

# Chapter 1: Introduction

## 1.1 Polymers

Polymers are any of various complex organic compounds produced by polymerization, capable of being molded, extruded, cast into various shapes and films, or drawn into filaments used as textile fibers. Plastics form the major part of polymers.

### 1.1.1 Plastics

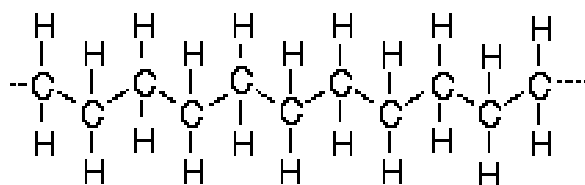
The term "plastics" encompasses organic materials, such as the elements carbon (C), hydrogen (H), nitrogen (N), chlorine (Cl) and sulfur (S), which has properties similar to those naturally grown in organic materials such as wood, horn and rosin. Organic materials are based on polymers, which are produced by the conversion of natural products or by synthesis from primary chemicals coming from oil, natural gas or coal. The plastic production process begins by heating the hydrocarbons in a "cracking process." Here, in the presence of a catalyst, larger molecules are broken down into smaller ones such as ethylene (ethene)  $C_2H_4$ , propylene (propene)  $C_3H_6$ , and butene  $C_4H_8$  and other hydrocarbons. The yield of ethylene is controlled by the cracking temperature and is more than 30% at  $850^\circ C$  and such products as styrene and vinyl chloride can be produced in subsequent reactions. These are then the starting materials for several other types of plastics. Therefore, this process results in the conversion of the natural gas or crude oil components into monomers such as ethylene, propylene, butene and styrene. <sup>(1)</sup>

These monomers are then chemically bonded into chains called polymers. Different combinations of monomers yield plastic resins with different properties and characteristics. Each monomer yields a plastic resin with different properties and characteristics. Combinations of monomers produce copolymers with further property variations.

The resulting resins may be molded or formed to produce several different kinds of plastic products with application in many major markets. The variability of resin permits a compound to be tailored to a specific design or performance requirement. This is why certain plastics are best suited for some applications while others are best suited for entirely different applications. For instance, impact strength measures the ability of a material to withstand shock loading. Heat resistance protects the resin from exposure to excessive temperatures. Chemical resistance protects the resin from breakdown due to exposure to environmental chemicals; these different properties can be achieved by variation of chemical structure of polymers.<sup>(2)</sup>

### 1.1.2 Chemical Structure Of Polymers

The chemical bonding of many identical or related basic units creates polymers and those produced from a single monomer type are called homopolymers. These polymers are specifically made of small units bonded into long chains. Carbon makes up the backbone of the molecule and hydrogen atoms are bonded along the carbon backbone. Polymers that contain primarily carbon and hydrogen are classified as organic polymers. Polypropylene, polybutylene, polystyrene, and polymethylpentene are examples of these. Below is a diagram of polyethylene, the simplest polymer structure.



Even though the basic makeup of many polymers is carbon and hydrogen, other elements can also be involved. Oxygen, chlorine, fluorine, nitrogen, silicon, phosphorous, and sulfur are other elements that are found in the molecular makeup of polymers. Polyvinyl chloride (PVC) contains chlorine. Nylon contains nitrogen. Teflon contains fluorine. Polyester and polycarbonates contain oxygen. There are also some polymers that, instead of having a carbon backbone, have a silicon or phosphorous backbone and these are considered inorganic polymers. In order to achieve a commercial product, the polymer is subjected to further treatment and the

inclusion of additives that are selected to give its specified properties. Most polymers are blended with additives during raw material processing into their finished parts.<sup>(3)</sup>

### **1.1.3 The Additives**

Additives are incorporated into polymers to alter and improve their basic mechanical, physical or chemical properties. Additives are also used to protect the polymer from the degrading effects of light, heat, or bacteria; to change such polymer properties as flow; to provide product color; and to provide special characteristics such as improved surface appearance or reduced friction, these additives vary in such way to meet the desired application and some of them are:

- Antioxidants: for outside application
- Colorants: for colored plastic parts
- Foaming agents: for Styrofoam cups
- Plasticizers: used in toys and food processing equipment

These finished parts after different treatments are divided into three major categories.

## **1.2 Classification Of Polymer**

- Thermosetting types: these are polymers that undergo chemical change during processing to become permanently insoluble and infusible. Phenolic, amino, epoxy, and polyester resins are typical. They are also called thermohardening plastics.

- Thermoplastic types: these are resins that soften repeatedly when heated and harden when cooled. Most thermoplastics are soluble in specific solvents and support flame to some degree. Softening temperatures vary with polymer type and grade, so care must be taken to avoid degrading, decomposing, or igniting the material. Nylon, vinyl, cellulose acetate are typically thermosoftening plastics.

- Elastomers: elastomers are materials that can be stretched repeatedly to at least twice their original length (while at room temperature) and which will return with force to their approximate original length when an immediate stress is released. Polymers ranged as elastomers include modified thermoplastics as well as natural and synthetic rubbers. Most elastomers attain their properties by a process of vulcanization that

renders then incapable of reprocessing, as it possible with thermoplastics. Examples of elastomeric are silicon, urethane, nitrile rubbers, and chlorinated polyethylene. Thermoplastic and thermoset polymers are processed in different processing methods depending upon the finished parts.

### 1.3 Processing Methods <sup>(1)</sup>

There are a variety of different processing methods used to convert resins into finished products. Some include:

**Extrusion** - This continuous process is used for the production of semi-finished goods such as films, sheet profiles, tubs and pipes. They are termed "semi-finished" because they must be further processed before they become useful things. Plastic material is first loaded into a hopper and then fed into a long heated chamber through which it is moved by the action of a continuously revolving screw. At the end of the heated chamber, the molten plastic is forced out through a small opening called a die that is cast in the shape of the finished product. As the plastic extrusion comes from the die, it is fed onto a conveyor belt where it is cooled by blowers or by immersion in water. The operation's principle is the same as that of a meat mincer but with added heaters in the wall of the extruder. Examples of products include lawn edging, pipe, film and window trim.

**Injection molding** - Since this process can produce moldings of high quality and with great accuracy, it is very widespread. It is predominately used for thermoplastics but smaller amounts of thermosets and elastomers are also processed this way. In injection molding, plastic material is also put into a hopper, which feeds into a heating chamber. A plunger pushes the plastic through the heating chamber where the material is then softened into a fluid state. At the end of this chamber, the resin is forced into a closed mold. Once the plastic cools to a solid state, the mold opens and the finished product is ejected. This process is used to make such items as butter tubs, yogurt containers, closures, fittings and razors.

**Blow molding** - Blow molding is a process used in conjunction with extrusion. The die forms a molten tube of thermoplastic material. Using compressed air, the tube is then blown to conform to the interior of a chilled mold, which clamps around the

tube. Overall, the goal is to produce a uniform melt, form it into a tube with the desired cross section and blow it into the exact shape of the product. This process is intended for use in manufacturing hollow plastic products and its principal advantage is its ability to produce hollow shapes without having to join two or more separately molded parts. This method is used to make items such as commercial drums and bottles.

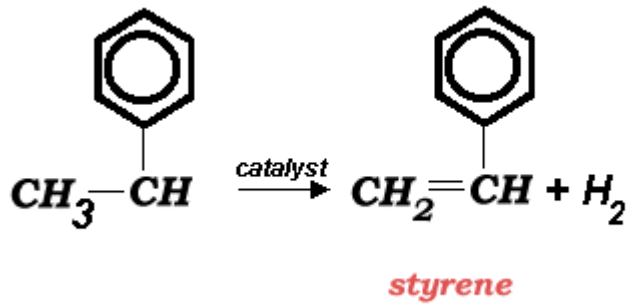
**Rotational Molding** - This process is relatively simple in concept since heat is used to melt and fuse a plastic resin inside a closed mold without using pressure. Rotational molding consists of a mold mounted on a machine capable of rotating on two axes simultaneously. Solid or liquid resin is then placed within the mold and heat is then applied. Rotation distributes the plastic into a uniform coating on the inside of the mold until the plastic part cools and sets. This process is used to make hollow configurations. Common rotationally molded products include shipping drums, storage tanks and some consumer furniture and toys.

One of the most popular thermoplastic polymer which is processed in different methods and meeting a variety of application is polystyrene.

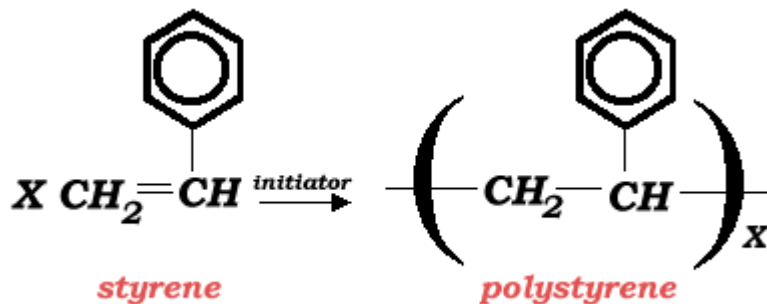
## **1.4 Polystyrene**

### **1.4.1 Introduction <sup>(2)</sup>**

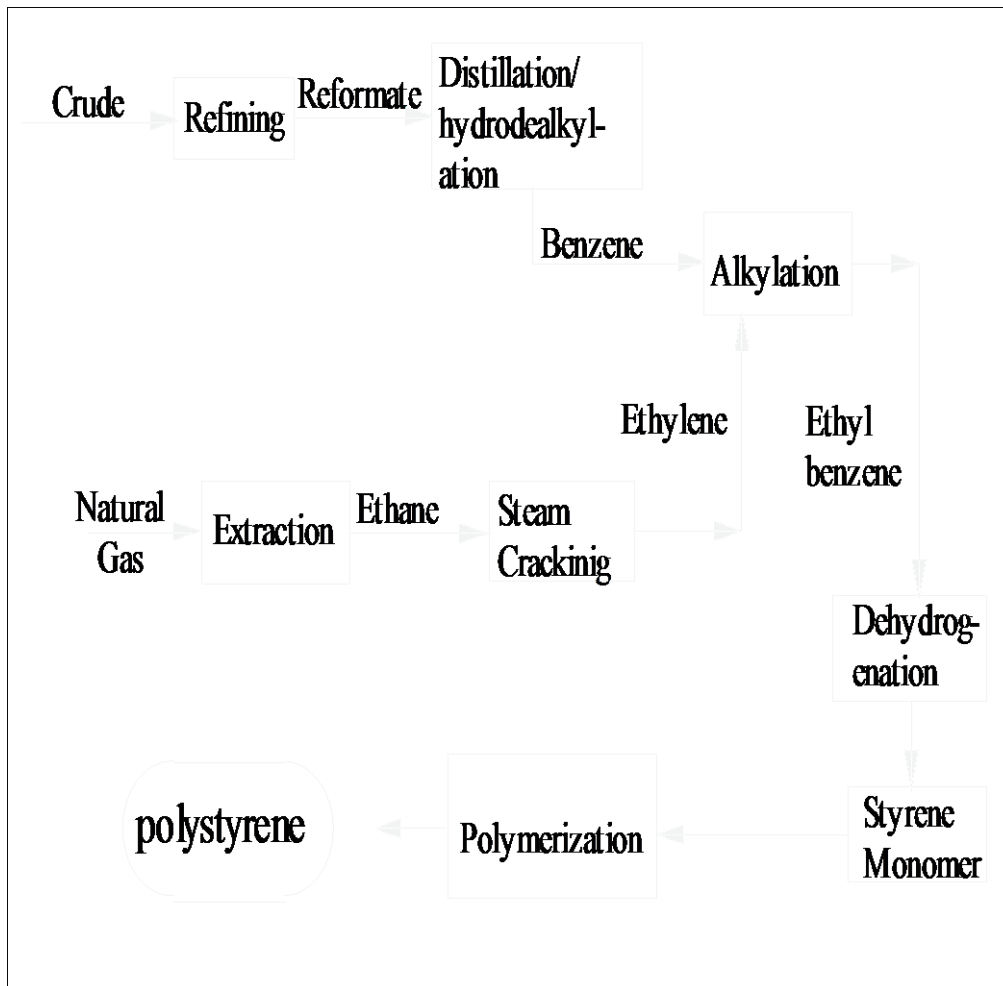
Polystyrene (PS) is a very versatile plastic that can be rigid or foamed. General-purpose polystyrene is clear, flammable, hard and brittle. On a per-pound basis, it is a very inexpensive resin. It is a rather poor barrier to oxygen and water vapor and has a relatively low melting point, but starts to soften at (T=185 F). Generally, polystyrene's density varies from 1.04 to 1.14 g/cm<sup>3</sup>, depending upon composition. Typical applications include protective packaging, containers, lids, bottles, trays and tumblers. Polystyrene itself is made from styrene, which is a petroleum by-product, through a chemical reaction process known as polymerization. Styrene is produced by high temperature dehydrogenation of ethylbenzene (EB) in the presence of a catalyst. The chemical representation of this reaction is as follows:



In most cases, the catalyst is a form of iron oxide carried on an inert substrate in the form of small-extruded granules. The catalyst is a fixed bed, and is replaced on a routine basis at 2 to 3 year intervals. Benzene and toluene are co-produced in the process. Styrene monomer is used almost exclusively (about 94%) as the feedstock for a wide variety of homopolymers and copolymers (e.g. ABS resins, S/B copolymer latexes, SBR elastomers and latexes, unsaturated polyester resins, and SAN resins). Polymers made from styrene are also used extensively today in the manufacture of automobile parts, electronic components, personal computer housings, boats, recreational vehicle, and synthetic rubber products. The reactive chemical intermediate styrene monomer (SM) is the immediate precursor for all forms of polystyrene (PS). The polymerization reaction is represented as below:



Polymerization is affected by a free radical mechanism, and can be initiated by heat alone or more effectively by heating in the presence of a free radical provider, such as benzoyl peroxide. The polymerization of styrene monomer is highly exothermic, and the properties of the polymer are governed by control of catalyst concentration, temperature, and time of the reaction. A schematic representation of the steps involved in the main route to the formation styrene monomer (SM), the precursor to polystyrene (PS), is shown in **figure(1-1)** below:



**Figure(1-1):**the main routes for polystyrene synthesis

When polystyrene is produced there are three main, commercially available, types of polystyrene are crystal polystyrene, impact polystyrene and expandable (foamed) polystyrene which is commonly known (Styrofoam) which is the major well spread used, in these three types, the molecular structure is atactic, i.e. the phenyl ( $C_6H_5-$ ) groups are randomly placed on either side of the polymer chain.

Syndiotactic polystyrene, in which the phenyl groups alternate regularly from one side of the polymer chain syndiotactic polystyrene has some superior properties compared to atactic one, but is still only commercially available in small quantities.

## **1.4.2 Types Of Polystyrene<sup>(3)</sup>**

### **1.4.2.1 Crystal Polystyrene**

Historically, crystal polystyrene was produced by polymerization of styrene monomer (SM) suspended in water. Agitation (stirrer speed) and suspension agents control the bead size, and the heating cycle and catalyst control the molecular weight (MW) and MW distribution, which in turn determine the polystyrene properties. The resulting beads are then converted, by extrusion, into strand-cut granules. In this stage, the properties of the polystyrene are further influenced by incorporation of ultra violet (UV) stabilizers, anti-static agents, flame-retardants, etc. These granules are the form in which the product is shipped and soled.

Although crystal polystyrene (PS) is still produced as described above, there is an increasing tendency to use continuous mass polymerization, with a series of stirred reaction vessels, and heat-exchanger zones to control the reaction temperature. The resultant hot polymer is fed to an extruder, where the additives package is introduced, and strand-cut granules produced for subsequent shipping and sale.

Crystal polystyrene (PS), in addition to other applications, is also the feedstock for the production of foam board by extrusion. The beads are mixed with a solid foaming compound, which releases the blowing agent at the extruder temperature, and produces the foaming effect at the die-plate.

Crystal polystyrene polymers have high clarity and stiffness and are used for cup, tumbler, and cassette and CD cases. They are also chemically inert and water-resistant, and thus have an advantage in electronics, food, automotive and medical applications.

### **1.4.2.2 Impact Polystyrene**

Impact polystyrene produced by incorporating small proportions of polybutadiene elastomers into the polystyrene (PS). High impact grades typically include 6-12% elastomer, and medium impact grade contain 2-5%. The elastomer is dissolved in the styrene monomer (SM), and the mass polymerization process as described above is used to produce copolymers with the required properties. As suggests, these products are more impact resistant than crystal polystyrene and compete with polyethylene and polypropylene products in some applications. Impact polystyrene polymers are used in appliance and electronics housings such as refrigerator linings and TV cases.



### 1.4.2.3 Expandable or Foamed Polystyrene (EPS)

EPS in the form of beads is produced by the batch suspension polymerization of styrene monomer as described previously in crystal polystyrene in the latter stages of the production cycle, the reaction vessel is closed, the blowing agent introduced, and the reactor temperature increased. Under these conditions, the blowing agent (usually a saturated aliphatic hydrocarbon in the C<sub>4</sub> to C<sub>6</sub> range or carbon dioxide CO<sub>2</sub> which is nontoxic, nonflammable, and does not contribute to low-level smog, nor it deplete the stratospheric ozone layer. Its use in this manufacturing process results in no net addition of carbon dioxide CO<sub>2</sub> to the atmosphere), is absorbed into the beads, where it remains when the reaction vessel contents are cooled and removed. In further continuous processing, the beads are dried, sieve-cut into the bead size range for the particular application, and packed into sealed containers in order to maintain the blowing agent content. This is the form in which the product is shipped and sold.

The EPS beads are steam-expanded by the fabricator into expanded polystyrene beads. Generally, the largest bead cuts are moulded into large blocks, and then cut into sheets for thermal insulation; medium beads are moulded to shape protective packaging; and small beads are used for moulding into disposable drinking cups. EPS is made up of 98% air and, due to its extremely low weight, its use for packaging does not significantly add to the weight of the total product. This in turn means that fuel consumption is improved and the consequent emissions are lower than with the heavier materials. The reduction in emissions means less impact on global warming.

For these packaging applications, it is worth underlining following properties of expandable polystyrene (EPS):

- Shock absorption: the material has a high-energy absorption index should it fall or be knocked and this makes it the ideal material for protecting sensitive products during transport and storage.
- Thermal insulation: protecting product, especially food stuffs, from sudden change in temperature.
- Low weight: its low density reduces the packaging weight and consequently provides savings in transport.
- Retention of vitamin C: when packed on EPS, fruit and vegetables, as recently studies have shown, keep longer the content of vitamin C of these food stuffs.

- Resistance to humidity: its excellent mechanical and thermal properties are maintained by the fact that it does not absorb water. This is very significant because climatic hostility like rain can affect other material, but not EPS.
- Compressive resistance: This allows stacking of merchandise-filled packages and packs without any difficulties in storage, transport or at point of sale.
- Chemical resistance: allows many products to be packed without the goods being affected.
- Display effect (promoting sales): given its appealing appearance and the ease with which it can be colored, printed on, stacked and subjected to other product dressing techniques to attract customers.
- Hygienic nature: since the material is inert, inalterable and innocuous it can come into direct contact with food stuffs whilst complying with the laid down health and safety standards.
- Adaptability: it easy to adapt to any product or any design.

### **1.4.3 Processing Of Polystyrene**

Polystyrene and closely related thermoplastics such as the ABS polymers may be processed by such techniques as injection moulding, extrusion and blow moulding. Of less importance is the processing in latex and solution form and the process of polymerization casting. The main factors to be borne in mind when considering polystyrene processing are:

- 1-The negligible water absorption avoids the need for pre-drying granules.
- 2-The low specific heat (compared with polyethylene) enables the polymer to be rapidly heated in injection cylinders, which therefore have a higher plasticizing capacity with polystyrene than with polyethylene. The setting-up rates in the injection moulds are also faster than with the poly-olefins so that faster cycles are also possible.
- 3-The strong dependence of apparent viscosity on shear rate, this necessitates particular care in the design of complex extrusion dies.
- 4-The absence of crystallization gives polymers with low mould shrinkage.
- 5-Molecular orientation.

Although it is not difficult to make injection mouldings from polystyrene, which appears to be satisfactory on visual examination it is another matter to produce mouldings free from internal stresses. This problem is common to injection mouldings of all polymers but is particularly serious with such rigid amorphous thermoplastics as polystyrene.

Internal stresses occur because when the melt is sheared as it enters the mould cavity the molecules tend to be distorted from the favoured coiled state. If such molecules are allowed to freeze before they can re-coil (relax) then they will setup a stress in the mass of the polymer as they attempt to regain the coiled form. Stressed mouldings will be more brittle than unstressed moulding and are liable to crack and craze, particularly in media such as white spirit. They also show a characteristic pattern when viewed through crossed polaroids. It is because compression mouldings exhibit less frozen-in stresses that they are preferred for comparative testing.

To produce mouldings from polystyrene with minimum strain it is desirable to inject a melt, homogeneous in its melt viscosity, at a high rate into a hot mould at an injection pressure such that the cavity pressure drops to zero as the melt solidifies. Limitations in the machine available or economic factors may, however, lead to less ideal conditions being employed.

A further source of stress may arise from incorrect mould design .For example, if the ejector pins are designed in such away to cause distortion of the moldings, internal stresses may develop. This will happen if the mould is distorted while the centre is still molten, but cooling, since some molecules will freeze in the distorted position. On recovery by the moulding of its natural shape these molecules will be under stress. A measure of the degree of frozen-in stresses may be obtained comparing the properties of mouldings with known, preferably unstressed samples, by immersion in white spirit and noting the degree of crazing, by alternately plunging samples in hot and cold water and noting the number of cycles to failure or by examination under polarized light. Annealing at temperatures just below the heat distortion temperature followed by slow cooling will in many cases give a useful reduction in the frozen-in stresses. The main reason for extruding polystyrene is to prepare high-impact polystyrene sheet. Such sheet can be formed without difficulty by vaccum forming techniques. In principle the process consists of clamping the sheet above the mould, heating it so that it softens and becomes rubbery and then applying a vaccum to draw

out the air between the mould and the sheet so that the sheet takes up the contours of the mould.

Many grades of resins for commercial polystyrene are available to suit a variety of end uses, styrene is also copolymerized or blended with other thermoplastics to improve properties or modified with additives to aid processing.

#### **1.4.4 Grades Of Polystyrene <sup>(4)</sup>**

Polystyrene is available in a number of grades. These may conveniently be grouped as follows:

##### **1.4.4.1 General Purposes Grades**

In these grades a balance is attempted to obtain good heat resistance, reasonably high setting-up temperature, good flow properties and reasonable impact strength.

##### **1.4.4.2 High Molecular Weight Grades**

Polystyrene has little strength if its molecular weight is below 50000 but increase rapidly, with molecular weight up to 100000. An increase in molecular weight above 100000 has little further effect on tensile strength but continues to have an adverse effect on the ease of flow. Such higher molecular weight grades are sometimes used where improved impact strength is required without the loss of clarity that occurs with the toughened polystyrenes. .

##### **1.4.4.3 Heat Resistant Grades**

By reducing the amount of volatile matter the softening point of the polystyrene can be raised. For example, by reducing the monomer content from 5% to 0% the softening point may be raised from 70C to 100C. Commercial heat-resisting grades usually have a softening point about 7C above the softening point of general purpose polystyrene.

##### **1.4.4.4 Easy Flow Grades**

By incorporating an internal lubricant such as butyl stearate or liquid paraffin, by using a polymer of lower molecular weight, by careful control of granule shape and size and by lubrication of the granules with an external lubricant such as zinc stearate, the flow properties of polystyrene may be improved with little effect on other properties apart from reduction of up to 10C in the softening point. These materials are very useful for thin-wall mouldings, for moulding with minimum frozen-in strains

or other products where the moulding is rather intricate. They have not however, replaced general-purpose polystyrene because of their lower setting-up temperature, which causes a prolongation of the injection moulding cycle.

#### **1.4.4.5 Chemical Resistant Grades**

A copolymer of styrene and acrylonitrile improves chemical resistance. Called SAN types, these resins are molded, extruded, and thermoformed into products requiring resistance to acids, mineral oils, and detergents.

The final stage in a product's life cycle in the waste management process is disposal. Despite the fact that plastics are used in every thing from medical products to beverage containers, only very tiny fraction of the waste contains plastics. And this is due to advanced programs of recycling, incineration, land filling, and biodegradation.

### **1.5 Disposal Ways <sup>(5)</sup>**

**1.5.1 Land Filling:** it represents a missed opportunity to recover valuable resources, many plastics waste are an ideal materials for land filling because they remain inert, non toxic, odour-free and non biodegradable by design

**1.5.2 Incineration:** plastics are composed mainly of carbon and hydrogen, when incinerated in a licensed and properly operated modern incinerator; some plastics have a high combustion energy which contributes to a more efficient, cleaner, and complete burn. More over only carbon dioxide, water, and trace amounts of ash remain after waste-to-energy conversion.

**1.5.3 Biodegradation:** many plastics products do not biodegrade significantly, and this feature may be beneficial, "the fact that plastics do not biodegrade, which is often cited as one of its great defects, may actually be one of its greatest virtues'. Since biodegradation can lead to the release of harmful methane gas or leachate, which can contaminate ground water, its preferable to place non biodegradable rather than biodegradable products in landfills, when land filling is the appropriate choice for disposal

**1.5.4 Recycling:** an obvious benefit of recycling is that it reduces the requirement for disposal of waste material. Items that are recycled are, by definition, diverted from the waste stream. In many, though not all, cases, another obvious benefit of recycling is cost reduction. Use of regrind, for example, became routine because of the monetary savings it provided. Similarly, certain plastics industries of years have relied on a combination of off spec and recycled plastics because of their lower price. More recently, the desire to benefit from consumer preferences for recycled material coupled, in some cases, with legislative pressure have led to the anomalous situation of recycled plastic some times being worth more per pound than virgin resin. Less obvious benefit from recycling of plastic result from the fact that use of recycled resin displaces use of virgin materials. Thus, use of recycled plastics can result in significant energy savings, since in general more energy is used to make plastics article than to recover and remold the article.

Polystyrene is a type of plastic that maintains much of its integrity as it is melted and reformed into new pellets. This quality makes polystyrene ideal for being recycled over and over again.

## **1.6 Recycling of polystyrene**

In order to recycle polystyrene, it is necessary to check the solubility of polystyrene, in many solvents to achieve a polymer solution, to be manipulated in such away to form other forms of articles with different properties.

### **1.6.1 Polymer Solubility <sup>(6)</sup>**

A chemical will be a solvent for another material if the molecules of the two materials are compatible, i.e. they can co-exist on the molecular scale and there is no tendency to separate.

This statement does not indicate the speed at which solution may take place since this will depend on additional considerations such as the molecular size of the potential solvent and the temperature. Molecules of two different species will be able to co-exist if the force of attraction between different molecules is not less than the forces of attraction between two like molecules of either species. If the average force of attraction between dissimilar molecules A and B is  $F_{AB}$  and that between similar

molecules of type B is FBB and between similar molecules of type A is FAA, then for compatibility  $F_{AB} \geq F_{BB}$  and  $F_{AB} \geq F_{AA}$ .

If either FAA or FBB is greater than FAB, the molecules with the highest intermolecular attraction will tend to congregate and they will expel the dissimilar molecule with the result that two phases will be formed.

It is now becomes necessary to find some suitable measure of the forces of attraction holding molecules together. If we first consider like molecules we might expected the latent heat of vaporization (L) to provide a useful basis, but this would exceed the value of interest to us by an amount corresponding to the mechanical work done on evaporation, an amount approximating to RT where R is the gas constant and T the absolute temperature. The value of (L-RT), the energy of vaporization, will also clearly depend on the molecular size, a parameter that would not be expected to have large effect on the forces of attraction between two dissimilar molecules. More relevant will be the terms (L-RT)/M (a measure of the energy of vaporization per unit weight) and (L-RT)/(M/D) the energy of vaporization per molar volume, (where M is the molecular weight). This latter term is known as the cohesive energy density and has often been expressed in unit of (cal/cm<sup>3</sup>). However, these units are contrary to the SI system where the unit will be expressed as MPa. More commonly encountered in qualitative studies is the square root of the cohesive energy density, which is known as the solubility parameter and given the symbol ( $\delta$ ), i.e.:

$$\delta = [(L-RT) / (M/D)]^{1/2} = (\text{cal/cm}^3)^{1/2} \text{ or } (\text{MPa})^{1/2}.$$

The solubility parameter  $\delta$  is thus an experimentally determinable property although special methods are necessary with polymers, which cannot normally be vaporized without decomposition. It is found that there is a wide range of solvent for polystyrene in the solubility parameter range of 17.2-19.7 MPa<sup>1/2</sup>, such as benzene, toluene, chloroform, and ethyl acetate with 18.7, 18.2, 19, and 18.6, respectively.

A solvent for a macromolecule may be considered good by either of two separate standard, one kinetic, the other thermodynamic. A kinetically good solvent is one, which will dissolve the polymer quickly. (Reducing the particle size of the polymeric solute, since a grater surface is exposed to solvent also facilitates rapid solution). For a solvent to be good in the thermodynamic sense, the solvent must be capable of strong interaction with the solute brought about because of the similarity in their chemical structure. Thus, a kinetically good solvent is fast; a thermodynamically good solvent is thorough.

The aim of this scientific explain is to predict the solubility of any polymer in any solvent, and this is valid for experiments in the labs, on the other hand, other than solvent power (solvent volume reduction) is used to convert the solid polymer to its melt, such as heat and friction (heating volume reduction) as described later in the following section.

Recycling process of large scale production of polystyrene is determined by several steps, and which is based mainly on the fact that the recycled polystyrene has almost their original properties, using heating volume reduction (melting by heating) or pulverizing volume reduction (pulverized).

In order to recycle any polymer it should be born in mind that this recycled polymer has to attain most of its original properties, especially their mechanical properties. So what is meant by mechanical properties?

## 1.6.2 Mechanical Properties

For materials used as structural element such as glassy polymers, we can usually not tolerate strains of more than a fraction of 1%. It is therefore customary to employ measures of infinitesimal strain. In a tensile test, we usually take a specimen with tabs at the end and stretch it well. One end of the sample is typically fixed, whereas the other is moved outward at a constant velocity. The force is necessary to carry out the stretching deformation is monitored as a function of time along with the instantaneous sample length. From the measured load, we can calculate the stress.

$$\text{stress } \sigma = \frac{f}{A_c}$$

Where  $f$  is the applied load and  $A_c$  is the cross sectional area.

If the cross sectional area is un-deformed, original cross sectional area, the stress is called engineering stress, and if the actual, instantaneous area is used, the true stress is measured.

$$\text{strain } \epsilon = \frac{L - L^{\circ}}{L^{\circ}}$$

Where  $L_0$  is the initial sample length,  $L$  is the final length, strain  $\epsilon$  is called engineering strain. There is also true strain  $\epsilon_{\text{true}} = \ln(1 + \epsilon_{\text{eng}})$ , the two strain measures are identical for small strain.

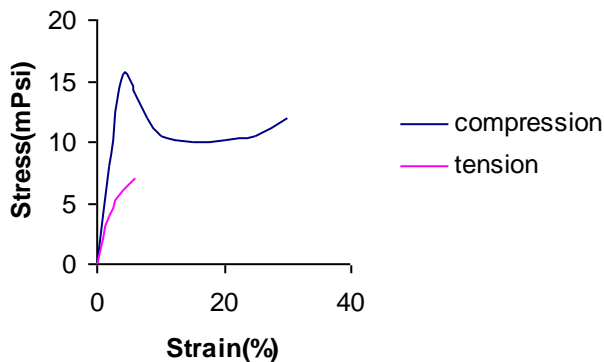


As the sample is stretched in the z direction, its cross sectional area decreases, and this implies that the material suffers a negative strain in the x direction, which is perpendicular to the stretching direction. This is quantified using the Poisson's ratio  $\nu$  defined as:

$$\epsilon_x = -\nu\epsilon_z$$

For incompressible materials such as rubber, it is easy to show that Poisson's ratio  $\nu$  equals 0.5. For glassy polymers, the sample volume increases somewhat on stretching, and Poisson's ratio ranges from 0.3 to 0.4.

Typical stress-strain data for glassy polystyrene are shown in **figure (1.2)** in both tension and compression. The slope of the stress-strain curve evaluated at the origin is termed the elastic modulus (E), and is taken to be a measure of the stiffness of the material. It is seen in this particular case that the modulus in tension differs from that in compression. The stress at fracture is called the strength of the material. Because materials fracture due to the propagation of cracks, the strength in tension is usually less than that in compression since a compressive deformation tends to heal any cracks that form. The strain at fracture is known as the elongation-to-break; the larger the value of this quantity, the more ductile is the material being tested.



**Figure (1-2)** stress-strain behavior of polystyrene under tension and compression.

Glassy polystyrene is not ductile in tension; indeed, it is quite brittle. Finally the area under the stress strain curve is called the toughness and has unit of energy per unit volume. For design purposes, the materials generally sought are stiff, strong, ductile, and tough. For materials that are liquid-like such as polymers above their softening point, it is easier to conduct shear testing than tensile testing. This conceptually

involves deforming a block of material. The force is again monitored, but as a function of the displacement  $\Delta u_x$ . Stress and strain are defined as follows:

$$\text{shear stress, } \tau = \frac{\text{force}}{\text{surface area}}$$

$$\text{shear strain, } \gamma = \frac{\Delta U_x}{\Delta y}$$

At temperatures above the polymer glass transition temperature, shear testing is done using a variety of viscometer. For elastic materials the moduli in shear and tension are related by the following expression:

$$E=2G(1+\nu), E=3G, \text{ for incompressible, elastic polymers.}$$

### 1.6.3 Large Scale Recycling Of Polystyrene (7)

The recycling of expanded or foamed polystyrene (EPS), occupies the first rank of recycling process of poly styrene, and this is due to well-known characteristics and uses, which leads to high demand on it.

Foamed polystyrene recycling steps:

1. **Receiving:** Post consumer expandable polystyrene is shipped to recycling facility in clear bags and manually unloaded.
2. **Sorting:** Before the foam can be recycled, it must be inspected for any contaminants, such as paper, metals, and food wastes.
3. **Conveying:** Once sorted, conveyors move the inspected foam up an incline. At the end of the inclined conveyor, the foam drops into the grinder.
4. **Grinding:** Grinders process the foam into "fluff".
5. **Washing & Drying:** This proprietary process is used only for contaminated material. Typically, the fluff moves directly from the grinder to the silos thus passing this operation.
6. **Storing:** The fluff is held in temporary storage silos before extrusion. Storing fluff in silos assures a continuous supply to the extruder.

- 7. Mixing:** The mixer combines the separate silo feeds into one.
- 8. Extruding:** Heat and friction change the fluff from a solid into a melt. This process removes all of the air trapped in the melt. The melt exits the extruder as strands of polystyrene.
- 9. Pelletizing:** As water-cools the strands of polystyrene, a high-speed blade cuts them into pellets. Process water is then filtered and reused throughout this process.
- 10. Drying:** Water and pellets enter the bottom of the dryer. A screw, spinning at high speed, moves the slurry up through the unit. Centrifugal force pulls the water away from the pellets. Dry pellets exit near the top.
- 11. Packaging:** Once dried, pellets are sorted by size and boxed by color.
- 12. Shipping:** Boxed, recycled polystyrene is then sent to various manufacturers to be made into many durable consumer goods. Some of the products manufactured from recycled polystyrene include rulers, videocassette shells, toys, sun visors, and building insulation. Additional items include flower pots, egg cartons, push pins, landscape supplies, and desk top accessories, to name a few.

## Chapter 2: Experimental Work

### 2.1 Materials

**A**-Virgin polystyrene, which is supplied by (Tosaf Company) as shown in **figure (2.1)**, was used as a thermoplastic material in preparing sheets by thermo-stamping apparatus.



**Figure (2.1)** virgin polystyrene pellets.

**B**-Crushed cups of foamed polystyrene (Styrofoam) as shown in **figure (2.2)** which is supplied by (Poly Bid Company), was used as a thermoplastic material in preparing sheets by thermo-stamping apparatus.



**Figure (2.2)** crushed foamed polystyrene cups

**C**-Acetone (Propanone) was used as a solvent for a Styrofoam, which is supplied (Frutarom Company).

## 2.2 Apparatus

Thermo-stamping apparatus was designed by the project team to carry out different sheets of specific properties. This apparatus consists of a heater with maximum power (1KW), two plates for compression moulding, on-off temperature control system with  $\pm 10\text{C}$  error, with maximum operating temperature (400C) as shown in **figure (2.3)**.



**Figure (2.3)** thermo-stamping apparatus

## 2.3 Processing

### A-Partial removal of acetone for foamed polystyrene

10 g samples of crushed cups of foamed polystyrene were put respectively in 30ml volumes of acetone for one minute, then they were transferred to dry in still air for 20 min, then they were placed in sheet thermo-stamping apparatus. Several samples were prepared and shown at different temperatures in **table (2.1)**.

**Table (2.1):** samples of Styrofoam produced by partial removal of acetone.

Sample#	%Volume of acetone	T°C
1	45	50
2	45	70
3	45	80
4	45	90
5	45	100
6	45	110
7	45	130
8	45	150
9	45	200
10	45	230

### B-Relatively total removal of acetone for foamed polystyrene

As mentioned above, 10 g samples of crushed cups of foamed polystyrene were put respectively in 30ml volumes of acetone for one minute, and then they were transferred to dry in still air for 24 hours. Then they were placed in the thermo-stamping apparatus. Several samples were prepared and shown at different temperatures in **table (2.2)**.

**Table(2.2):** samples of Styrofoam produced by total removal of acetone.

Sample #	% Volume of acetone	T°C
1	30	150
2	30	200
3	30	230

**C-Without removal of acetone for foamed polystyrene**

10 g samples of crushed cups of foamed polystyrene were put respectively in 30ml volumes of acetone for one minute, and then they were transferred directly to thermo-stamping apparatus. Several samples were prepared and shown at different temperatures in **table (2.3)**.

**Table(2.3):** samples of Styrofoam produced without removal of acetone.

Sample #	% Volume of acetone	T°C
1	65	80
2	65	100
3	65	150
4	65	200
5	65	230

**D-Foamed polystyrene without acetone**

10 g samples of crushed cups of foamed polystyrene were placed respectively in thermo-stamping apparatus. Several samples were prepared and shown at different temperatures in **table (2.4)**.

**Table (2.4):** samples of Styrofoam produced without acetone.

Sample#	% Volume of acetone	T°C
1	0	150
2	0	180
3	0	200

**E-Virgin polystyrene**

10 g samples of a virgin polystyrene were placed respectively in thermo-stamping apparatus at a temperature of 210 C. Each sample was subjected to several number of recycling and they were prepared and shown in **table (2.5)**.

**Table (2.5):** samples of virgin polystyrene produced by several number of recycling.

Sample#	# Of Recycling	T <sup>o</sup>
1	0	210
2	1	210
3	2	210
4	3	210
5	4	210

**F-Mixture of virgin and foamed polystyrene:**

10g samples of virgin and foamed polystyrene were placed respectively in thermo-stamping apparatus at different compositions of Styrofoam at constant temperature which is 210 C. Several samples were prepared and shown in **table (2.6)**.

**Table (2.6):** samples of different composition of foamed and virgin polystyrene.

Sample#	% Weight Of Styrofoam	T <sup>o</sup>
1	30	210
2	50	210
3	70	210

## 2.4 Sample Testing

**A-Tensile Test**

Tensile test of the polystyrene sheet samples was carried out by using a (Gunt Humburg Apparatus WP 310). Three trials of each sample were done, the average width and thickness of the samples were (23mm) and (2.5mm) respectively.

**B-Appearance Test**

Appearance test was carried out by inspection for each sheet sample; it was used to determine the effect of operating temperature on the clarity of the sheet samples.



## Chapter 3: Results and Discussion

### 3.1 Results

#### 3.1.1 Tensile Test

Tensile tests were carried out to measure the tensile strengths of polystyrene sheets, those prepared from virgin and foamed polystyrene, in order to compare among various methods, and to observe, by which method it is possible to get better properties, also to study the effect of processing parameters on the tensile strength.

Tensile test was done by using a Gunt-Humburg machine for the samples mentioned in tables (2.1), (2.2), (2.3), (2.4), (2.5), and (2.6).

The results are listed in tables (3.1), (3.2), (3.3), (3.4), (3.5), and (3.6).

**Table (3.1):** tensile strength for Styrofoam samples prepared by partial removal of solvent.

Sample #	Recycling Temperature °C	Tensile Strength (MPa)
1	50	1.93
2	70	3.28
3	80	4.05
4	90	4.22
5	100	5.53
6	110	6.91
7	130	8.37
8	150	7.45
9	200	9.51
10	230	4.33

**Table (3.2):** tensile strength for Styrofoam samples prepared by total removal of solvent.

Sample #	Recycling Temperature ©	Tensile Strength (MPa)
1	150	6.10
2	200	5.18
3	230	4.96

**Table (3.3):** tensile strength for Styrofoam samples prepared without removal of solvent.

Sample #	Recycling Temperature ©	Tensile Strength (MPa)
1	80	2.89
2	100	5.05
3	150	5.83
4	200	4.88
5	230	4.48

**Table (3.4):** tensile strength for Styrofoam samples prepared without solvent.

Sample #	Recycling Temperature ©	Tensile Strength (MPa)
1	150	3.07
2	180	2.67
3	200	1.77

**Table (3.5):** tensile strength for virgin polystyrene with several times of recycling at constant temperature 210 C.

Sample #	Number of recycling	Tensile strength (MPa)
1	0	10.22
2	1	9.20
3	2	5.58
4	3	5.47
5	4	4.24

**Table (3.6):** tensile strength for mixture of foamed and virgin polystyrene at constant temperature equals to 210 C.

Sample #	Percentage Mass Of Foamed Polystyrene	Tensile Strength (MPa)
1	0	10.22
2	30	4.54
3	50	5.23
4	70	6.28
5	100	2.5

### 3.1.2 Appearance Test

Appearance test was carried out to observe the effect of operating conditions (temperature and %volume of solvent) on the clarity of sheet samples for both Foamed and virgin polystyrene. The results are shown in **table (3.7)**.

**Table (3.7):** clarity of various sheet samples prepared by different methods.

Sample#	Case	Recycling Temp ©	Appearance
1	Partial removal of solvent	50	Opaque, white
2	=	70	Opaque, white
3	=	80	Opaque, white
4	=	90	Opaque, white
5	=	100	Less opaque, white
6	=	110	Less opaque, white
7	=	130	Less opaque, white
8	=	150	Translucent, white
9	=	200	Transparent, white
10	=	230	Transparent, yellowish white
11	Total removal of solvent	150	Opaque, white
12	=	200	Translucent, white
13	=	230	Transparent, white

14	Without removal of solvent	80	Opaque, white
15	=	100	Opaque, white
16	=	150	Translucent, white
17	=	200	Translucent, white
18	=	230	Transparent, white
19	Without solvent	150	Translucent, white
20	=	180	Opaque, yellowish white
21	=	200	Translucent, yellowish white
22	Virgin polystyrene, 0 recycle	210	Transparent, white
23	Virgin polystyrene, 1 recycle	210	Transparent, white
24	Virgin polystyrene, 2 recycle	210	Transparent, white
25	Virgin polystyrene, 3 recycle	210	Transparent, white
26	Virgin polystyrene, 4 recycle	210	Transparent, yellowish white
27	0% foamed polystyrene	210	Transparent, white
28	30% foamed polystyrene	210	Transparent, white
29	50% foamed polystyrene	210	Transparent, white
30	70% foamed polystyrene	210	Transparent, white
31	100% foamed polystyrene	210	Transparent, yellowish white

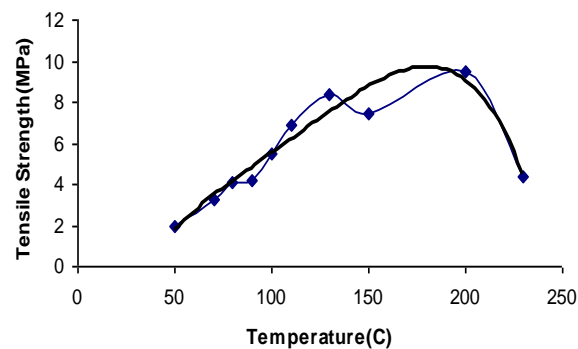
### 3.2 Discussion

It is clear from previous results, that there is an effect of the processing variables on the tensile strength and appearance of the sheet samples prepared.

The main objective was to determine the best operating condition (temperature and percent volume solvent); satisfying the needs of attaining most of original properties in foamed and virgin polystyrene.

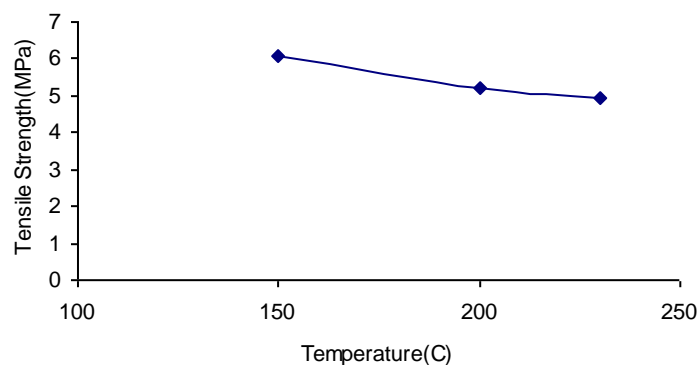
#### -Effect of temperature:

It can be concluded from carrying out partial removal of solvent process, that the tensile strength increases with increasing forming temperature up to 200 C, then a sudden decrease occurred; that is because an elevated temperatures cause distortions in molecular structure of foamed polystyrene as shown in **figure (3.1)**.



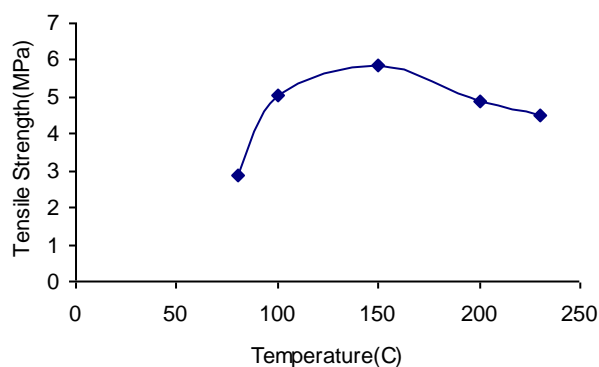
**Figure (3.1)** effect of temperature on tensile strength for partial removal of solvent.

For case of total removal of solvent, it can be observed that, as forming temperature increases, the tensile strength decreases, thus the sample solidify more and more, then it needs more heat to be melted, hence damage will occur to molecular structure. It was found that the best forming temperature was 150 C as shown in **figure (3.2)**.



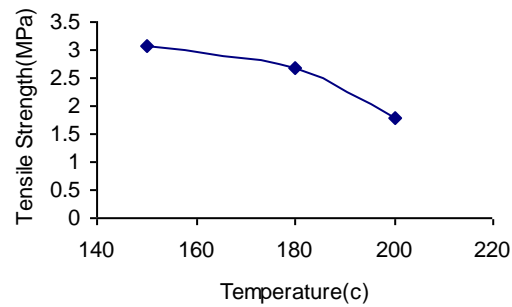
**Figure (3.2)** effect of temperature on tensile strength for part total removal of solvent.

Results for case in which solvent was not removed from foamed polystyrene showed consistency with behavior of (polymer-solvent) rich solution, it was observed that as the forming temperature increases, the tensile strength increases till 150 C (because of, incapability of low temperatures on eliminating holes resulted by solvent in the sheet samples), then a slight decrease occurs above 150 C, and this is because a destruction in molecular forces will start at higher temperature as shown in **figure (3.3)**.



**Figure (3.3)** effect of temperature on tensile strength for without removal process.

Sheet samples produced in without solvent process, suffered from low tensile strength values, it is noticed that a narrow range temperatures within samples can be made as shown in **figure (3.4)**.

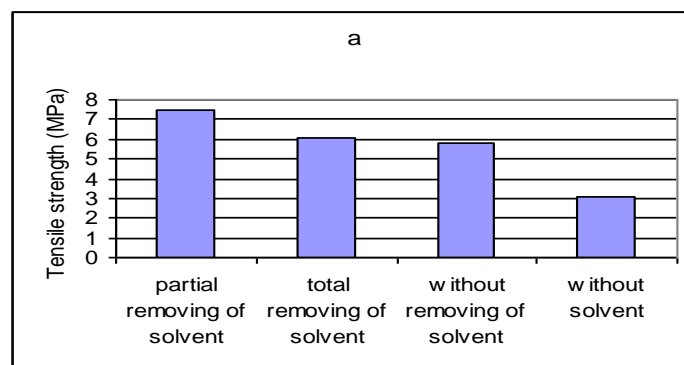


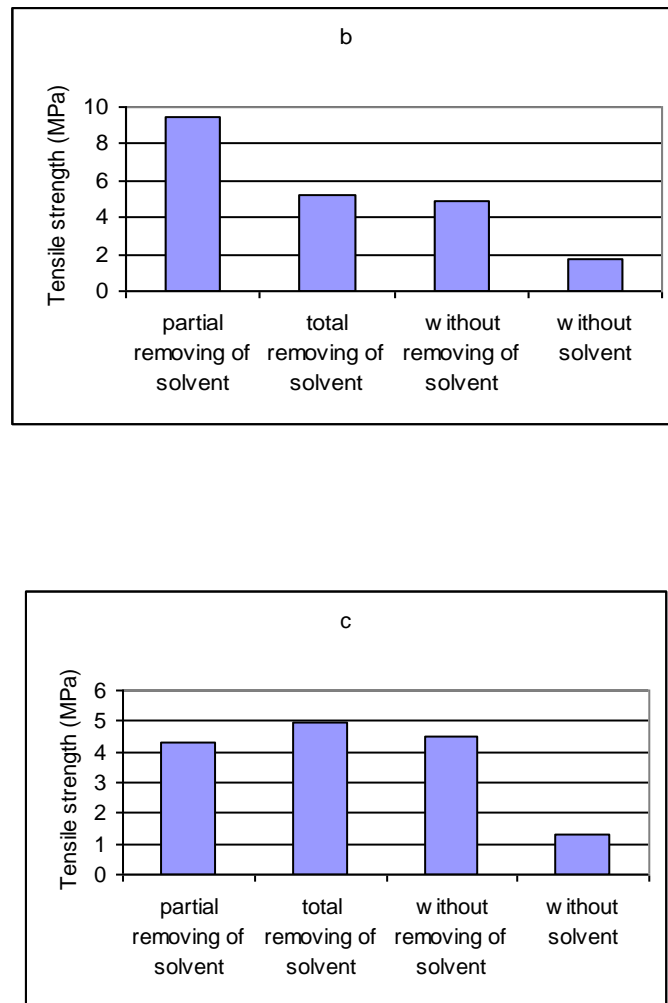
**figure (3.4)** effect of temperature on tensile strength for without solvent process.

**-Effect of solvent (acetone):**

A satisfying explanation for solvent effect on such polymer (foamed polystyrene) is that for an amorphous polymer which is composed of a tangled network of flexible chains in continued motion, when the foamed polystyrene is immersed in a solvent, the network swells from osmotic action of solvent, the segmental motion of the individual chains consequently increases, so long as the solvent is available, the polymer will continue to expand increasing its freedom of motion. When the solvation process has progressed sufficiently to permit translational motion to the chains, they will begin to separate, forming a true solution, and allowing for chains to reordering their sites in such way that they branched and become more attached.

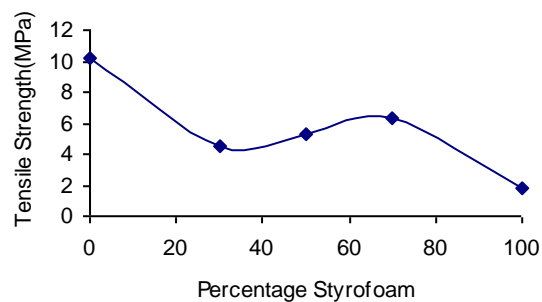
After temperature and solvent effects were observed on recycled foamed polystyrene it can be seen from **figure (3.5)** that at 150 & 200 C the partial removing method was the best, whereas at 230 C total removing was the best for achieving maximum tensile strength.





**Figure (3.5) a:** at temperature 150 C, **b:** at temperature 200 C, **c:** at temperature 230C.

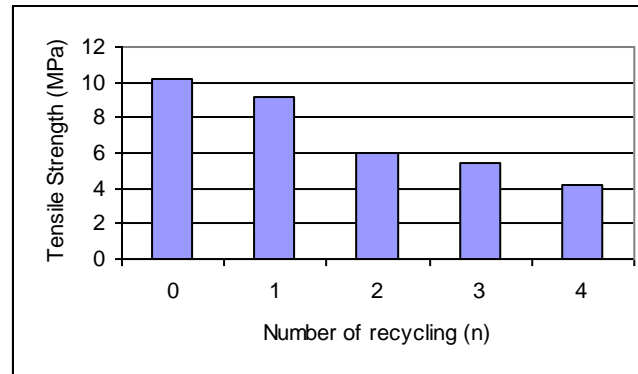
It is clear from **table (3.6)** that there was an effect of percent foamed polystyrene on the decreasing of tensile strength for sheet samples to some value (4.54 MPa), and then gradually increased to (6.28 MPa) and then a sudden decreasing tensile strength occurs as shown in **figure (3.6)**.



**Figure (3.6)** effect of percentage Styrofoam on tensile strength.



In order to estimate the percentage of recovery of tensile strength for polystyrene sheet samples after n-time recycling, it was necessary to know how much time polystyrene can be recycled with attaining of almost its mechanical properties it was noticed from **table (3.5)** that there were a gradual decrease in tensile strength with increasing the number of recycling process as shown in **figure (3.7)**.



**Figure (3.7)** effect of number of recycle on tensile strength.

By considering the method of processing and forming temperatures for each sheet samples, in two cases with partial and total removal of solvent from polystyrene, it is noticed that the appearance depends on the forming temperature, and in the less importance on the method of processing with solvent. So, as the temperature increases, transparency increases, and the sample begin to change from opaque icy white until this white color converts gradually to yellowish white and becomes translucent as shown **figures (3.8)&(3.9)**

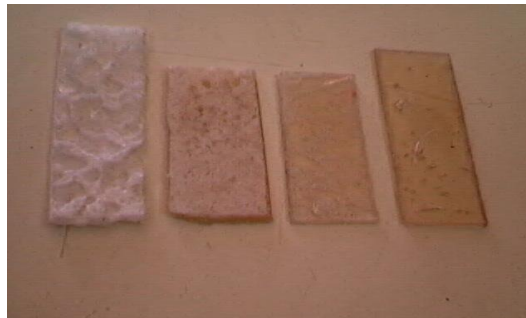


**Figure (3.8)** effect of temperature on the appearance of the in part A (temperature increases to the right).



**Figure (3.9)** effect of temperature on the appearance of the sheet samples in part B (temperature increases to right).

In case of without removal of solvent, it was seen how holes increased in the sample as the temperature decreased due to the presence of solvent inside those holes, thus transparency was decreased as shown in **figure (3.10)**.



**Figure (3.10)** effect of temperature on the appearance in part C (T increase to right).

For virgin polystyrene it was seen that the number of recycle has relatively no effect on the appearance of the recycled sheets as shown in **figure (3.11)**.



**Figure (3.11)** effect of number of recycles on appearance (number of the recycle increase to left).

## Chapter 4: Conclusions and Recommendations

- **From the previous mentioned results the following can be concluded:**
  - 1- According to the total number of cups that recycled in various ways, which equals to (200 cups), and compared to the volume of these cups before recycling, it is clear that the total resulted volume from the recycling of these cups is small, this explains why the recycling process for foamed polystyrene is a volume reduction process, this reduction of volume helps in dealing with the solid waste problem.
  - 2- The tensile strength and appearance are affected by the processing variables(Temperature, percent volume of solvent, number of the recycling times, and percent weight of Styrofoam), during cold recycling and thermo-stamping processing, they increase with increasing stamping temperature and percent volume of solvent and they decrease with increasing number of recycling. For case of mixture of foamed and virgin polystyrene, the best range of percent weight of poly styrene to give high tensile strength is between (30 and 70)%.
  - 3- The percentage recovery of mechanical property is satisfactory for both recycled foamed and virgin polystyrene.
- **The recommendations for this project are:**
  - 1- Recycling of polystyrene in two forms (normal and foamed) can be used in many applications which satisfy the needs of strength for protective requirements.
  - 2- It is suggested that cold recycling(with solvents) and forming process , can be successfully implemented for polystyrene wastes(energy saving process).
  - 3- It is recommended that, the optimum recycling temperature is 200 C for foamed polystyrene, good appearance can be achieved.
  - 4- Several uses for recycled polystyrene, include kid toys, protective films, video cassette and flower pots.
  - 5- The studying of just two properties of recycled polystyrene is not sufficient to prove that recycling process is economical and successful, so more tests other than tensile and appearance tests are needed .

## Nomenclature

		<b>Unit</b>
<b><math>\delta</math></b>	solubility parameter	cal/cm <sup>3</sup> (MPa)
<b>L</b>	latent heat of vaporization	cal/mol
<b>R</b>	gas constant	cal/mol.k
<b>T</b>	absolute temperature	K
<b>M</b>	molecular weight	g/mol
<b>D</b>	density	g/cm <sup>3</sup>
<b>F<sub>xx</sub></b>	attraction force between molecules	N
<b><math>\sigma</math></b>	shear stress	MPa
<b>G</b>	shear rate	GPa
<b><math>\epsilon</math></b>	strain	-
<b><math>\nu</math></b>	Poisson's ratio	-
<b><math>\gamma</math></b>	shear strain	1/sec
<b>E</b>	modulus of elasticity	Pa

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