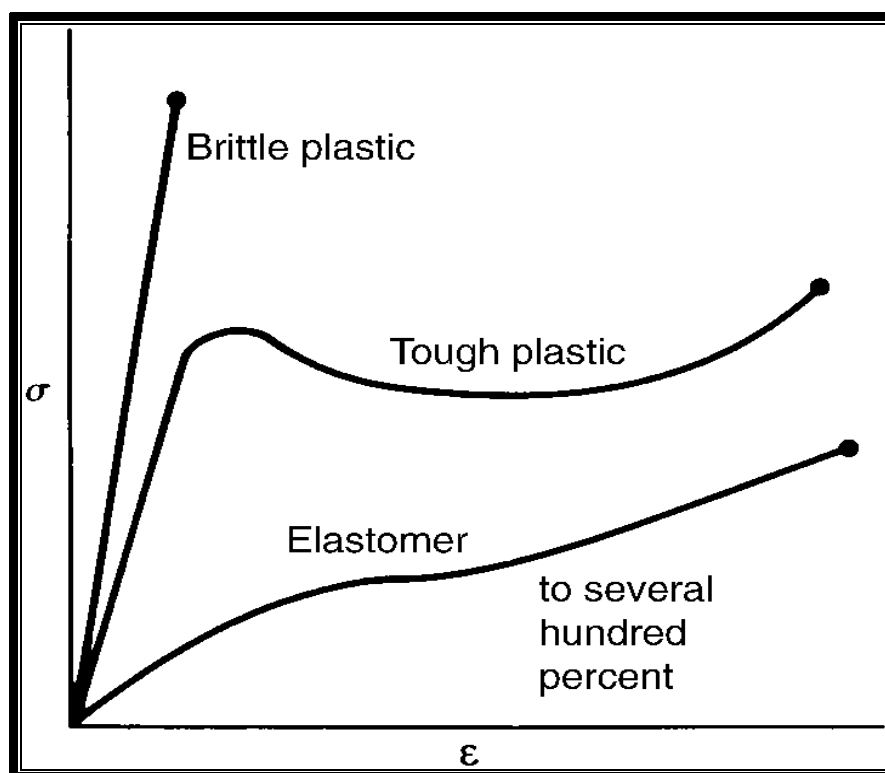


Fig. (2-10): Stress–strain behavior of three types of polymeric materials <sup>[33]</sup>.

An example of a tough plastic is polyethylene, which is semicrystalline, with the amorphous portions above  $T_g$ . Its Young's modulus, given by the initial slope of the stress–strain curve, is somewhat lower than that of the brittle, glassy plastic. Typically this class of polymer exhibits a yield point, followed by extensive elongation at almost constant stress. This is called the plastic flow region and is clearly a region of nonlinear viscoelasticity. Stresses in the range of 2 to  $5 \times 10^7$  Pa are commonly exhibited in this range. Extension at constant stress in the plastic flow region is often referred to as cold drawing. Finally, the polymer strain hardens, then ruptures. Many tough plastics break at about 50% elongation.

The third type of stress–strain curve is that exhibited by elastomers. The equation of state for rubber elasticity governs here, with its peculiar

nonlinear curve. Elongation to break for the elastomer may be of the order of several hundred percent and is indicated by the dot at the end of the curve. For crystallizing elastomers such as natural rubber, the curve swings upward rather sharply at the point of crystallization, and tensile strengths of 2 to  $5 \times 10^3$  psi ( $2-3 \times 10^7$  Pa) are common. Noncrystallizing elastomers such as SBR have much lower tensile strengths, often below 1000 psi. However, with the addition of reinforcing fillers such as finely divided carbon black, the tensile strength is much increased. Of course, this last material is widely used for automobile tires, one of the toughest materials known <sup>[33]</sup>.

### ***2-5-2 Effect of temperature on stress-strain curves of polymers***

Polymers such as polystyrene and poly(methyl methacrylate), PMMA, with a high tensile modulus at ambient temperatures fall into the category of brittle materials, since they tend to fracture prior to yielding. “Tough” polymers, or those that undergo some deformation prior to failure, can be typified by cellulose acetate. These two categories of behavior are illustrated in Figure (2-11), along with their respective temperature dependences. It can be seen from Figure (2-11) that the effect of temperature on the characteristic shape of the curves is significant. As the temperature increases, both the rigidity and the yield strength decrease, while the elongation generally increases. For cellulose acetate, there is a ductile–brittle transition at around (273 K), above which the polymer is softer and tougher than the hard, brittle polymer below 273 K. For PMMA, the hard, brittle characteristics are retained to a much higher temperature, but it eventually reaches a soft, tough state at about 320 K. Thus, if the requirements of high rigidity and toughness are to be met, the temperature is important <sup>[34]</sup>.

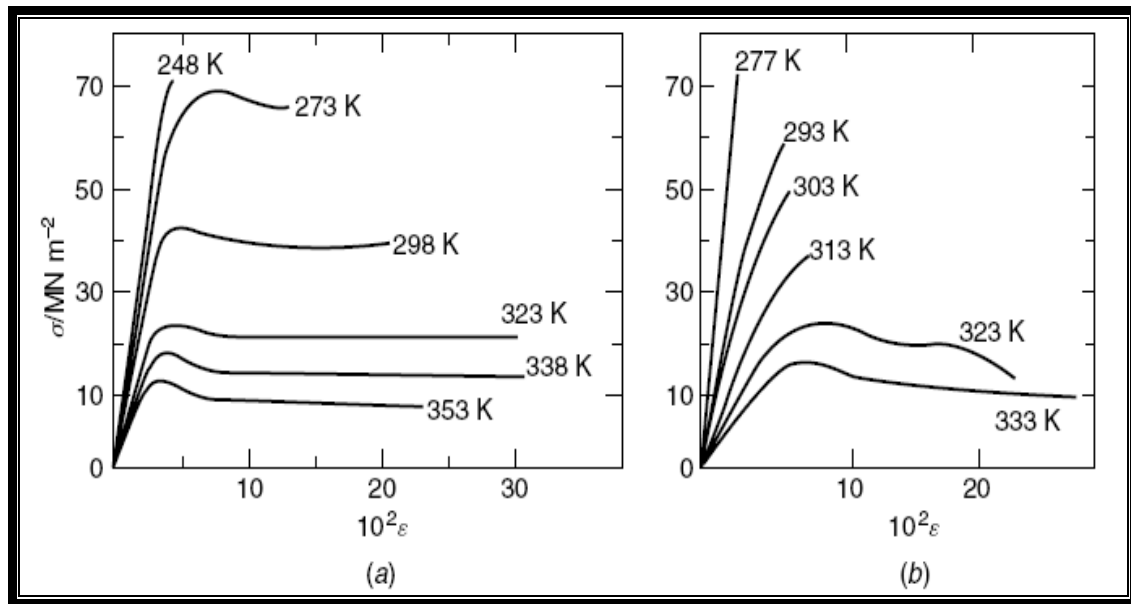


Fig. (2-11): Influence of temperature on the stress–strain response of (a) cellulose acetate and (b) poly(methyl methacrylate) <sup>[34]</sup>.

### ***2-5-3 Effect of strain rate on stress-strain curves of polymers***

For many material, the stress-strain curves are sensitives to the strain rate  $\dot{\epsilon}$ . The tensile tests are usually conducted in the range  $10^{-4} \text{ s}^{-1} < \dot{\epsilon} < 10^{-2} \text{ s}^{-1}$ . Materials can be tested over a wide range of strain rates; however, standardized tensile tests require well-characterized strain rates that do not exceed a critical value. High strain rate tests are often used to obtain information on the performance of materials under dynamic impact conditions<sup>[55]</sup>.

Figure (2-12) shows the effect of different strain rate on the tensile response of PMMA <sup>[16]</sup>.

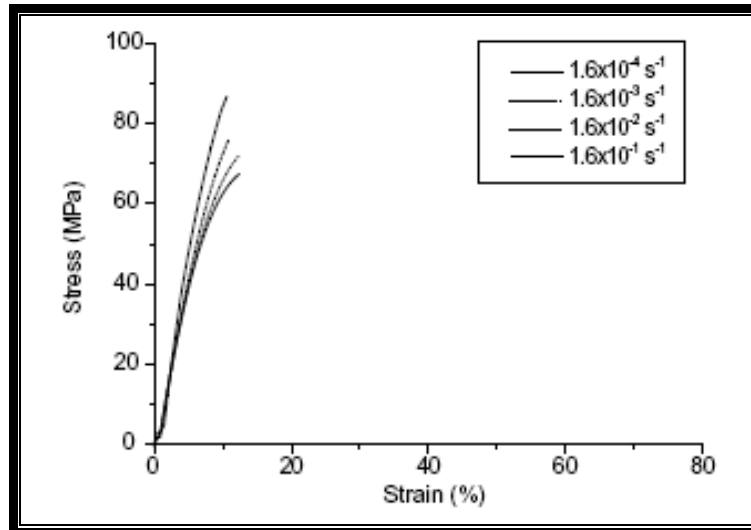


Fig. (2-12): Tensile tests made at different rates for PMMA <sup>[16]</sup>.

## **2-6 Impact properties of polymer**

### ***2-6-1 Introduction***

Plastics products are most likely to fail in a brittle manner under impact conditions, both due to strain rate effects and because large forces can be generated by low energy impacts on stiff structures <sup>[56]</sup>.

Impact strength of many polymers is raised by introducing reinforcements in them. Toughness of many plastics is also improved by the addition of rubber material in them. These additions are called toughness modifiers <sup>[36]</sup>.

### ***2-6-2 Factors affecting the impact strength of polymeric materials***

#### ***2-6-2-1 Nature of impact Tests***

Impact tests can be broadly divided into two separate classes:

(a) Low velocity impact by a large mass, which is generally a swinging pendulum, where the breaking energy is determined from the

loss in kinetic energy of the pendulum, or a falling weight in which the breakage energy is determined from the weight of the ball and the height from which it is dropped. The impact speeds normally attainable lie in the range of 2 to 6 m/s.

(b) High velocity impact by a small mass using a gas gun or some other type of ballistic launcher. For such special test purposes, projectiles with impact speeds of 50 to 100 m/s are generally used <sup>[57]</sup>.

### ***2-6-2-2 Effect of Notches***

The state of the surface of a solid has a profound influence on its impact strength. The notch in the Izod specimen serves to concentrate the stress, minimize plastic deformation, and direct the fracture to the part of the specimen behind the notch. Hence the impact strength of the notched specimens is less than that of the unnotched specimens <sup>[58]</sup>.

### ***2-6-2-3 Effect of Temperature***

The impact strength of most polymers increases as the temperature is raised to the neighbourhood of their glass transition temperature,  $T_g$ . This is due to the fact that at temperatures in the neighbourhood of the glass transition temperature, the potential molecular motion is great enough to relieve any stress concentrators that may be present in the material <sup>[59]</sup>.

### ***2-6-3 Impact testing of polymers***

The ability of a component to withstand a sudden impact is obviously of great importance for any practical application of the material. The impact testing of polymers is therefore equally important. By using standardized techniques it is fairly straightforward to obtain results that

allow the comparison of one type of polymer with another, but it is less easy to obtain fundamental data.

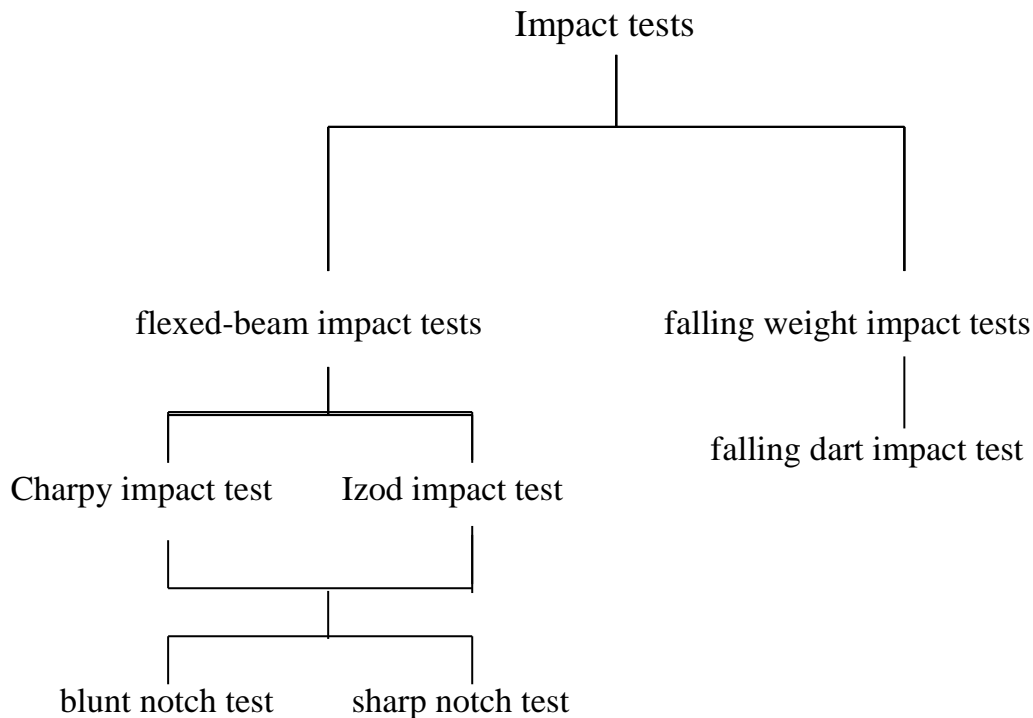


Fig. (2-13): The various kinds of impact tests <sup>[35]</sup>.

Figure (2-13) shows the principal types of test. In the Charpy test a beam of the polymer is held at each end and is struck at its centre by a hammer with one or two knife edges, giving a three- or four-point impulsive bending stress, respectively. Figure (2-14) shows a diagram of a standard Charpy impact tester. Charpy testing is usually reported in units of  $J/m^2$ , or energy required to create a unit area of crack.

In the Izod test the specimen is held at one end and struck at the other. For either test a notch is cut in the sample at the point where it is to break and the sample is placed in the tester with the notch pointing away from the hammer, so that the blow tends to widen the notch. If the blow is strong enough the sample cracks at the foot of the notch and fractures. The standard type of specimen has a blunt notch, which is a V-shaped

notch with a tip radius of 0.25 mm, but sometimes a sharper notch is made, into the foot of which a razor blade is driven to provide a starting place for a crack. Izod testing is usually reported in units of J/m (Joules per meter of crack), based on samples of 12.7 mm wide, 3.2 mm thickness, and 65 mm length.

In the falling-dart test a circular sample of polymer is supported horizontally and a pointed steel dart is allowed to fall so that it strikes the centre of the disc. The standard dimensions for this test are radius of test disc 6 cm, thickness of disc 2 mm and radius of dart tip 1 mm. The disc is supported horizontally by an annulus of 4 cm aperture to which it is clamped by a second annulus. The behavior of the sample can be studied under a variety of different degrees of severity of impact simply by varying the height from which the dart is allowed to fall <sup>[35]</sup>.



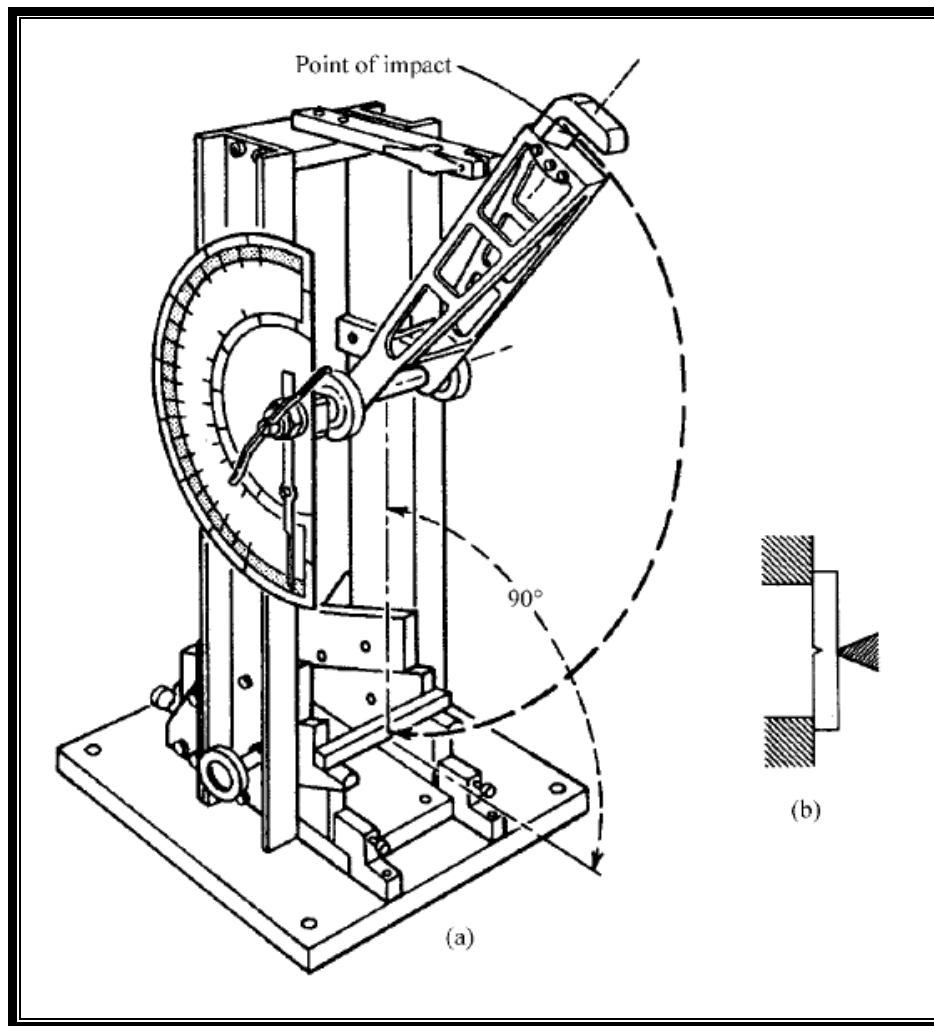


Fig.(2-14): The Charpy impact test: (a) the pendulum tester, ASTM 256; and (b) the sample and striking hammer tip <sup>[35]</sup>.

#### ***2-6-4 Ductile-to-brittle transition***

A Charpy test at one temperature is not sufficient, however, because the energy absorbed in fracture drops with decreasing test temperature. The temperature at which a change occurs from a high-energy fracture to a low-energy one is called the ductile-brittle transition temperature (DBTT). However, since, in practice, there occurs not a sharp change in energy, but instead, a transition zone, it becomes difficult to obtain this DBTT with precision.

The appearance of the fractured surfaces after an impact test also gives information about the type of fracture that has occurred <sup>[55]</sup>.

## **2-7 Fatigue of polymers**

### **2-7-1 Introduction**

Fracture of components due to fatigue is the most common cause of service failure, particularly in shafts, axles, aircraft wings, etc., where cyclic stressing is taking place. With static loading of a ductile material, plastic flow precedes final fracture, the specimen necks and the fractured surface reveals a fibrous structure, but with fatigue, the crack is initiated from points of high stress concentration on the surface of the component such as sharp changes in cross-section, slag inclusions, tool marks, etc., and then spreads or propagates under the influence of the load cycles until it reaches a critical size when fast fracture of the remaining cross-section takes place. The surface of a typical fatigue-failed component shows three areas, the small point of initiation and then, spreading out from this point, a smaller glass-like area containing shell-like markings called “arrest lines” or “conchoidal markings” and, finally, the crystalline area of rupture.

Fatigue failures can and often do occur under loading conditions where the fluctuating stress is below the tensile strength and, in some materials, even below the elastic limit. Because of its importance, the subject has been extensively researched over the last one hundred years but even today one still occasionally hears of a disaster in which fatigue is a prime contributing factor <sup>[60]</sup>.

Similar to metals, polymers can deform plastically and thus can fail in a similar way under cyclic loading. However, the microscopic mechanisms are not the same as in metals <sup>[52]</sup>.

### **2-7-2 Thermal fatigue**

Polymers deform viscoelastically. Under cyclic loads, the stress-strain curve upon unloading is not the same as upon loading. Therefore,

there is a hysteresis between stress and strain, causing energy dissipation during the deformation, thus producing heat. The heat generated under cyclic loads cannot easily dissipate into the surroundings because the thermal conductivity of polymers is small. If heat generation exceeds heat dissipation, the temperature increases in each cycle until the temperature-dependent strength of the material is exceeded and the material fails. If the stress is reduced, the heat generation reduces as well, and the number of cycles to failure increases. For this reason, this phenomenon is called thermal fatigue. If the stress is reduced further, an equilibrium between heat generation and heat dissipation will be established without exceeding the strength.

Thermoplastic polymers fail by plastic yielding under thermal fatigue because the yield strength decreases with increasing temperature. Elastomers and duromers can also fail by thermal fatigue due to the reduction of Young's modulus with temperature which causes a continuously growing deformation.

If thermal fatigue occurs, the load frequency can strongly influence fatigue life. On the one hand, longer cycles provide more time to dissipate the heat, on the other hand, Young's modulus and the size of the hysteresis in the stress strain diagram are dependent on the frequency. If sufficiently long unloading occurs between the cycles, the generated heat can be dissipated, and there is no thermal fatigue. The geometry of the component is also important, for it determines the heat dissipation <sup>[52]</sup>.

### ***2-7-3 Mechanical fatigue***

If the temperature increase during cyclic loading is sufficiently small so that no thermal fatigue occurs, the polymer fails by mechanical fatigue. Similar to metals, we can distinguish the stages of crack initiation and crack propagation.

Cracks can form in a polymer in different ways, depending on the dominating deformation mechanism. Fracture of single chain molecules or sliding of chain molecules can weaken the material locally and thus serve as initiating points for cracks. In many polymers (for example, polystyrene, polycarbonate, PMMA), crazing plays an important role, as it does in plastic deformation. Under cyclic loads, crazes may form and grow even if the loads are comparatively small, until they have grown sufficiently to act as microcracks. If a crack propagates, the stress concentration near the crack tip can initiate further crazes that coalesce with the crack. Because crazing depends on the hydrostatic stress state, the mean stress is especially important in this case. Alternatively, shear bands may form and be starting points for microcracks. If there are phase boundaries within the polymer, for example, between the amorphous and crystalline regions of a semi-crystalline polymer or between chemically different phases in a copolymer, these boundaries may initiate cracks due to the stress concentration they cause. Nevertheless, the fatigue strength of semi-crystalline polymers is in most cases superior to that of amorphous polymers.

Whether a polymer fails by mechanical or thermal fatigue is determined by many factors e. g., the load frequency, the stress level, the temperature, and the geometry of the component. In general, polymers with weak viscoelastic effects, which produce only a small amount of heat in each cycle, fail by mechanical fatigue. Among these are polystyrene and many duromers. Thermal fatigue is important in materials with a large hysteresis in the stress-strain diagram, for example polyethylene, polypropylene, and polyamide. Finally, both effects can interact because the increase in temperature changes not only the static, but also the dynamic material properties. In this case, the material heats

up initially, and crack propagation sets in afterwards. This phenomenon can be observed in PMMA, PET and polycarbonate [52].

#### ***2-7-4 S-N curves of polymers***

We first define some important parameters, these parameters are as follows:

$$\text{cyclic stress range, } \sigma = \sigma_{\max} - \sigma_{\min}, \quad \dots\dots\dots (2-2)$$

$$\text{cyclic stress amplitude, } \sigma_a = (\sigma_{\max} - \sigma_{\min})/2, \quad \dots\dots\dots (2-3)$$

$$\text{mean stress, } \sigma_m = (\sigma_{\max} + \sigma_{\min})/2, \quad \dots\dots\dots (2-4)$$

$$\text{stress ratio, } R = \sigma_{\min} / \sigma_{\max} \quad \dots\dots\dots (2-5)$$

where  $\sigma_{\max}$  and  $\sigma_{\min}$  are the maximum and minimum stress levels, respectively.

Traditionally, the behavior of a material under fatigue is described by the S-N (or  $\sigma$ -N) curves, where S (or  $\sigma$ ) is the stress and N is the number of cycles to failure. Such an S-N curve is frequently called a Wöhler curve, after the German engineer who first observed that kind of fatigue behavior [55].

There are four categories of cyclical stresses to consider. The first is called a reversed stress cycle, in which the stress alternates equally between compressive and tensile loads. A repeated stress cycle occurs when the maximum and minimum stress of a reversed stress cycle are asymmetric relative to the zero stress level. Other types of cyclical stresses include a fluctuating stress cycle, which has a maximum and minimum tensile or compressive load (but not both), and a random stress cycle, in which the stresses are neither periodic nor uniform in the magnitudes [34].

The fatigue behavior of polymers strongly depends on the load frequency because of their viscoelastic properties. If the frequency is sufficiently large, the polymer can fail by thermal fatigue due to the heat

generated during deformation. This is shown for the example of a thermoplastic polymer in Figure (2-15). At low frequencies, the thermoplastic fails by crack formation and propagation, similar to a metal, at higher frequencies, thermal fatigue occurs, and the fatigue strength strongly decreases. The load frequency is for this reason usually limited to 10 Hz.

However, as Figure (2-15) shows, this may be due to thermal fatigue, and in this case the horizontal part of the curve meets the curve for true mechanical fatigue at higher numbers of cycles.

S-N curves of polymers have to be used with caution in designing components.

The fatigue strength depends much more strongly on the load frequency than in metals because the equilibrium between heat production and dissipation plays a crucial role. To design components, experiments should be as close to real service conditions as possible <sup>[52]</sup>.

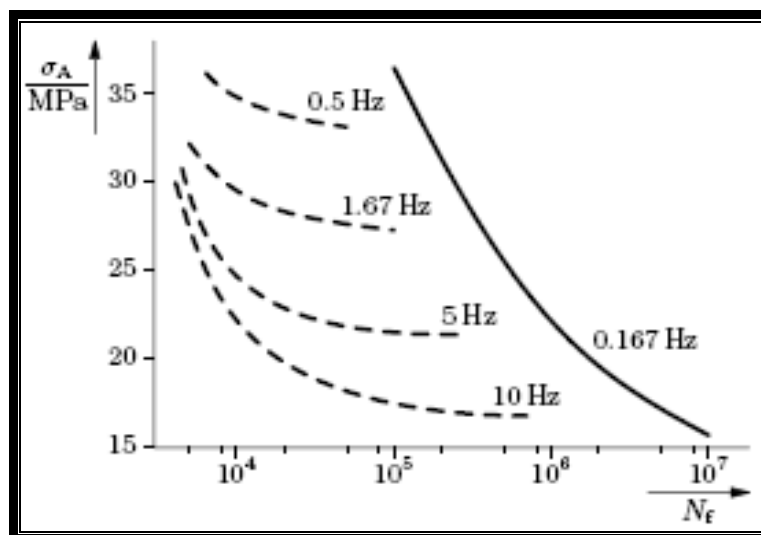


Fig. (2-15): S-N diagram of polyoxymethylene (polyacetal) at different loading frequencies <sup>[52]</sup>.

Phenomenologically there are three regions in the stress versus number of cycles to failure (S–N curves); see Figure (2-16): For a sample undergoing cyclic stress–strain exercises, first there is a region where there may be no externally apparent damage. This is followed by a region of crack propagation, where the crack grows steadily with each cycle. The last region involves catastrophic failure, where one or two cycles more causes total material fracture. Fatigue response in this way is commonly observed: A material in service appears to be fine, and then breaks with little or no warning. Of course, the cracks may be propagating internally, not easily seen without instrumental examination. The number of cycles to failure depends on the stress level, as illustrated in Figures (2-16) and (2-17). In some cases a so-called endurance limit is observed below which fatigue failure does not occur in realistic lifetimes of experiments.

The fatigue phenomenon is not an all-or-nothing situation. First, it is assumed by many investigators that all materials are flawed as made, even if the flaws are too small to be ordinarily noticed. On repeated stressing, these tiny flaws initiate cracks. In the next stage, these cracks propagate slowly, perhaps growing a bit with every cycle, or sometimes intermittently. Finally, the material fails, the crack growing through the sample in one stress cycle<sup>[33]</sup>.

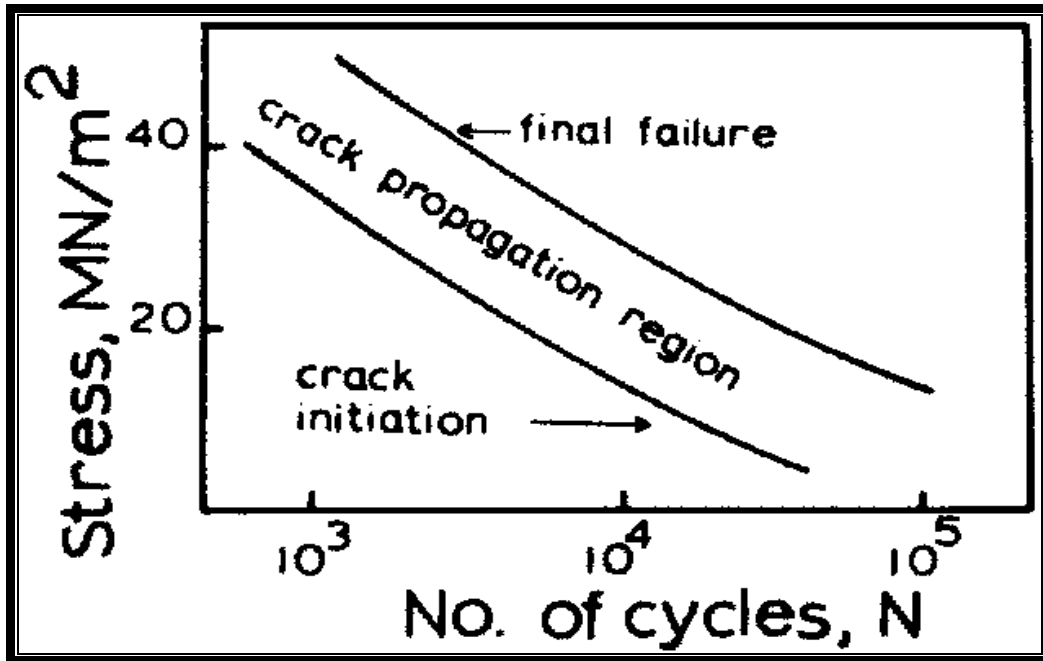


Fig. (2-16): The fatigue response of a polymer [33].

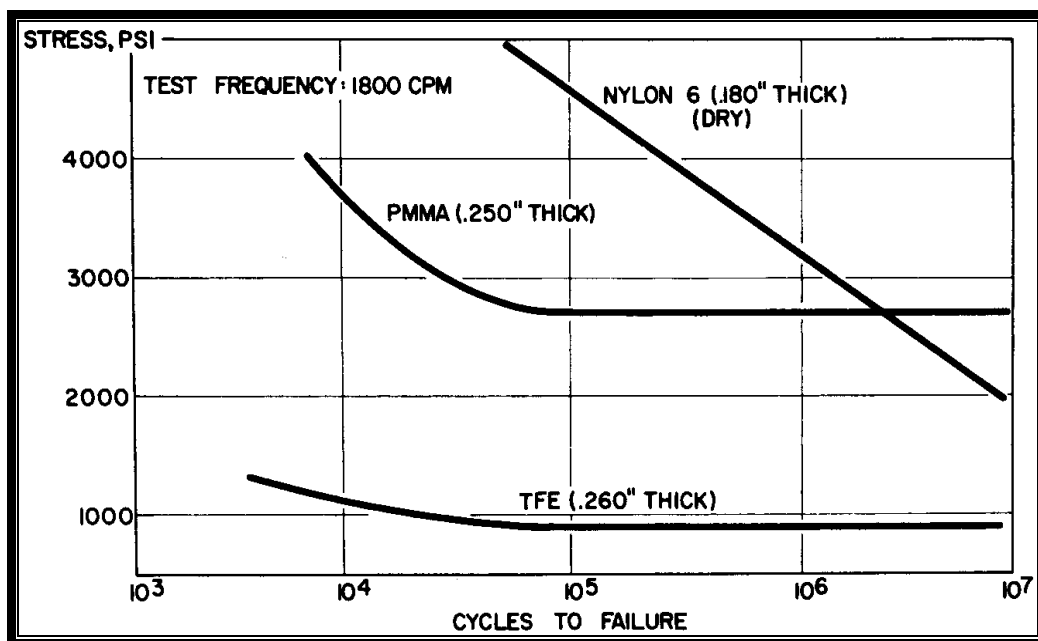


Fig. (2-17): Fatigue lifetimes versus stress level for nylon 6, poly(methyl methacrylate), and polytetrafluoroethylene [33].



### 2-7-5 *Fatigue Crack Propagation*

Fatigue crack propagation relates to the slow growth of cracks caused by cyclic stressing. In many fatigue crack propagation experiments, a notch is deliberately introduced in the specimen at a convenient location. The rate of growth of this crack and the morphology of the crack surface outline areas of current interest.

For a crack of length  $a$ , the fatigue crack growth rate is  $da/dn$ , where  $n$  represents the number of stress cycles. The stress intensity factor range is given by

$$\Delta K = K_{\max} - K_{\min} \quad \dots\dots\dots(2-6)$$

where  $K_{\max}$  and  $K_{\min}$  are the maximum and minimum values of the stress intensity factor during the cyclic loading. The crack growth rate is related to the stress intensity factor range by the equation (Paris' law)

$$da/dn = A_1 \Delta K^m \quad \dots\dots\dots(2-7)$$

where  $A_1$  and  $m$  are parameters dependent on material variables, mean stress, environment, and frequency. While the rate of crack growth increases with crack length, equation (2-7) implies a straight line when  $\log da/dn$  is plotted against  $\Delta K$ , frequently observed over much of the range in  $\Delta K$  (Figure 2-18). The actual rates of crack growth depend on several factors. First is the temperature of the experiment. Under fatigue propagation conditions, the crack tip may get quite hot even if the experiment is at room temperature.

This is important because viscoelastic motions depend strongly on the temperature and the frequency of the loading. Either the glass transition or secondary transitions such as the  $\beta$  transition may be involved, but the latter is usually the more important because most engineering plastics are well below their glass transition temperatures. The frequency sensitivity, defined as the multiple by which the fatigue crack propagation rate

changes per decade of frequency, goes through a maximum at the temperature where the  $\beta$  transition segmental jump frequency is comparable to the test machine loading frequency.

Second, the rates of crack growth depend on the value of  $\Delta K$ . If  $\Delta K$  is low enough, the rate of crack growth may be essentially zero. If  $\Delta K$  is high enough, one cycle may produce fracture. This results in a sigmoidal character to the fatigue crack growth curve.

Third, fatigue propagation depends inversely on the weight-average molecular weight. Below a critical value of  $M_w$ , the sample is brittle. At higher molecular weight ranges, the fatigue crack propagation rate decreases. Indeed, higher molecular weight samples are stronger in a variety of experiments<sup>[33]</sup>.

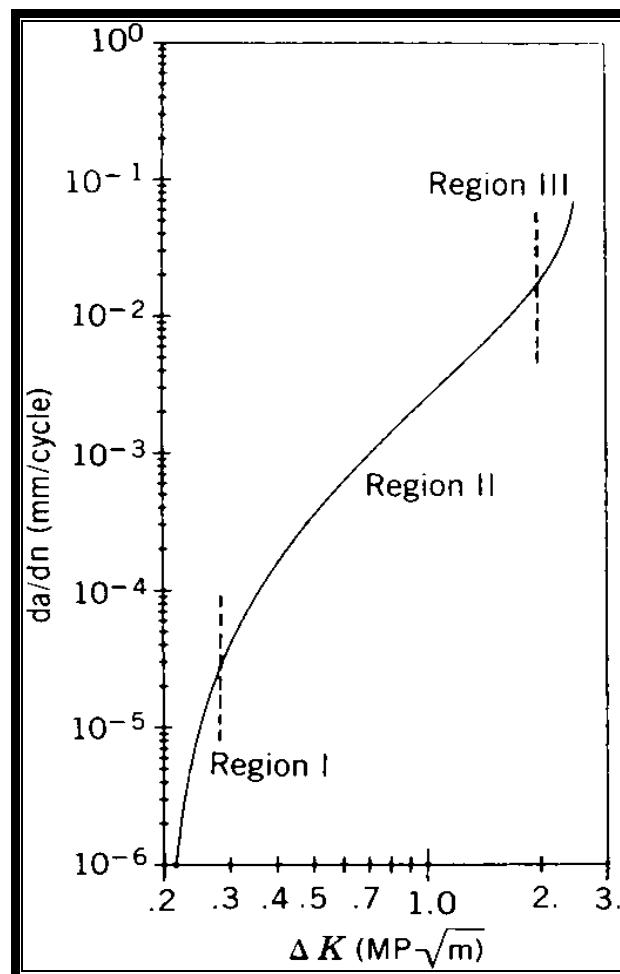


Fig. (2-18): Fatigue propagation in plastics<sup>[33]</sup>.

### 2-7-6 Fatigue testing

Fatigue tests are usually carried out under conditions of rotating - bending and with a zero mean stress as obtained by means of a Wohler machine.

From Fig. (2-19), it can be seen that the top surface of the specimen, held “cantilever fashion” in the machine, is in tension, whilst the bottom surface is in compression. As the specimen rotates, the top surface moves to the bottom and hence each segment of the surface moves continuously from tension to compression producing a stress-cycle curve <sup>[60]</sup>.

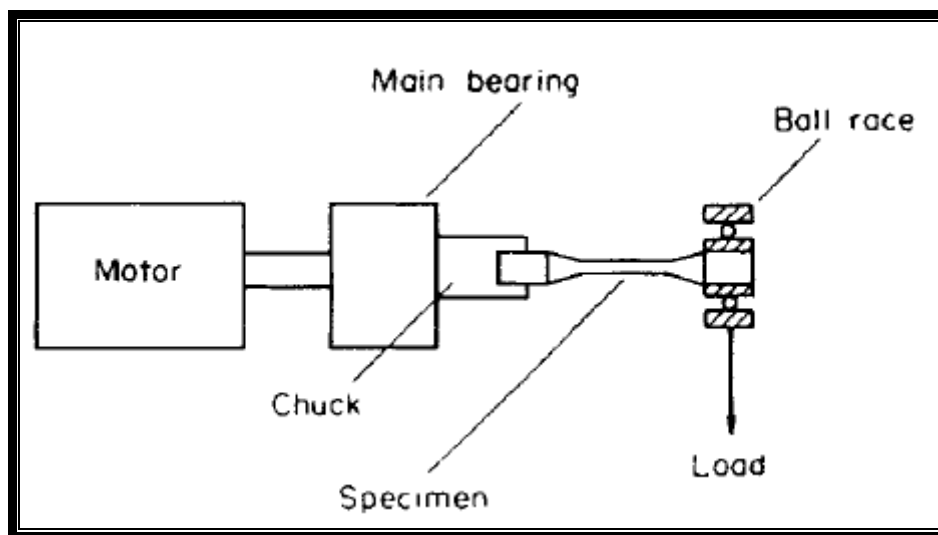


Fig. (2-19): Single point load arrangement in a Wohler machine for zero mean stress fatigue testing <sup>[60]</sup>.

