MODULE –IV

Property requirements and polymer utilization.

Combination of properties unique to polymers is evidence in each of major uses including elastomers, fibers and plastics to which the macromolecules are put. Here the property requirements of these end uses are described and related to polymer structure.

Elastomers: All the substances exhibiting a high degree of the rubber like elasticity containing long-chain structures. The restoring force leading to the elastic behavior results directly from the decrease in entropy associated with the distortion of chain macromolecule from its most probable conformation.

I. Two additional property requirements are imposed by the condition that there may be sufficient freedom of molecular motion to allow distortions to take place rapidly.
   - First the polymer must be at its use temperature above Tg.
   - It must be amorphous in nature at least in the undistorted state.

II. In contrast to the high local mobility of chain segments, the gross mobility of chains in elastomers must be low. The motion of one chains pass on another must be restricted in order that the material can regain its original shape when the stress as released. This restriction of gross mobility usually obtained by the introduction of a network of primary bond cross-linking in the material (it cannot be obtained through secondary bond).

III. The cross-linking must be relatively few and widely separated, hence stretching to large extensions can takes place without rupture of primary bonds.

IV. The requirements of low cohesive energy limit the family of elastomers to polymers which are largely hydrocarbons (Fluorocarbons on silicones) in nature with polar groups distributed at random and is not too great in number, so that crystallinity is absent and Tg is sufficiently low, ideally in the range of 50 to 80 ^{0}C.

V. In contrast to its equilibriumproperties a stretched elastomer should have high tensile strength and modulus usually awaited with crystalline plastics. Thus rubbers in which crystallinity can develop on stretching such as natural rubber and its steno regular synthetic counter parts usually have more desirable properties than those with less stereo -regularstructures.

VI. However, a neon forcing filler can sometimes impart to a rubber properties similar to those obtained on the development of crystallinity. Thus neon forcedstyrene- butadiene rubber has properties meanly equivalent to those of neon forced natural rubber, when its properties are due to cross-linked but not reinforced.

(2) Fibers: (i) In contrast to elastomers, the requirements of high tensile strength and modulus characteristics of fibers are almost always obtained by utilizing the combination of the molecular symmetry and high cohesive energy associated with high degree of crystalline. Usually the fibers are oriented to provide optimum properties in the direction of the fiber axis.

(ii) The fibers particularly those involving textiles leads to the restriction of several properties. The T_m must be above a certain minimum say 200^{0}C if the resulting fabric is to the subjected to tailoring. On the other hand,spinning the polymer in to a fiber requires either that $T_{m\ must}$ be below say 300^0Cand iswell below the temperature of decomposition of the polymer.

(iii) The requirement of orientation in the fiber usually implies that Tg being is not too high (since orientation by cold drawing and ironing are carrier out above this temperature are too low (since orientation and related characteristics such as crease retention after ironing must be maintained at room temperature).

(iv) Thus the selection of polymer for us as a fiber involves a number of compromises usually met by choosing a mean polymer with high symmetry and high intermolecular forces resulting from the presence of polar groups high toughness and high molecular weight so that tensile strength and related properties are fully developed.

(v) Breaking in the polymer chain is in general detrimental to the fiber properties because breakingpoints disrupt the crystalline lattice, lower the crystalline M.P and

decreases stiffness. Cross-linking on the other hand offers the possibility of offering strong interchange bonding. If crosslinks are formed after the polymer is span microfiber and are relatively few in number, improvement in fiber properties may result.

(vi) Thus polyvinyl alcohol, polyurethanes, and protein fibers may be cross-linked with formaldehyde to give higher M.P, lower solubility and low moisture regain.

(3) General purpose and specially plastics: The wide range of the use of plastics requires a variety of property combination correspondingly a wide variety of structure. Generally, the properties of plastic are intermediate between fibers and elastomers with much overlapping on either end. Thus plastics have cohesive energies higher than those of elastomers but lower than those of fibers. The different applications of plastics are as follows.

(**i) Optical application: -** The requirement of good optical properties, especially in massive pieces imposes several limitations on the structure of the polymers, in general crystallinity must be absent and most of the amorphous polymers areextremely shows softness and brittleness which include them for many applications. In this films structural requirements are not so severe since crystallinity can after being tolerated if the material can be processed to give sufficiently smooth surfaces. Thus normally incompatible requirements of clarity and toughness both have to be meet.

(ii) Electrical Applications: To achieve low dielectric loss over a wide frequency range, the structure of a polymer must be selected on the basis of low polarity and all other requirements are considerably less important. Polyethylene and PTFE are the best materials for low loss application, particularly at high frequencies whereas at low frequencies however other plastics such as PVC are useful.

(iii) Mechanical application: The most important property requirement for the use of polymers Is its mechanical applications is toughness. This property is usually achieved by the selection of a polymer with a moderate but not too high, degree of crystallinity often a delicate balance of the structural features is need a to achieve the desired combination of properties.

(iv) Economic aspects: The major factor in the selection of the appropriate plastic for a given use is economic. In many as a mass market is achieved by sacrificing properties for price. The plastics manufacturer must therefore consider what structure give the optimum combination of melt and it properties. He would thus like to lower the M.W to achieve low melt viscosity and more rapid fabrication but he must maintain the levels of M.W consistent with the development of good mechanical properties. The selection of raw materials is also important. The cost polymerization itself appears less important in most cases and closely related to cost of the monomers. Hence it is clear that monomers which are expensive to polymerize have is opportunity to yield large – volume plastics.

(v) Engineering plastics: (i)The term engineering polymers or plastics is applied to those materials which command a premium price usually associated with relatively low production volume, because of their outstanding balance of properties which allows them to compete successfully with other materials (metals, ceramics) in engineering applications.

(ii) These are strong, stiff, tough, abrasion- resistance materials, capable of withstanding wide ranges of temperature and resistance to attack by weather, chemicals and other hostile conditions.

(ii) The outstanding properties of engineering plastics come primarily from their crystalline nature and strong intermolecular forces. Most of them have quite high M.P good physical properties to high temperature and good toughness over wide range of temperature.

(iv) The necessary high M.P can be obtained in several ways. These include combining high degree of crystallinity with still polymer chains of finding structural features substituting for crystallinity in imparting rigidity to the total material structure. This can be done in two ways i.e. cross-linking and utilizing composite structure with an extremely rigid material such as glass fibers.

(v) Glass fibers are usually used to reinforce glassy plastics such as polyester-styrene copolymers but the cross- linking polymers are not crystallizable. The combination of two or more of these enhances the properties.

Example: The development of ladder polymers combining the features of cross-linking with crystalizability and the use of high- performance inorganic fibers (such as born) to reinforce crystalline plastics.

(vi) The role of plastics among materials: In the last decades the production of all the plastics has increased about 3-5 fold as compared to a 2-5-fold increase for chemicals and smaller values for metals and ceramics. Engineering pasties have increased proportionately more about 6- fold.

This means that on a weight basis the annual production of plastics now exceeds that of Cu and Al but falls far short of the production of steel.

We cannot help concluding that the burgeoning expansion in the use of polymeric materials we have seen in the last decade will continue for the foreseeable future.

Mechanical Behaviors of Polymers:

A polymer in the molten state is amorphous and possesses random chain orientation. This structure can be prevented at a low temp. through quench. The stress=strain relationships are not like those of metals, because the modulus of elasticity is increased when stress is applied directly against the polymer chains after alignment has occurred.

(i) If polymers are subjected to the same time-dependent phenomenon like metal, the molecular movement are more complicated than the atomic movement due to large size and weaker bonding forces of the polymer molecules. Hence high creep rates are developed.
(ii) Instantaneous stressing results only elastic response, while prolonged exposure to even weak stresses allows plastic deformation to occur.

This different behaviors of the polymeric materials are as follows:

(i) **Stress – Relaxation:Definition**: Stress relaxation time is defined as the time takes for the stress to be reduced by 1/e of its original value.

Stresses are relaxed with time in those applications where they are initially developed from elastic elongation.

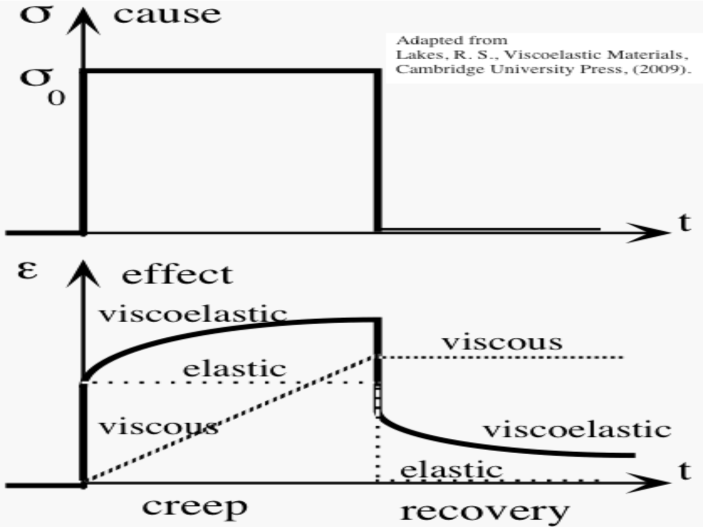
The time required for the adjustment of stresses is called as relaxation time.

Anelasticity: The time dependent elastic behaviors of the polymer is known as an elasticity.

- An elasticity of a polymeric material is due to the following reason. Diffusion of thermal energy of interstitial atoms or substitution atoms.
- Grain boundary effects, dislocation and thermal currents within the crystals. This effect is also a result of retarded elasticity and is called as "**elastic after effect**". In some polymeric materials an elasticity magnitude is insignificant and is called "Viscoelastic behavior".

Viscoelasticity: Viscoelasticity is a third kind of deformation (other two kinds are elastic and plastic deformation) which is found in may polymers such as plastic. When the elastic range of the materials are completely removed, the material will not completely recover to its original size.

i. An amorphous polymer behaves like a glass at low temp., a rubbery solid at an intermediate temp., and a viscous liquid with further raise in temperature.
ii. An intermediate condition of temp. is termed as Viscoelasticity of the polymer.
iii. The Viscoelasticity behavior of a polymeric materials is dependent of both time and temperature.



Adapted from
Lakes, R. S., Viscoelastic Materials,
Cambridge University Press, (2009).

iv. It has been observed that most of the polymers exhibits both elastic as well as viscous response to the external forces. Thus the models for such Viscoelasticity behavior comprise of viscous as well as elastic elements.

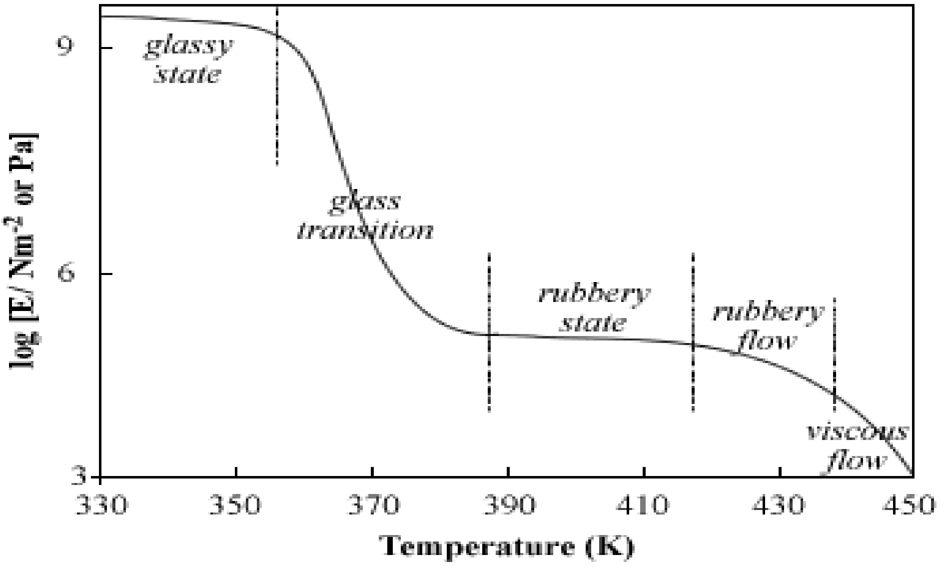
v. Further more stress relaxation occurs with time if the stresses are developed by elastic deformation. The time required for the adjustment of stresses is known as "Relaxation time".

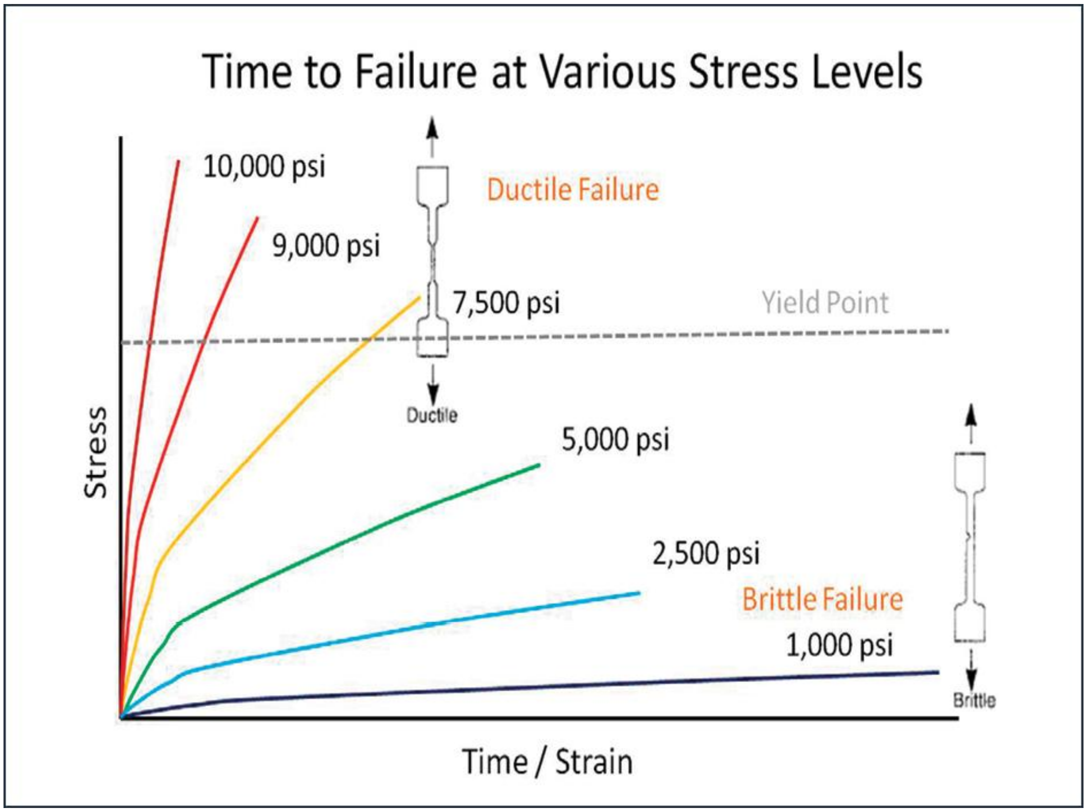
$$\sigma = \sigma 0 \ \ e - 1/\lambda$$

$\sigma 0$=original stress σ =stress after time 't'

λ - relaxation time.

If a graph is platted between stress and strain at different temp. below transition temp, the polymer deforms by elastic deformation (-40^{o}C to 68^{0}C) and above T_g it shows plastic deformation (122^{o}c to 140^{o}c)





Increase in temperatureProduces the following

(a) A decrease in elastic modulus
(b) A reduction in tensile strength.
(c) An enhancement of ductility.

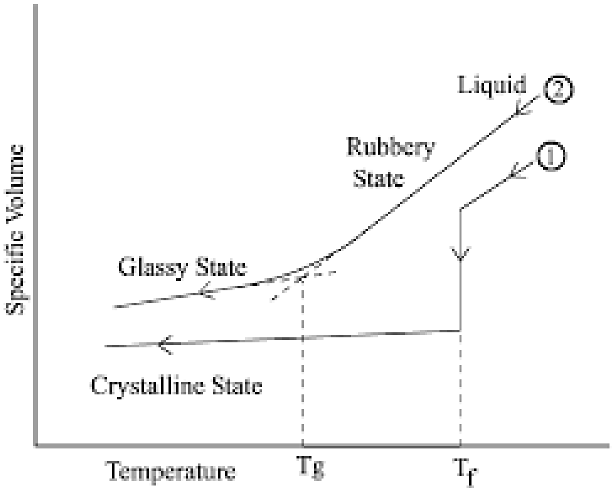
Further the mechanical properties of the polymeric material depend as following.

(i) It directly depends on its average molecular mass.
(ii) Increasing crystallinity of a polymer generally increases its mechanical properties.
(iii) Increasing the degree of cross-linking inhabit relative chain motion and strengthen the polymer and makes it brittle.
(iv) Highly dependent on the magnitude of week Vander Waals forces.
(v) Strength of thermoplastic can be considerably increased by the addition of reinforcements.
(vi) Strength of thermoplastic can be done by the introduction of phenylene rings in the main carbon chain.

The glassy state and the glass transition: -

(i) All amorphous polymers assume at sufficiently low temperatures the characteristics of glasses, including hardness, stiffness and brittleness. One property associated with the glassy state is a low volume coefficient of expansion. This low coefficient occurs as the result of a change in the slope of the curve of volume vs temperature at the point called glass transition temperature (Tg). this behavior is shown for natural rubber.
(ii) In the high temp. region, the slope of the curve (expansion coefficient) is characteristics of a rubber, below Tg at about -70^{o}C, it is a characteristics of glass.
(iii) Another general phenomenon, in which the amorphous region in partially crystalline polymers also assume a glassy state, Tg being independent of degree of crystallinity to a first approximation. The magnitude of the phenomenon associated with Tg decreases with decreasing amorphous content. As a result, T_g is sometimes difficult to defect in highly crystalline polymers.

In contrast to crystalline melting at a temperature Tm (about 10^{0}c.) there is not an abrupt change in volume at Tg but only a change in the slope of the volume and temperature. Curve.



Measurement of Tg: The glass transition temp. can be detected in a variety of experiments which can be roughly classified into those dealing with bulk properties of the polymer, and those measuring the nature and extent of molecular motion.

The classification is some extent arbitrary which is indicated below.

Bulk Properties: Perhaps the most common way of estimating Tg is by means of the volume expansion coefficient. Other bulk properties whose temp. Coefficient undergoes marked changes at Tg and which can therefore be used for its determination include heat content.

Molecular motion: Experiments which are sensitive to the onset of molecular motion is polymer chains may be used to defect the Tg. Such methods include the measurement of the internal friction, dielectric loss in polar polymers and NMR spectroscopy.

Phenomena Related to Tg: The onset of brittleness as measured in impact tests and the suffering of amorphous polymers as measured in thermal tests of various sorts, takes place at temperature near Tg.

Time effects near Tg:- If a polymer sample is cooled rapidly to a temperature just below Tg, its volume continues to decrease for many hours. The value is observed as Tg in a volume-temperature experiment depends on the time- scale of the measurement.

For similar reasons other tests for Tg give results somewhat dependent on the time scale of the experiments, with tests requiring shorter times yielding higher values for Tg. The brittleness. as determined in an impact test is normally somewhat higher than Tg as otherwise measured.

Fracture of the polymeric materials:

The fracture of the polymeric materials can be considered to be either brittle or ductile or intermediate in between the two extremes.In general, thermosetting plastics are considered to fracture primarily in a brittle mode, on the other hand thermoplastics may fracture primarily by the brittle or ductile manner.

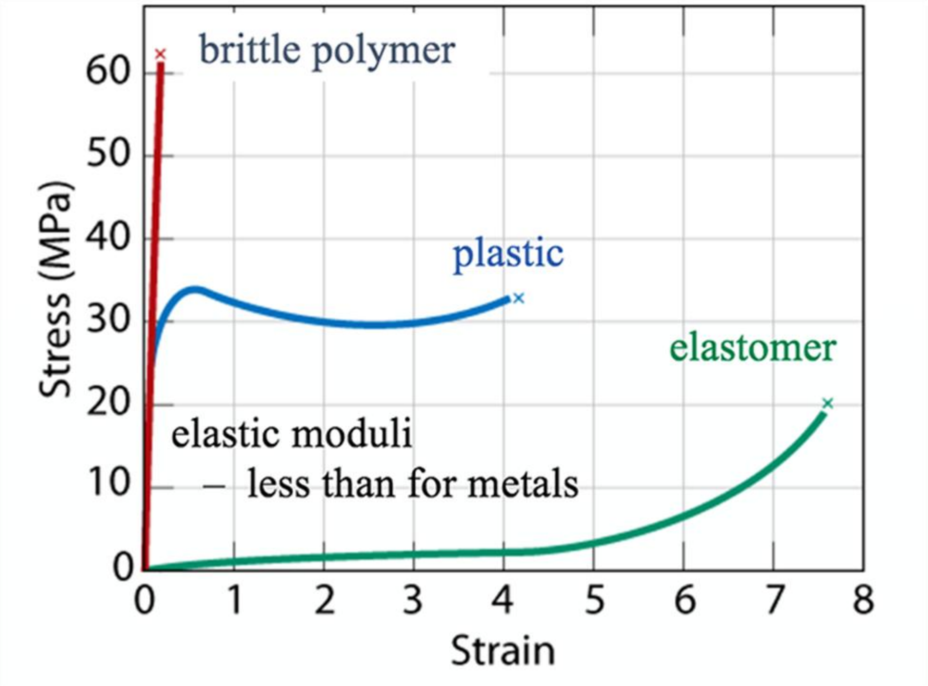
If the fracture of a thermoplastic takes place below its Tg. Then its fracture mode is primarily brittle whereas if fracture takes place above its Tg its fracture mode will be ductile. Thus the temp can greatly affect the fracture mode of thermoplastics.

Thermosetting plastics heated above room temperature become weaker and fracture occur at a lower stress level but still fracture occurs primarily in a brittle mode because the covalent bonding network is retained at elevated temperature.

Strain rate is also an important factor in the fracture behavior of the thermoplastics with slower strain rates favoring ductile fracture because a slow strain rate allows molecular- chain realignment.

Brittle fracture of the polymericmaterials: -

- The surface energy required to fracture an amorphous brittle glassy polymeric material such as PS on PMMA is about 1000 time greater than that which would be required if the fracture involves just simple breaking of C-C bonds on a fracture plane.
- The glassy polymeric materials such as PMMA are much tougher than inorganic glasses. The energy required to fracture glassy thermoplastics is much higher because of the distorted localized regions called **crazes** formed before cracking occurs.
- **Definition:** A craze in a glassy thermoplastic is formed in a highly stresses region of the materials and consists of an alignment of molecular chains combined with a high density of intendispersed voids.
- If the stress is intense enough a crack forms though the “Craze”. As the crack propagates along the craze, the stress concentration at the top of the crack extends along the length of the “Craze”. The work done in aligning the polymer molecules within the craze is the cause of the relatively high amount of work required for the fracture of glassy polymeric materials. This explains why the fracture energy of PS and PMMA are between 300 to 1700 J/m^2 instead of about 0.1J/m^2, which is the energy level that would be expected if only covalent bonds were broken in the fracturing process.



Ductile fracture of the polymeric materials:

Thermoplastics above their glass transition temperature (Tg) can exhibit plastic yielding before fracture. During the plastic yielding the molecular linear chains uncoated and stop pass each other gradually align closer together in the direction of the applied stress. When the stress on the chain becomes too high the covalent bonds on the main broken down and the fracture of the material occurs. Elastomeric materials deform essentially in the same way except they undergo much more chain uncoiling (elastic deformation) but if the stress on the materials is too high and the extension of their molecular chairs are too great, the covalent bonds of the main chains will break causing fracture of the materials.

Feature Mechanics: All materials contain flaws and that fracture occurs by the stress induced extension of these defects. The theory derives from the work of A.E Griffith who attempts to explain the observation that the tensile strength of the fine glass filaments were inversely proportional to the sample diameter.

Tensile strength= $\frac{Breaking\ \ force}{Initial\ \ cross-sectinal\ \ area}$

He assumed that every object contained flaws, that failure is more likely the larger the defect and that larger bodies would break at lower tensile stresses because they contained larger cracks. The basic concept is that a crack will grow only if the total energy of the body is lowered. Hence that is to say, the elastic strain energy which is released by the crack growth must exceed the energy of the newly created surface. If is also important that the presence of a crack or inclusion changes the stress distribution around it and the strew may be amplified greatly around the tips of the sharp cracks.

The relation which was derived between crack size and failure stress is known as Griffith-contagion.

$\sigma f\left[\frac{2\lambda y}{\pi a}\right]1/2$………………………… (I)

Where σf- future stress based on the initial cross section.

a- Crack depth.

λ-Surface energy of the solid material (The factor ‘2’ is inserted because fracture generates two new surfaces) Y- Young’s modulus.

Eq (i) is applied to completely elastic fractures, where all the applied energy is consumed in generating the fracture surfaces. Real materials are vey seldom completely elastic but however a more general application of this concept allows for additional energy dissipation in a small plastic deformation region near the crack up.

With this amendment q(i) is applicable with the 2r term replaced by ‘G’ the strain energy release rate which includes both elastic and plastic surfaces work done in extending a preexisting crack.

$\sigma f \left[\frac{2\lambda y}{\pi a}\right] 1/2$………………………… (2)

The general equation to describe the applied stress field around a crack tip us

$\sigma f \left[\frac{2\lambda y}{\pi a}\right] 1/2$………………………… (3)

Where K- stress intensityfactor Eq (3) applies at all stresses, buth the stress intensity reaches a critical value ‘Kc’ at the stress level where the cracks begin to grow. Kc is a material property calles the fracture toughness and the corresponding strain energy release rate called the critical strain energy release rate (G)

The eq(3) is for an ideal semi-infinite plate with no boundary effect. Application to real specimens requires calibration factors so that fracture toughness Eq(3) at the critical point is given by

Kc= $\sigma f \mathrm{C}\,(\pi a)\, {}^{1}\!/_{2}$…………… (4)

Garma is a calibration factor which is itself a function of specimen geometry and crack size.

The instrumented impact tests yield values for the specimen fracture energy U_f with such data, the critical strain energy release rate can eb calculates as

Gc= $\frac{u}{BD\emptyset}$…………………… (5)

B and D – specimen width and depth respectively ∅ is the calibration factor and is a function of the specimen geometry and the ratio of the crack depth and specimen width.

The total work of crack formation =G_c X crack area.

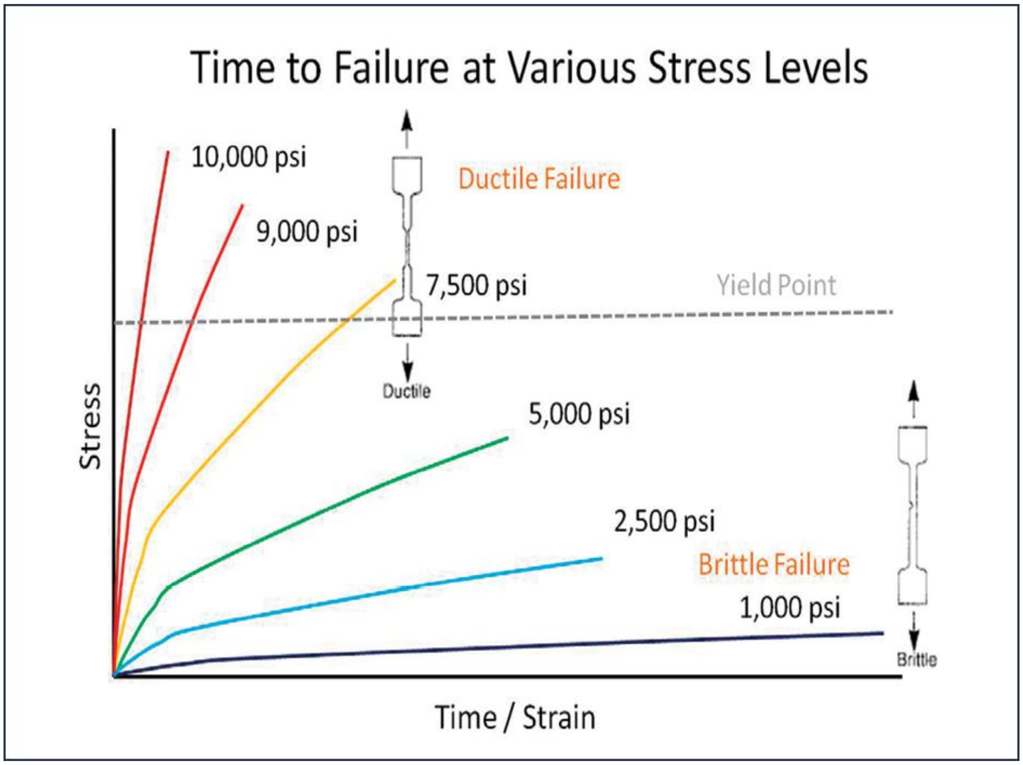
The catastrophic failure is predicted to occur when

$$\sigma\,(\pi a)\, {}^{1}\!/_{2} = (\gamma a c)\, {}^{1}\!/_{2} =$$

Where Kc and Gc are the parameters usedin Linear elastic fracture Mechanics (LEFM). Bo the factors are defined at the point of place stress conditions. To understand the term plane stress, it was imagined that the applied stress is resolved into three components along Cartesian coordinates plane stress occurs when are component=0, such conditions are more likely occur when the specimen is thin.

Fracture occurs with a lower level of energy absorption in a thick specimen. The crack tip in a thin specimen will be in a state of plane stress while the corresponding condition in the thick specimen will be plane strain. Plane strain will be the more dangerous condition.

The parameters which apply the plane strain fracture are Gc and Kic where the subscript 'I' indicates that the crack opening is due to tensile force.



To illustrate the differences between plane stress and plane strain fracture modes, thin polycarbonate specimen with thickness < 3 mm reported to have G_c value of 10K5 /m^2 while the G_{Ic} of thickness specimen is 1.5k5/m^2

CONDUCTING POLYMERS: Most of polymers are electrically insulating in nature. The polymeric materials are usually characterized by a strong covalent bonds along the polymer chain, while the bonding between the polymer chains are considerably weaker. Now a day there are very large numbers of organic monomers are available to make angelic polymers for getting a wide range of applications by modifying the properties of the polymer. Although the polymers are electrical due to their wide band gap, a low carrier mobility and a low melting point, using new synthetic methods, highly conductingdoped polymers are developed. These are doped conjugated polymers and act as conductor.

Example-Polyamine and polyp role are semi-conducting conjugated polymers are converted into conducting polymers when doped with. Sufficient concentrations. These are used as battery electrodes conductive coatings for electrostatic speakers, capacitor electrolyte transparent conductive coating, interconnecting wines in the IC circuits instead of copper.

The transport of charge carriers in these conducting polymers involves the transport rate, scattering, trapping process recombination.

A few polymeric materials made during past two decades showed high enough electrical conductivity (>0.1Scm-1) some polymers becomes conducting after incorporation of some departs (usually inorganic electron acceptors like ASF_5 or I_2) such polymeric materials which shows electron conductively are called conducting polymers (synthetic metals)

The electrical conducting behaviors exhibited by such polymers and that of copper was given by (fig-1) commercial applications of conducting polymeric material.

(a) For making field effect transistors and Scotty diodes: Example: poly acetylene, politico here, poly parole.

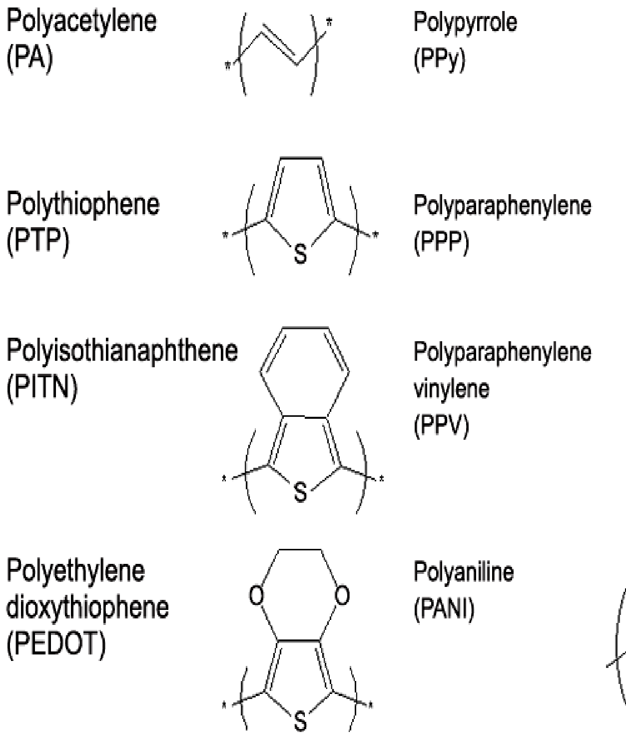
(b) For making large area light emitting device (LEP) displays

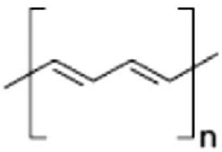
Example: Poly (P- pherylenevinylene)
Poly (P-diethyrylenepherylene)
Poly (ary-leneviry lenes)
Poly (p=pyridines)
Polythopheres

For making photo conductors:
Example: Poly (N- virylcarbazole)
Poly (vorylpyrene)
Poly- (2-vinylcarbazole)

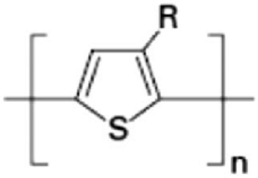
Some Conductivity of some Conductive Polymers

Compound	Conductivity (S cm-1)
trans-Polyacetylene	103 - 105
Polythiophene	103
Polypyrrole	102 - 7.5 · 103
Poly(p-phenylene)	102 - 103
Polyaniline	2 · 102
Poly(p-phenylene vinylene)	2 · 104

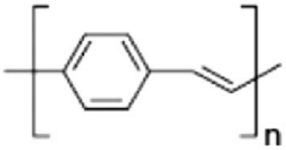




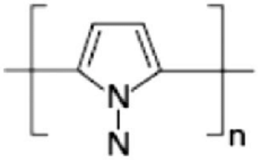
Polyacetylene



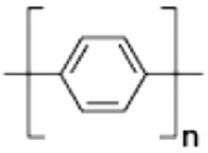
Poly(3-alkylthiophene)



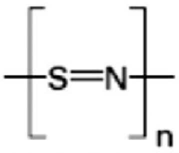
Polyphenylene vinylene



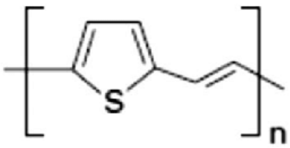
Polypyrrole



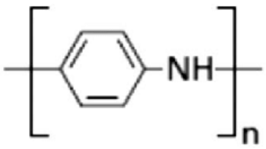
Polyphenylene



Polythiazyl



Polythienyl vinylene



Polyaniline

Note: Trans- Poly acetylene is a week semiconductor as such in bulk form but behaves like conducting when doped with ASF_5. The incorporation of ASF_5 is believed to be giving rise to charge transfer completes at various points.

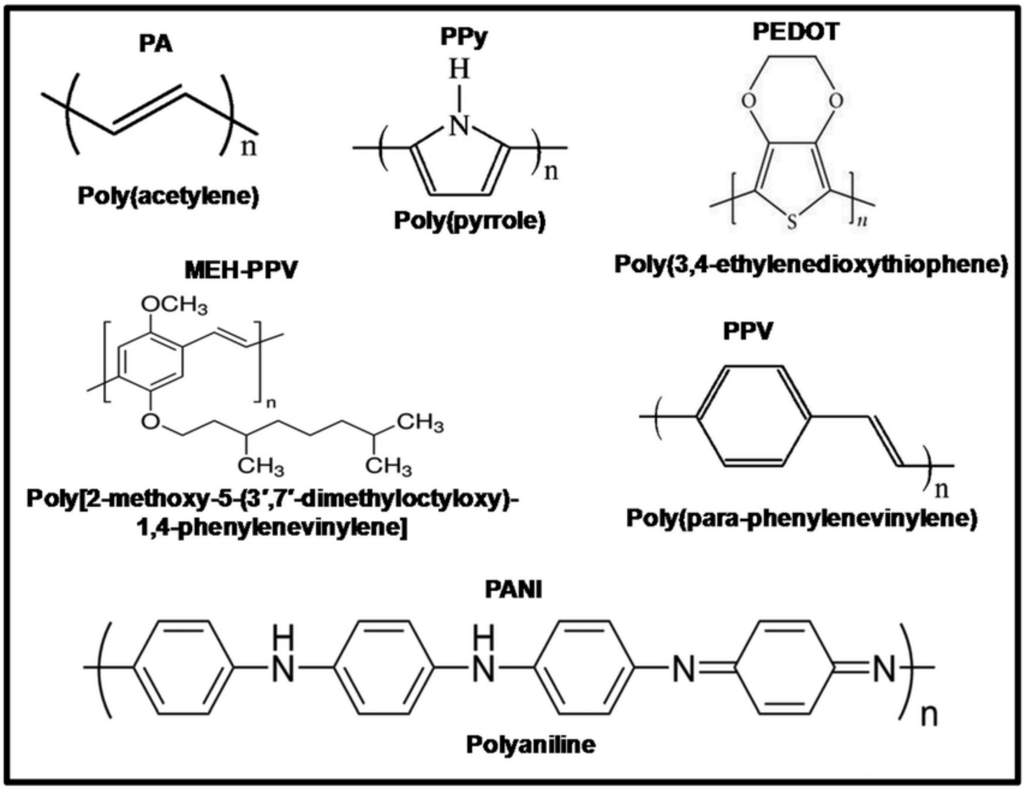
$(CH=CH)_n$ CH=CH- + ASF_5 – (CH=CH) $_n$ CH- CH

The strong electron wish drawing nature of ASF_5 molecule pulls out the electronic charge from the conjugated chain. The resultant +ve charge is stabilized by its delocalization over the section of (CH-CH) n with n=14. Thus the +ve charge can be considered as the mobile +ve hole which moves and which moves and transfers electric charge interestingly, the conducting behavior of doped poly acetylenes increases when it is stretched due to the alignment of the chain. Doped poly acetylenes offer a particularly high electrical conductivity per unit density of the material (thrice that of metal)

Organo-metallic polymers with novel electrical and optical properties and their mechanical and thermal characteristic improved for their use as conductions. The disadvantages of use of the conducting polymers are their high cast, problems in the processing due to their insolubility, infusibility and brittleness and long term instability

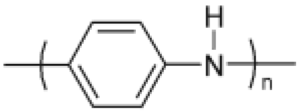
Inducement or enhancement of electrical conductivity on exposure to light or irradiation is called photoconductivity.

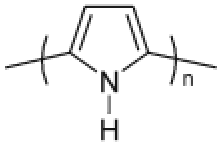
Photoconductive polymers are commonly insulators in the dark and they behave as semi-conductor when exposed to light, genuine photoconductors do not contain free charge Carrier but the charge carriers are generated in them by the action of light. The electrical charge carriers may also be photo- generated extrinsically in an adjacent photoconductor and then transferred to the polymer that would act as a charge transporting medium.

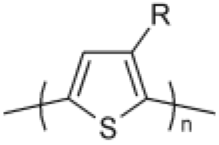


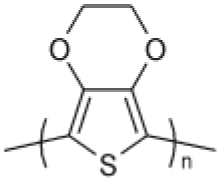
Inherently conducting polymers: Inherent conducting polymers (ICP) also commonly known as conducting metals or synthetic metals- somehow possess electrical, electronic magnetic properties and optical properties of a metal while also exhibiting the physical and mechanical properties, rheological features and process usability associated with a conventional polymer. The applicability of the concept of “doping” is the unifying theme that dusting wishes the inherently conducting polymers (ICPs) form all others. Addition of electron donors or accretions causes doping that results in dramatic electronic and magnetic charges in the ICPs along with increase in conductivity to or approaching the metallic.

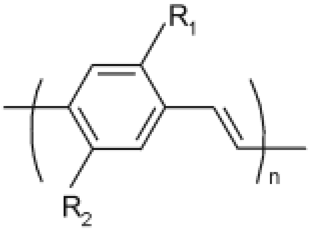
Doping is reversible removal of do pant on deposing produces the original low-conducting, semi-conducting or insulating (base) polymer usually without degradation of the polymer backbone.


Polyaniline


Polypyrrole


Polythiophenes


Polyethylenedioxythiophene


Poly(p-phenylene vinylene)s

MOLECULAR WEIGHT OF POLYMERS OF DIFFERENT TYPES

The molecular weight of a polymer depends upon the no. of repeating units. i.e. upon the degree of polymerization (DP). A polymer consists of molecules of different molecular weights and hence, its molecule weight is expressed in terms of an average value:

There are four types of average molecular weights.

(i) The number- average molecular weight (Mn)
(ii) Weight average molecular weight (Mw)
(iii) Sedimentation average molecular weight or Z- average molecular weight (Mz)
(iv) Viscosity – average Molecular weight (Mv)

Number – Average Molecular weight (Mn):-

Definition: The number average molecular weight can be defined as the sum of the product of the molecular weight of each fraction multiplies by its mole fraction.

For a sample consisting of ‘n’ polymer molecules containing $n_1$monomer molecules of molar mass M1, n2 molecules of molecular mass M_2 etc. The number average molecular mass as defined as

$$M_n=\frac{n_1 M_{1}+n_2 M_{2}+\ n_3 M_{3}+\cdots\ldots\ldots}{n_1+n_2+n_3\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots}=\frac{\varepsilon niMi}{\varepsilon ni}\ldots\ldots\ldots(i)$$

It is obtained by dividing the total weight of the dispersed material with the number of molecules present.

Weight – Average Molecular weight (Mw)

Definition: The weight average molecular weight is defined as the sum of the products of the molecular weight of each fraction multiplied by its weight fraction.

$$\bar{M}_n = \frac{\sum_{i=1}^{3} N_i M_i}{\sum_{i=1}^{3} N_i} = \frac{\sum_{i=1}^{3} w_i}{\sum_{i=1}^{3} (w_i/M_i)} = \frac{1+2+2}{\frac{1}{10,000} + \frac{2}{50,000} + \frac{2}{100,000}} = 31,250$$

$$\bar{M}_w = \frac{\sum_{i=1}^{3} N_i M_i^2}{\sum_{i=1}^{3} N_i M_i} = \frac{\sum_{i=1}^{3} w_i M_i}{\sum_{i=1}^{3} w_i} = \frac{10,000 + 2(50,000) + 2(100,000)}{5} = 62,000$$

$$\mathrm{PDI} = \frac{\bar{M}_w}{\bar{M}_n} = \frac{62,000}{31,250} = 1.98$$

Where n_1, n_2, n_3 ……………… are the number of molecular having molecular masses M_1, M_2, M_3….respectively.

Mw is always greater than M_n for all synthetic polymers

Z-average Molecular weight

$$\overline{M_z} = \frac{\sum_{i=1}^{N} N_i M_i^{\alpha}}{\sum_{i=1}^{N} N_i M_i^{\alpha-1}} = \frac{\sum_{i=1}^{N} w_i M_i^{\alpha-1}}{\sum_{i=1}^{N} w_i M_i^{\alpha-2}}$$

Generally weight average molecular weight us found by light scattering ultracentrifugation and diffusion methods.

Viscosity average Molecular Weight:

$$\overline{M}_v \equiv \left(\frac{\sum_i N_i M_i^{1+a}}{\sum N_i M_i} \right)^{1/a}$$

The light scattering, osmotic pressure, ultracentrifugation and viscosity methods are used to get Mn Mw Mv and Mz

NOTE: The ratio $\frac{Mw}{Mn}$ is known as polydisperity and as used to measure the breath of the molecular weight distribution.

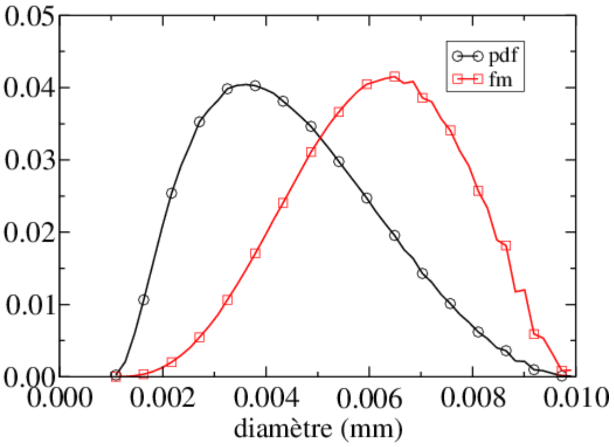
For monodies parse system

y$\overline{Mz}$>$\overline{Mw} > \overline{Mv} > \overline{Mn}$ is in the order

Polydispersity--It is a very important parameter and given and idea of the lowest and the highest molecular weight species to know about the degree of poly disparity, we can determine Mw and Mn by two different experimental methods ane we have to compute. $\overline{Mw}/\overline{Mn}$

The ratio is the indicative of the extent of the polydispersity. For all the synthetic polymers this ratio is always greater than 1. As the molecular weight distribution becomes broader, the value of$\overline{Mw}/\overline{Mn}$ increases.

The poly disparity arises due to the variation in the degree of polymerization attained by different molecules during the polymerization process. One would therefore expect polymers obtained by different polymerization techniques to show different poly dispersive and this is indeed the case.



Molecular weight and Degree of Polymerization:

The degree of polymerization represents the numbers of structural or nonnumeric units contained in a polymer.

D_p is related with molecular weight of the polymer as

M=D_p.m……………… (i)

M= Molecular weight of the polymer

D_p= Degree of polymerization

M= Molecular wt of the monomer or Repeat unit.

D_p and Molecular wt depends upon the size of the polymer molecules. Thus Dp can be expressed in terms of the average value.

The number average degree of polymerization can be expressed as.

$(D_p)\mathrm{n} \;\; = \frac{Eni\ (Dp)i}{Eni}$…………………………..(2)

And weight average degree of polymerization can be expressed as.

$(D_p)\mathrm{n} \;\; = \frac{Eni\ (Dp)i}{Eni\ (Dp)i}$…………………………..(3)

MEASUREMENT OF MOLECULAR WEIGHT: There are various physical and chemical methods are employed to determine on measure molecular wt of polymers. All these methods are absolute except dilute solution viscosity method. By these methods the molecular weight can be calculated directly. Dilute solution viscosity method (Viscometer) however molecular weight methods requires solubility of the polymer and all involve extrapolation to infinite dilution or operation in a solvent in which ideal solution behavior is attained.

The molecular weight of the polymer may be determined either on the colligative properties on the estimation of the size of the polymer chains. As expected the former methods will yield. Mn while the letter gives Mw. In addition to these two methods another method besed on estimation of chemical functional groups present as end groups in the polymer chainis also wed to get

(i) End group analysis
(ii) Osmometry
(iii) Light scattering
(iv) Ultra centrifugation
(v) Viscometer.

Measurement of Number Average Molecular weight (Mn):

End- group Analysis: Molecular weight determination through group analysis requires that the polymer contains a known number of determinable groups per molecule. The long chain nature of polymers limits such group analysis. Since methods of end-group analysis court the number of molecules in a given weight of polymer sample, they give Mn. Presently available techniqueallows a practical upper limit of molecular measurement of about 50,000. Some of the current methods of end-group determination includes as follows.

(i) Titration using either indicators or potation metric techniques.
(ii) Elemental analysis of element- specific end groups.
(iii) Measurement of the activity of a radioactive-tagged end going.
(iv) UV spectroscopic determination of end group with a characterized chromo phone. IR and NMR spectrospic techniques are of more limited use.

Points to be kept in mind in applying end-group analysis are the following.

(i) The method cannot be applied to branched polymers unless the number of branches is known with certainly, thus it is practically limited to linear polymers.

(ii) In a linear polymer there are twice as many end group as polymer molecules.

(iii) If the polymer certain different group at each end of the chain and only one-character sable end group is being measured, the number of this type is equal to the number of polymer molecules.

(iv) Measurement of molecular- weight by end-group analysis is only meaningful when the mechanism of initiation and termination are well understood.

In this method, first the total no of functional groups [-OH, -COOW, -CHO, -NH2, - OCOR etc] present in a given weight of the sample is determined by usual chemical methods.

This is expressed as functional group equivalent 100gm from the knowledge of functional group equivalent and functionality, the Mn can be calculated by using the equation.

Mn= $\frac{Functionality}{Fractional\ \ group\ \ equivalent}$

Functionality is defined as the number of reactive functional groups present in each macromolecule. Thus the functionality of carboxyl-terminated and hydroxyl-terminated poly butadiene's (CTPB and HTPB) is two, as each molecule possesses two reactive functional groups.

Hooc-R-CH_2-CH=CH_2 R-CooH.

H-R - R-CH_2-CH=CH_2 R-ow

The procedure is as follows.

An accurately weighed quanty (less than 1gm) of for example CTPB is dissolved in the ethanol-tolune(1.3) mixture. This is titrated against 0.IN alcoholic KoH solution. Using phenol phthaleon as an indicator. The end point is the appearance is of slightly pink column.

Then,

Carbonyl value = $\frac{VXN\ \ (56,1)}{W}$ my of KOH / gm

V= Vol. of KOH consumed in ml.

N- Normality of KOH solution.

W=wt. of the sample taken in gram.

Carboxyl equivalent / 100gm $\frac{VXN\ \ (56,1)}{W\ (1000)} X\ \frac{100}{56.1} = \frac{VN}{10W}$

In a particular experiment if 0.8734gm of the sample has consumed 5.1ml of 0.1242N alc. KOH solution then.

Carboxyl equivalent / 100gm = $\frac{5.1X\ 3.1242}{10X0.8734}$ = 0.0725

Assuming a functionality of ‘2’ we get

Mn= $\frac{2X100}{0.0725} = 2760$

This method is valuable of linear polymer molecules having determinable end groups and for those obtained by a known polymerization mechanism without side reactions. This is because side reactions during polymerization may introduce errors in the assumed functionality and hence lead to erroneous results.

(2) Colligative property measurement (osmometry)

The colligative property methods are based on vapour-pressure lowering, elevation is boiling point (ebulliometry), depression in freezing point (cryoscopy and the osmotic pressure (osmometry) . The colligative properties and molecular weight for infinitely dilute solutions are related to each other. When the solute concentration becomes sufficiently low then the activity of the solute in a solution becomes equal to its mole fraction as the solute concentration becomes sufficiently small. The depression of the activity of the solvent by a solute is equal to the mole fraction of the solute.

The following equations are used for polymer solutions to determine the number average molecular weight (Mn)

$$\frac{lom\ \ \Delta Tb}{C-10\ \ C} = \frac{RT^2}{\Delta Hv}\frac{1}{M}$$

$$\frac{lom\ \ \Delta Tb}{C-10\ \ C} = \frac{RT^2}{\Delta Hf}\frac{1}{Mn}$$

$$\frac{lom}{C-10\ \ C}\pi/c = \frac{RT}{Mn}$$

Where ΔT_b , ΔT_f and $'\pi'$ are boiling point elevation freezing point depression and osmotic pressure respectively.

- Density of the solved

ΔH_v, ΔH_f - Enthalpies of vaporization and Enthalpies of fusion respectively.

C- Solute con. In gms / ml.

T- freezing point or boiling point.

The then moody nominal relationships derived for infinite dilute solutions are.

There are two types of osmotic pressure methods are used to determine the molecular weight.

(a) Vapour- pressure osmometry

(b) Membrane osmometry.

(a) Vapour- pressure osmometry

Principle: (i) It is generally willful for determining molecular weights below about 25,000 , white no membrane is used, the thermodynamic principle involved in analogous to that the membrane osmometry.

(ii) The technique is governed by the principle that the vapour pressure of a liquid is lowered on addition of a solute and this lowering as dependent on the no of molecules present and is based on the idea of isothermal distillation.

(iii) It is an indirect measurement of vapour pressure lowering. This method is used for measuring Mn of a polymer sample and based on the principle that at a given temperature the vapour pressure of a solution is less than that of the pure solvent.

(iv) In this method a drop each of pure solvent and the solution is kept in an atmosphere saturated with solvent vapour. Since V.P of the solution is lower than that of the pure solvent, conversation of the solvent takes place from the saturated vapour (pressure) phase on to the solution droplet. The solution droplet, therefore, starts getting diluted as well as heated up by the latent heat of condensation of the solvent condensing on it.

(v) Due to temp. raise and increased conc. of the solvent, the vapour pressure of the solution droplets increases. The process of condensation and temp. raise continues till the vapor pressure of the solution droplet becomes equal to that of the pure solvent.

(vi) An important assumption of this method is that this temp. difference is proportional to the vapor-pressure lowering of the polymer solution of equilibrium and thus to the Mn because of heat loss.

(vii) The total raise in temperature $'\Delta T'$ will be proportional to the mole fraction of the solute ‘n’ in the solution.

$$\Delta T = \frac{RT^2 n}{\Delta Hv} \text{ -------------------- (1)}$$

ΔHv - Heat of vaporization.

The apparatus used for this method is called as Vapoun-pressure osmometry (VPO). The solution and the solvent droplet are placed directly on two thermostats in a wheat stone bridge circuit in such a way that the temperature rose can be measured very accurately as a function of output voltage (ΔV)

'ΔV' is related to the molecular weight of the solute (polymer) by the equation.

$\frac{\Delta V}{C} = \frac{K}{M_n} + KBC$………………………… (2)

Where K- calibration const. that can be determined by doing the similar experiment with any polymer sample of known molecular weight.

Thus a plot between Av/$_C$$\sim C$ gives a linear behavior, the intercept of which will provide Mn.

B- viral coefficients.

$\Delta V = \left(\frac{RT^2}{\gamma 100}\right) m \ldots\ldots\ldots\ldots\ldots\ldots (3)$

n- heat of vaporization pen gm of solvent and moss the modality.

Instrumentation: The solvent vessel made of glass is placed in an 'As' block. This 'Al' block is closed by a stainless steel did through a Teflon gasket. This vessel provides the space for the atmosphere of solvent vapour wherein the transistors are suspended. The stainless steel lid is covered by another metal block through which several syringes for placing the solution and solvent drop on the them stores are introduced. The entire assembly is thermo stated to maintain a constant temperature.

Method: (i) At first the solvent is added to the solvent vessel through a syringe and solvent drops are also placed on each thermostat. Since there will not be any conversation on either of the thermostats, there is obviously no temp. difference and hence the instrument should need zero.

(iii) In the next step, the instrument is calibrated with a standard sample of a known molecular weight. Now 4 to 5 solutions of known different concentrations are prepared. A drop of the solution of one particular concentration is placed on a thermostat. Now the solvent starts condensing on the solution droplet and the rise in temperature occurs which is directly measured as the bridge imbalance output value '$\Delta V'$.

The process is repeated with solutions of different concentrate and ΔV values for each concentration are no

A graph of Av/$_C$$\sim C$ is plotted and extrapolated to zero concentration. The ordinate intercept will them be (Av/$_C$)$_{C\text{-}10}$, then K can be calculated by using the equation.

K=M(Av/$_C$)$_{C\text{-}10}$……….. (1)

M- Molecular weight of the standard sample.

The molecular weight of the unknown sample can be calculated by repeating the same procedure with the same solvent. By knowing the ordinate intercept $(Av/_{C})_{C\text{-}10}$, the molecular weight of the unknown sample is given by.

$Mn=\left(\frac{K}{\Delta V/c_{C-0}}\right)$ …………………… (2)

Membrane Osmometry:

Principle: (i) The two compartments of an osmometry are separated by a semi-permeable membrane through which only solvent molecules are penetrated and which is closed except for capillary tubes.

(ii) This technique is used to determine the number-average molecular weight of polymers. It is based on the phenomenon of osmosis.

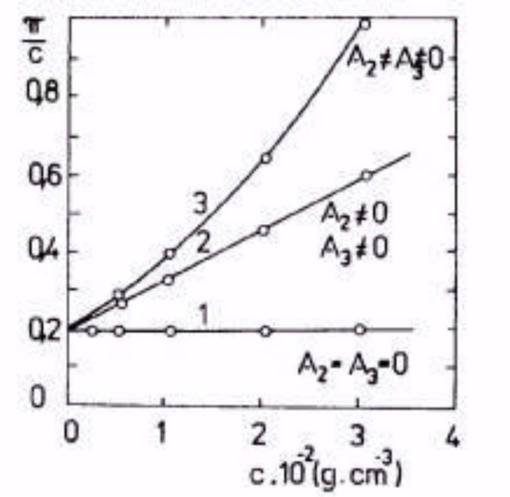
(iii) The membrane osmometry apparatus basically measures osmotic pressure of polymer solutions of known concentration.

(iv) The membrane osmometry (static) suffers with a disadvantage that often long time (several hours for a single measurement of mol. Wt.) is required as the achievement of equilibrium is a slow process.

Also since no membrane can be perfectly ideal, small sized molecules of a poly dispensed polymer sample can pass through the membrane causing error in the molecular weight determination.

(v) Osmotic pressure measurements are asked for studding polymers because osmotic changes are larger than the changes in boiling point elevation, freezing point depression and vapour pressure lowering.

$$\frac{\pi}{c} = RT\left(\frac{1}{M_n} + A_2c + A_3c^2 + \ldots\right)$$



Another advantage of osmotic pressure method is that the presence of a slight trace of an impurity of low molecular weight may cause serious error in freezing point or boiling point elevation where as it would pass through the cellophane membrane and therefore, would not change the pressure measured.

Osmotic pressure (π) of a solution is defined as the pressure that must be applied to the solution so as to totally present the flow of the solvent through the semi permeable membrane into the solution.

There are different types of osmometers. These are divides into two categories depending on the static on dynamic equilibrium.

(i) Static equilibrium method
(ii) Dynamic Equilibrium method
(iii) Static equilibrium method.

Apparatus: The apparatus consists of two metallic blocks made of stainless steel, one face of each block having a series of concentric grooves. These grooves are interconnected by vertical-horizontal channels. A semi permeable membrane is placed in between these grooved faces of the two metallic blocks. On bolting the apparatus, the two internal grooved faces of the metallic blocks come in close contact through the semi permeable membrane. The solvent and the solution are kept in the space formed between the grooves on the two blocks and are prevented from freely mixing by the membrane separating them.

The vertical channels of the blocks are connected to the glass capillaries through a drill in the metallic blocks of the solvent and solution compartment.

Experimental: First the two compartments are filled with solvent and the solution of known concentration. Due to the somatic pressure, the solvent will start passing through the membrane to the solution side. So the liquid level in the capillary attached to the solution side will nice. This will continue until the hydrostatic pressure developed in the capillary due to rose of solution level exactly balances the osmotic pressure. Once the osmotic equilibrium is attained, the solvent stops entering the solution side. Then the height difference between the solution and solvent levels in the two capillaries is measured. This difference is known as the osmotic head. The same procedure is repeated with solutions of different concentrations and the corresponding osmotic heads are measured.

Theory: The van't Hoft equation relating the osmotic pressure of a polymer solution with the mular mass of the polymer

$$\frac{\pi}{c} = \mathrm{RT}\left[\frac{1}{Mn} + A2C + B3C2 + \cdots \dots \dots \dots \dots \dots \dots\right]$$

$\frac{\pi}{c}$= Reduced osmotic pressure and are the secure third viral coefficient.

Dynamic Equilibrium Method: The high speed membrane osmometry (HSMO) is commonly used now a day it is a rapid method and attains equilibrium within 5 to 7 minutes. There are two pants I this osmometry. The upper part contains the sample solution while the lower part contains the solvent. The two parts are separated by a semi permeable membrane. The movement of an air bubble inside the capillary indicates the solvent flow to the solution. Such movement of the air bubble is detected by a photocell.

The servo mechanism is used to move the solvent reservoir in the upward or downward direction and also to adjust the hydrostatic pressure such that the solvent flow is totally stopped. The pressure head of two reservoir gives the osmotic head.

Behavior of Adhesives: Adhesives are substances often polymeric materials (natural or synthetic) that are used to glue two surfaces together.

(i) Plant excavates have been used as adhesives by Egyptian for about 6000 years for bonding ceramic vessels. Stanch and sugar, casein (from milk) and glue from animals and fish have been used for 4000 years.

(ii) The adhesives often work on the principle that they from either primary covalent bond or interact with the surface through physical forces (secondary bond).

(iii) There are several types of adhesives. The solvent based adhesives ae dissolved in solvent and the solvent is then allowed to evaporate in the presence of surface to theglued. The evaporation of the solvent that leads to the formation of a thick or thin solid coating.

(iv) Latex adhesives (which are directly used as the dispersion of the polymer made by emulsion polymerization) must have below Tg. It gives a flow and good surface contact on evaporation of water from a water based latex.

(v) Pressure sensitive adhesives (PSA_ are viscous polymers which melts at room temperature. The adhesives flow on applying pressure and thereafter on releasing the pressure, the high viscosity of the polymer provides the adhesion

(vi) Hot melt adhesives work on similar principle except here the material flows on applying heat.

Important and highly effective of all the adhesives are reactive adhesives which are low molecular weight liquid polymers and solidify due to the cross linking.

Example: Cyan cry lattes, phenolic resins, silicones epoxy polymers and unsaturated polyesters.

There are many different types of industrial adhesives on the market today, used in different construction and tasks by numerous industries. All these types have a few things in common; the most important is that they are designed and developed to reduce the amount of money and time required when using them. Companies spend significant amounts of money in developing efficient and effective industrial adhesives; therefore, it seems that there is a win-win situation for both users and manufacturers. The different types of adhesives are classified based on their composition or properties. There is also an additional classification based on the cure mechanism of the adhesive. Curing is the process of hardening the product using different methods, such as chemicals or ultraviolet light. The most common types of industrial adhesives are:

1.Resins

Resins are a type of polymer of synthetic origin. Resins can be thermosetting and thermostatic types of adhesive, which means that they can be either remolded at high temperatures or they cannot be remolded once the curing process is over

2. Hot Melt

Hot melt adhesives allow the user to harden and soften them whenever they want, using cold or heat. Hot melt adhesives feature an excellent bonding quality and once heated can bond really fast to materials. One of the greatest advantages of the hot melt adhesives is that if the user makes any mistake during the construction, the adhesive can be easily rectified and used again

3. Contact Spray

Contact spray allows the user to bond different items both temporarily and permanently. Spray adhesive can be used on uneven and porous surfaces, and is waterproof and transparent. Contact sprays are flexible and do not stain. They are considered friendly to the environment because they do not contain any chlorinated ingredients

4. Acrylic

The acrylic adhesives require some time to set and dry, opposite from other types of adhesives. Acrylic adhesives use a radical mechanism that consists of 2 individual components that mix together, creating the bonding feature. You can find acrylic adhesives in 2 different types, the solvent and emulsion ones, which are both used in construction.

5. Anaerobic Adhesive

Anaerobic industrial adhesives can set without using oxygen or air, and are great for using when you need to form tight seals without the use of heat, oxygen or even light. This type of adhesive can bond numerous types of materials together such as paper, masonry, plastic, wood, rubber, glass, fabric, ceramic and elastomers.

6. Conductive:

The conductive adhesive is used in construction and industries that need to avoid electrostatic discharges, or radio and electromagnetic interference from occurring when not wanted. Conductive adhesives can improve heat dissipation because they form thermo-conductive layers between products and components.

7. Epoxy Adhesives

The epoxy adhesives are used widely in certain industries, such as the automobile and aircraft industries; this type of adhesive can cure fast and bonds concrete surfaces, as well. Epoxy adhesives are also used in manufacturing plywood.

8. Pressure Adhesives

These types of industrial adhesives are popular and common, since it is quite efficient and requires pressure to bond different surfaces together.