

# Polymers

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First lecture

The materials, which are derivatives of carbon, chemically combined with hydrogen, oxygen or any other non-metallic substance, and their structures, in most cases, fairly complex are known as organic materials.

Organic materials may be **natural or synthetic**, i.e. prepared or manufactured artificially. The naturally available organic materials include wood, natural rubber, coal, petroleum and food products, etc. The synthetic organic materials include, plastics, lubricants, rubber, soap oils, synthetic fibres, etc. Obviously, the range of organic compounds is very extensive as the thousands of hydrocarbon compounds and their derivatives are in existence. Plastics and synthetic rubbers termed polymers and wood and wood products are common engineering materials of industrial importance.

The organic materials are marked by their non-crystalline nature. However, the non-crystalline solid structures of organic materials is not completely random as they are composed of ordered atoms in several sub-units. The structures of all non-crystalline materials are such that the sub-unit arrangements are tangled very easily and completely in liquid state itself. However, on solidification it is impossible for them to get untangled. Such materials result into three dimensional network or long chain molecules due to the entanglement.

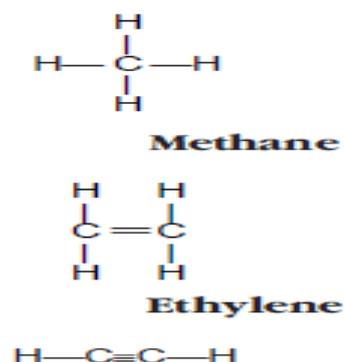
These non-crystalline organic materials may be elements or compounds and are usually referred to as amorphous solids. Glass is a common example of these materials.  $\text{SiO}_2$  (silica) is another example of amorphous materials. The most important amorphous materials are polymers

## polymers

As with metals and ceramics, the properties of polymers are intricately related to the structural elements of the material. Most polymers are **organic in origin** and are based on hydrocarbons, i.e. they are composed of hydrogen and carbon. Moreover, the intramolecular bonds are covalent. **Each carbon has four electrons that may participate in covalent bonding**, whereas every hydrogen atom has only one bonding electron. A single covalent bond exist when each of the two bonding atoms contribute one electron, as shown in for methane.

Double and triple bonds exist between two carbon atoms involve the sharing of two and three pairs of electrons, respectively. Figure 1 shows the structural formula for ethylene (C<sub>2</sub>H<sub>4</sub>). We note that in ethylene, the two carbon atoms are doubly bonded together, and each is also singly bonded to two hydrogen atoms. – and = denote single and double covalent bonds

respectively. Acetylene (C<sub>2</sub>H<sub>2</sub>) is an example of triple bond



Organic molecules that have double and triple bonds are termed unsaturated, i.e., in these compounds, each carbon atom is not bonded to the maximum (four other

atoms; as such, it is possible for another atom or group of atoms to become attached to the original molecule.

On the otherhand, for a saturated hydrocarbon, all bonds are single ones; (and saturated), i.e., no new atoms may be joined without the removal of others that are already bonded. Though the saturated organic compounds are three dimensional structures, yet they are represented by two dimensional structural formula for convenience.

Most polymers are organic (carbon-based) materials that contain molecules composed of **various combinations of hydrogen, oxygen, nitrogen and carbon**. These four elements are among the most common found in organic polymers. **Carbon forms the “spine” of the polymer chain**, and the other constituents attach themselves to the carbon. These polymer chains become entangled and form **irregular coils** which give them added strength. A portion of this entanglement is natural and can be further induced by additives and controlled processes.

Most polymers are based on hydrocarbons, where the elements of carbon and hydrogen form predictable combinations based on the relationship,  $C_nH_{2n+2}$ . These petrochemical intermediates are chemicals manufactured from **paraffins** in **petroleum** and natural gas, which are further processed into polymer products.

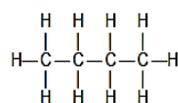
The chain like paraffin molecules include methane ( $CH_4$ ), ethane ( $C_2H_6$ ), propane ( $C_3H_8$ ), and butane ( $C_4H_{10}$ ). **Table 1** provides the compositions and molecular structures for some of paraffin molecules. The covalent bonds in each molecule are strong, but only weak hydrogen and Van der Waals bonds exist between molecules, and therefore these hydrocarbons have relatively low melting and boiling points.

However, boiling temperature rise with increasing molecular weight. These intermediates are the basis for almost all rubber and polymer products. Intermediates are also produced from coal. The most important of these intermediates is ethylene. These are called olefin intermediates and include acetylene, propylene, butylene, isobutylene, and butadiene. Most of these are used in the production of rubbers. Nylon is produced from butadiene; polyvinyl chloride is produced from acetylene.

**Table 17.1** Compositions and molecular structures for some of the paraffin compounds based on the relation  $C_nH_{2n+2}$

Name	Composition (formula)	Structure	Boiling point (°C)
Methane	CH <sub>4</sub>	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$	-164
Ethane	C <sub>2</sub> H <sub>6</sub>	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	-88.6
Propane	C <sub>3</sub> H <sub>8</sub>	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	-42.1
Butane	C <sub>4</sub> H <sub>10</sub>		-0.5
Pentane	C <sub>5</sub> H <sub>12</sub>		36.1
Hexane	C <sub>6</sub> H <sub>14</sub>		69.0

Hydrocarbon compounds with the same composition may have different atomic arrangement; a phenomenon called *isomerism*. For e.g., butane have two isomers. The structure of normal butane is shown in Fig. 17.4.



**Fig. 17.4** Normal structure of butane

Whereas the structure of isobutane is shown in Fig. 2. We may note that some of the physical properties of

hydrocarbons will depend on the isomeric state; for e.g., the boiling temperatures of normal butane and 2-methylbutane are  $-0.5$  and  $-12.3^{\circ}\text{C}$ , respectively.

There are several other organic groups, many of which are involved in polymer structures as mentioned above. Table 2 provides some common hydrocarbon groups, where R and R' represent organic radicals—groups of atoms that remain as a single unit and maintain their identity during chemical reactions. CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> and C<sub>6</sub>H<sub>5</sub> (methyl, ethyl and phenyl) groups are examples of singly bonded hydrocarbons.

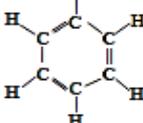
Family	Characteristic unit		Representative compound
(i) Alcohols	R—OH	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$	Methyl Alcohol
(ii) Ethers	R—O—R'	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{O}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	Dimethyl ether
(iii) Acids	$\begin{array}{c} \text{OH} \\ / \\ \text{R}-\text{C} \\ \backslash \\ \text{O} \end{array}$	$\begin{array}{c} \text{H} \quad \text{OH} \\   \quad / \\ \text{H}-\text{C}-\text{C} \\   \quad \backslash \\ \text{H} \quad \text{O} \end{array}$	Acetic acid
(iv) Aldehydes	$\begin{array}{c} \text{R} \\   \\ \text{C}=\text{O} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}=\text{O} \\   \\ \text{H} \end{array}$	Formaldehyde
(v) Aromatic hydrocarbons			Phenol
(a) The structure  represent a phenyl group:			
			

Table 2

for hydrogen atoms are shown adjacent to the appropriate corner of the hexagon. Figure 17.7 shows some aromatic compounds on this pattern.

Naphthenic intermediates is another category of intermediates in which cyclohexane is the most

important, being used in the production of nylon. Aromatic, naphthenic, and olefin intermediates are used to produce insecticides, detergents, rocket fuels, films, pharmaceuticals, explosives, alcohols, and other such products. Cellulosic plastics are produced from wood rather than petroleum, coal, or gas.

General characteristics of polymers can be summarized as follows:

**(i) Polymers have long chain structures. The individual molecule of a polymer is very large, i.e., it may**

**consists of thousands of similar small molecules, all bonded together covalently.**

**(ii) All polymers have one thing common, i.e., carbon, which further bonds with hydrogen, nitrogen, halogens or other organic or inorganic substances.**

**(iii) Although, polymer's structure may be crystalline in simple materials but generally they are noncrystalline**

**solids at room temperatures. No doubt, polymers pass through a viscous stage during formation.**

**(iv) Polymers have light weight and they can be easily fabricated and shaped. They are poor conductors of electricity and their thermal conductivity is also low. Moreover, the polymers are resistant to chemical attack and decay.**

Polymers are widely used in different fields. Polymers are used in indefinite number of forms, e.g. as **telephone sets, paints, radio and television cabinets, coatings, adhesive and other countless objects.**

Few notable developments in polymer materials are:

**(i) polymer materials far stronger than steel according to weight to weight ratio.**

**(ii) polymer materials suitable for repairing damaged kidney or heart.**

**(iii) materials act as adhesive so strong that the use of nails in wood and leather can be avoided.**

**(iv) lining for spacecraft to withstand high temperature, specially during re-entering into earth's atmosphere.**

**We know that there is increase in temperature due to friction when the spacecraft re-enters the earth's atmosphere.**

**(v) silicon film does not permit water to enter but allows dissolved oxygen, in water, to pass through it. Using polymers, under water tents have been prepared which allows a man to live and work.**

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