

CHAPTER II

THEORY

2.1 Coke

During the pyrolysis reaction, cokes are formed as a by-product from the dehydrogenation of hydrocarbon by ways of catalytic and pyrolytic reactions. As the pyrolysis reaction runs, the coke aggregates and accumulates on the inner walls of the reactor, alone or through a cooperative trap action. Such aggregation or accumulation of the coke on the inner wall of the reactor tubes interferes with the flow of fluids in the pyrolysis reactor, causing an increase in the pressure drop between the frontal and the postal zones of the reactor, and deteriorates the efficiency of the heat transfer through the inner walls. Sometimes coking may cause tube plugging and ultimately make the operation impossible. The coke formation in cracking furnace results in the reduction of the yields of the main product, the restriction of capacity and cracking severity and the increase of the energy consumption. Carburization may also occur into the metals of the reactor tubes, reducing the coil service life.

2.1.1 Classification of Coke

Typically coke formed in pyrolysis furnaces can be categorized as two types, catalytic and pyrolytic, as shown in Figure 2.1. Catalytic coke is formed by the reaction between hydrocarbon and metal surface components, mostly nickel and iron, of the reactor tube. The resulting catalytic coke is somewhat rigid and branch-like in structure, creating "trapping" sites that promote pyrolytic coke formation and accumulation. On the other hand, pyrolytic coke is softer and less structured than catalytic coke, and can be easily flushed through the system. It is formed by several related mechanisms, inclusive of dehydrogenation, polymerization and condensation, of both light olefinic, and heavy aromatic compounds.

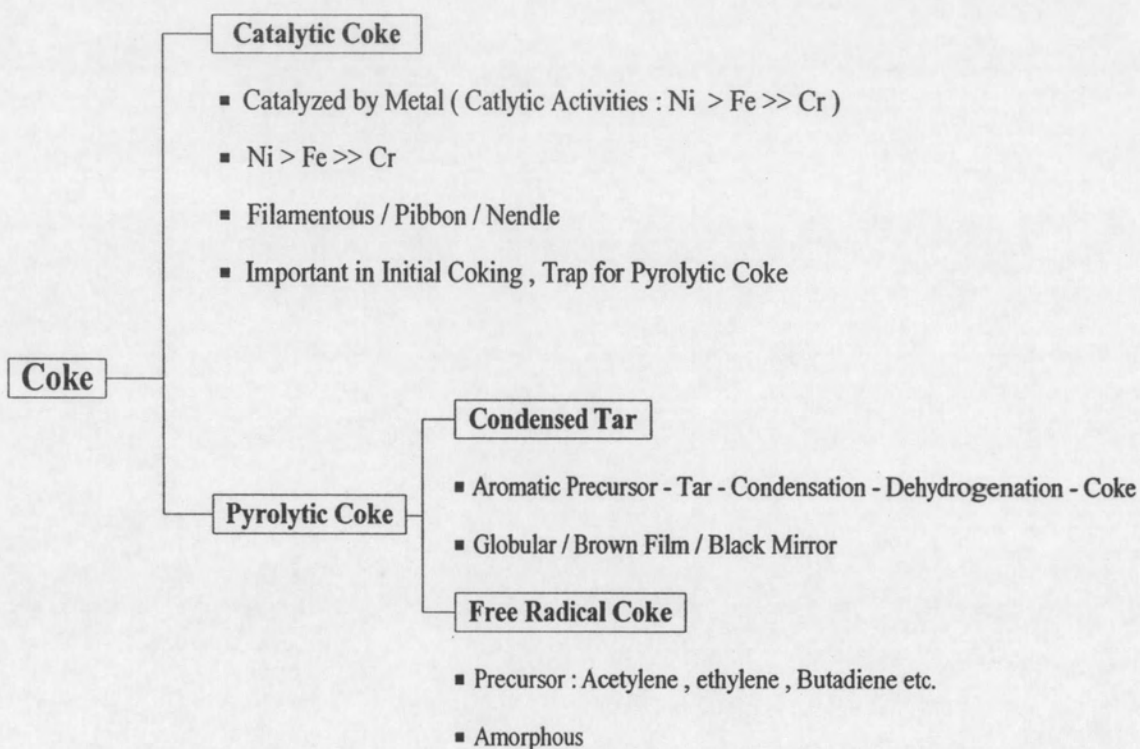


Figure 2.1 Classification of Coke [www.py-coat.com]

Catalytic coke is formed by the gas phase hydrocarbon reaction at 350~1050°C with catalysts of surface metals. Catalytic activities of metals are following; Ni>>Fe>>Cr, NiO>Ni, FeO>Fe>Fe₂O₃. Metals catalyze the reaction to form the filament and coil type coke by successive dehydrogenation.

Pyrolytic coke has various types and it is very difficult to define the shape. It is classified into globular, black mirror, fluffy and amorphous type according to the morphology and classified into gaseous and condensation coke according to the kind of hydrocarbon as precursor.

2.1.2 Coke Precursor

During thermal cracking, the coke is formed by the reaction of hydrocarbon with catalyst of the metal on the tube surface or the dehydrogenation of the highly olefinic radicals or the condensation / polymerization / dehydrogenation of the heavy aromatic droplets. In these reactions, the coke precursor plays the most important role.

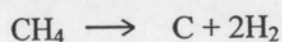
The typical coke precursors are the heavy aromatic droplets like tars, the microspecies that the molecular weight is below 100 such as acetylene, ethylene, butadiene and so forth, and the free radicals such as methyl, ethyl, propyl, benzyl etc. They affect the type of coke formed and the rate of coke accumulation.

Heavy aromatic droplets spread out on the tube surface and form the featureless coke or spherical coke etc. Microspecies, especially acetylene, form not only the filamentous coke by catalytic reaction but also the spherical coke by aromatization and dehydrogenation. Besides microspecies promote the growth of filamentous coke as well as spherical coke due to the low molecular weight and high diffusivity. Free radicals form the coke and promote the coking rate by condensing in gas phase or reacting with coke surface radicals.

2.1.3 Coke formation

One of the serious problems is the carbonaceous deposition. The formation of coke leads to catalyst deactivation and plugging problem in the reactor. It can be produced by the following reactions:

Catalytic methane decomposition reaction



These cokes have different crystalline structures, morphologies, and reactivities depending on the specific reaction taking place and the reaction conditions. On nickel surfaces, coke formation may take place mainly by three routes.

At lower temperatures (below 500°C), adsorbed hydrocarbons may accumulate on the surface and slowly be transformed into a non-reactive polymer film (gum) blocking and deactivating the surface. This phenomenon can be retarded by hydrogen. Note that because of the endothermic nature of the steam-reforming

reaction, high catalyst activity leads to a low temperature at the reaction site, resulting in a higher risk for carbon formation.

At higher temperatures, whisker carbon is the principal product of carbon formation on nickel catalysts. The underlying mechanism is quite comprehensive; it involves diffusion of carbon atoms through the metal particles.

Table 2.1 Routes to coke formation

Carbon type	Reactions involved	Phenomena	Critical parameters
Gum	$C_nH_m \rightarrow (CH_2)_n \rightarrow \text{gum}$	Blocking of surface by polymerisation of adsorbed C_nH_m radicals: progressive deactivation	Low S/C ratio, absence of H_2 , low temperature (below 500°C), presence of aromatics
Whisker carbon, amorphous carbon	$CH_4 \rightarrow C + 2H_2$ $2CO \rightarrow C + CO_2$ $CO + H_2 \rightarrow C + H_2O$ $C_nH_m \rightarrow nC + m/2H_2$	Break-up of catalyst pellet (whisker carbon: no deactivation of the surface)	Low S/C ratio, high temperature (above 450°C), presence of olefins, aromatics
Pyrolytic coke	$C_nH_m \rightarrow \text{olefins} \rightarrow \text{coke}$	Encapsulation of catalyst pellet (deactivation), deposits on tube wall	High temperature (above 600°C), high residence time, presence of olefins, sulfur poisoning

2.1.4 Mechanism of coke formation

The mechanism of coke formation is a very complex multi-step reaction sequence. It is not possible to find the exact answer for coking mechanism which can be applied to various systems. Different reaction schemes have been proposed for different system. In general we can summarize coke formation with four steps.

1. The hydrocarbon reacts as the surface metal catalyzes the reaction and forms the filamentous coke, which grows and offers the deposit site of various types of coke.
2. Radical coking causes the filaments to thicken. As the catalytic filaments grow, carbon begins to block the metal surface.
3. Tar formed by condensation coking collects in the filaments.
4. Filaments stop growing by catalytic coking when the metal particles are covered with carbon. Then, Radical coking and condensation are dominant.

Figure 2.2 illustrates the process of coke formation. First, active metal cluster is boosted by coke formed and keeps catalyzing and second, it grows up and finally begins to be covered with additional pyrolytic coke partially or totally. Thus, catalytic cokes grow up and collect pyrolytic cokes as catalytic goes on. If we suppress these catalytic functions on the tube metal then only pyrolytic coke formation will be remained on the surface, reducing the rate of coke accumulation remarkably.

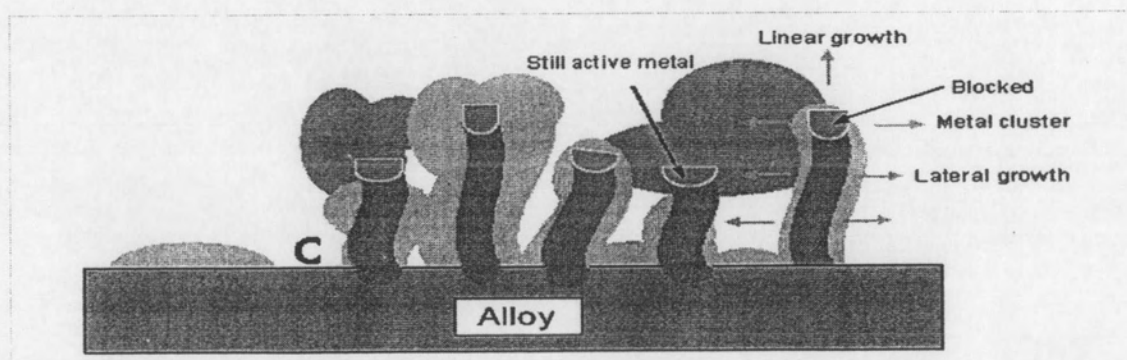


Figure 2.2 Coking Process [<http://www.py-coat.com>]

2.2. Composite processing [Coleman et al., 2006]

2.2.1 Solution processing of composites

The most common method for preparing polymer fillers composites has been to mix the fillers and polymer in a suitable solvent before evaporating the solvent to form a composite film. One of the benefits of this method is that agitation of the fillers powder in a solvent facilitates fillers de-aggregation and dispersion. Almost all solution processing methods are variations on a general theme which can be summarised as:

1. Dispersion of fillers in either a solvent or polymer solution by energetic agitation.
2. Mixing of fillers and polymer in solution by energetic agitation.
3. Controlled evaporation of solvent leaving a composite film.

In general, agitation is provided by magnetic stirring, shear mixing, reflux or, most commonly, ultrasonication. Sonication can be provided in two forms, mild sonication in a bath or high-power sonication using a tip or horn.

2.2.2 Melt processing of bulk composites

While solution processing is a valuable technique for both fillers dispersion and composite formation, it is completely unsuitable for many polymer types that are insoluble. Melt processing is a common alternative, which is particularly useful for dealing with thermoplastic polymers. This technique makes use of the fact that thermoplastic polymers soften when heated. Amorphous polymers can be processed above their glass transition temperature while semi-crystalline polymers need to be heated above their melt temperature to induce sufficient softening. Advantages of this technique are its speed and simplicity, not to mention its compatibility with standard industrial techniques.

In general, melt processing involves the melting of polymer pellets to form a viscous liquid. Any additives, such as carbon nanotubes can be mixed into the melt by shear mixing. Bulk samples can then be fabricated by techniques such as compression molding, injection molding or extrusion.

2.2.3 Processing of composites based on thermosets (Direct mixing)

The most common thermosetting polymers used in the formation of polymer filler composites are epoxy resins [Tang et al., 2003]. Generally these are polymers that cure when mixed with a catalyzing agent or hardener. In most cases the epoxy begins life in liquid form, facilitating filler dispersion by the techniques described in Section 2.1 Curing is then carried out to convert a liquid composite to a final solid state.

2.2.4 In situ polymerisation processing

This technique is particularly important for the preparation of insoluble and thermally unstable polymers, which cannot be processed by solution or melt processing. Depending on required molecular weight and molecular weight distribution of polymers, chain transfer, radical, anionic, and ring-opening metathesis polymerizations can be used for in situ polymerization processing. Here we consider only recent advances in situ polymerization processing, which resulted in new polymer-carbon nanotube composites with improved mechanical properties.

2.3 Polypropylene

Polypropylene (PP) is a linear hydrocarbon polymer, expressed as C_nH_{2n} . It is manufactured from propylene gas in presence of a catalyst such as titanium chloride. Besides PP is a by-product of oil refining processes.

2.3.1 Properties of polypropylene

- Light in weight
- Excellent resistance to stress and high resistant to cracking (i.e. it has high tensile and compressive strength)
- High operational temperatures with a melting point of 160°C
- Excellent dielectric properties
- It is highly resistant to most alkalis and acid, organic solvents, degreasing agents and electrolytic attack. On the contrary is less resistance to aromatic, aliphatic and chlorinated solvents and UV.
- Non-toxic
- Non-staining
- Easy to produce, assembly and an economic material

In order to improve some properties, PP compounds may include additives such as pigments, carbon black, rubbers, antioxidants, and UV stabilizer. PP is available as molding powder, extruded sheet, cast film, textile staple, and continuous filament yarn.

Table 2.2 Properties of polypropylene

Properties	ASTM	PP
Specific gravity	D729	0.90-0.91
Crystallinity (%)	-	82
Melt temperature (°C)	-	165-171
Tensile strength (MPa) ^a	D638	31-41
Tensile modulus (GPa) ^b	0638	1.10-1.55
Elongation-to-break (%)	0638	100-600
Impact strength,notched Izod (J m ⁻¹) ^c	0256	21-53
Heat-deflection temperature, at 445 kPa (66psi)	D648	225-250

^a To convert MPa to psi , multiply by 145.

^b To convert GPa to psi , multiply by 1.45×10^5 .

^c To convert J m⁻¹ to lbf in⁻¹ , multiply by 53.38.

2.3.2 Applications of polypropylene

In general homopolymers (i.e. with only one type of monomer) can be used for housing, housewares, packaging, cassette holders and fibers, monofilaments and film tapes; copolymers (i.e. different monomers are involved) are preferred for all applications exposed to cold and they are widely used for pipes, containers, boat hulls, seat shells and automotive parts e.g. battery cases and bumpers. PP can be manufactured to a high degree of purity to be used for the semiconductor industry. Its resistance to bacterial growth makes it suitable to be used in medical equipment. PP is used in most of non-woven fabrics such as rope used in a variety of industries,

including fishing and agriculture. PP can be used for flexible packaging applications (e.g. yogurt containers, syrup bottles, straws, etc.), construction.

2.4 Thermal properties

[<http://plc.cwru.edu/tutorial/enhanced/files/polymers/therm/therm.htm>]

2.4.1 Glass transition temperature

In the study of polymers and their applications, it is important to understand the concept of the glass transition temperature, T_g . As the temperature of a polymer drops below T_g , it behaves in an increasingly brittle manner. As the temperature rises above the T_g , the polymer becomes more rubber-like. Thus, knowledge of T_g is essential in the selection of materials for various applications. In general, values of T_g well below room temperature define the domain of elastomers and values above room temperature define rigid, structural polymers.

This behavior can be understood in terms of the structure of glassy materials which are formed typically by substances containing long chains, networks of linked atoms or those that possess a complex molecular structure. Normally such materials have a high viscosity in the liquid state. When rapid cooling occurs to a temperature at which the crystalline state is expected to be the more stable, molecular movement is too sluggish or the geometry too awkward to take up a crystalline conformation. Therefore the random arrangement characteristic of the liquid persists down to temperatures at which the viscosity is so high that the material is considered to be solid. The term glassy has come to be synonymous with a persistent non-equilibrium state. In fact, a path to the state of lowest energy might not be available.

To become more quantitative about the characterization of the liquid-glass transition phenomenon and T_g , we note that in cooling an amorphous material from the liquid state, there is no abrupt change in volume such as occurs in the case of cooling of a crystalline material through its freezing point, T_f . Instead, at the glass transition temperature, T_g , there is a change in slope of the curve of specific volume vs. temperature, moving from a low value in the glassy state to a higher value in the

rubbery state over a range of temperatures. This comparison between a crystalline material (1) and an amorphous material (2) is illustrated in the Figure 2.3.

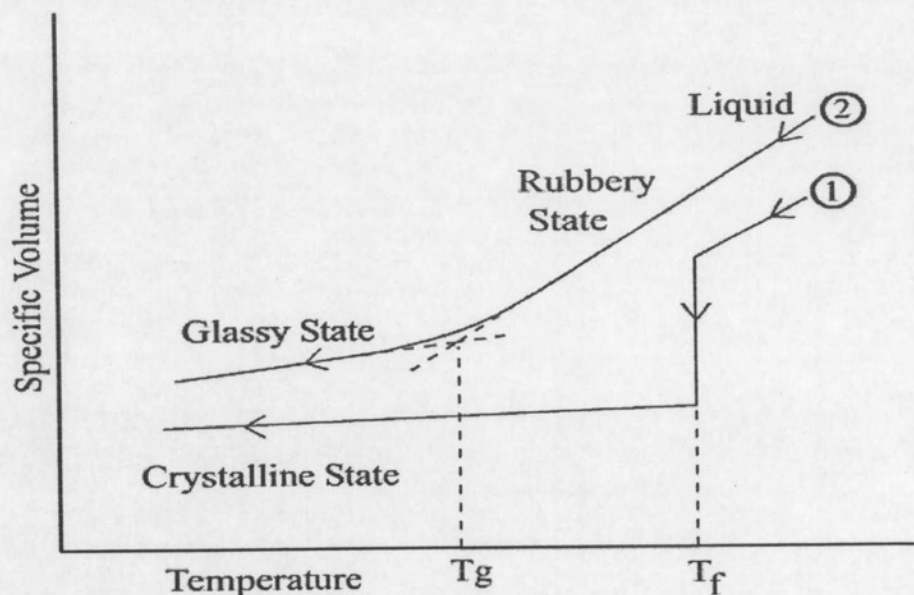


Figure 2.3 Glass transition temperature of (1) a crystalline material and (2) an amorphous material

2.4.2 Melting Temperature

Melting temperature, temperature at which a substance changes its state from solid to liquid. Under standard atmospheric pressure different pure crystalline solids will each melt at a different specific temperature; thus melting temperature is a characteristic of a substance and can be used to identify it. When heat is applied continuously and in sufficient quantity to such solids, the temperature rises steadily until it reaches the point at which liquefaction occurs. Here the rise ceases and no further change in temperature is observed until all of the substance has been converted to liquid.

2.5 Mechanical properties [Vishu Shah, 2003]

The material selection for a variety of applications is quite often based on mechanical properties such as tensile strength, modulus, elongation, and impact strength. These values are normally derived from the technical literature provided by material suppliers. The basic understanding of stress-strain behavior of polymer is of almost importance to design engineers. One such typical stress-strain diagram is illustrated in Figure 2.4.

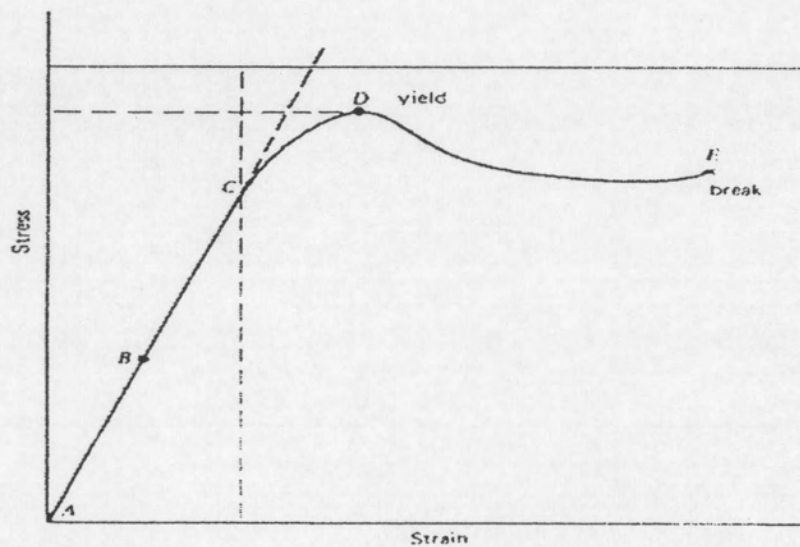


Figure 2.4 A typical stress-strain curve

For a better understanding of the stress-strain curve, it is necessary to define a few basic terms that are associated with the stress-strain diagram.

2.5.1 Stress-Strain diagram

2.5.1.1 Stress

Stress is the internal resistance, or counterforce, of a material to the distorting effects of an external force or load. These counterforces tend to return the atoms to their normal positions. The total resistance developed is equal to the external load. This resistance is known as stress. Although it is impossible to measure the

intensity of this stress, the external load and the area to which it is applied can be measured. Stress (σ) can be equated to the load per unit area or the force (F) applied per cross-sectional area (A) perpendicular to the force as shown bellows:

$$\text{Stress}(\sigma) = F/A$$

where: σ = stress (psi or lbs of force per in.²)
 F = applied force (lbs of force per in.²)
 A = cross-sectional area (in.²)

In mechanical properties, they are mainly interested in the effect of applying surfaces forces such as stress or pressure.

2.5.1.2 Strain

For mechanical engineering purposes, a given state of stress usually exists in a considerable volume of the material. Reaction of the atomic structure will manifest itself on a macroscopic scale. Therefore, whenever a stress (no matter how small) is applied to a specimen, a proportional dimensional change or distortion must take place. When forces are applied to a material, the atoms change position in response to the force and this change is known as strain. It is defined as ratio of the elongation to the gauge length of the test specimen, or simply stated, change in length per unit of the original length ($\Delta l/l$).

2.5.1.3 Elongation

The increase in the length of a test specimen produced by a tensile load (M) is called Elongation. Elongation is a type of deformation. Deformation is simply a change in shape that anything undergoes under stress. Usually they talk about percent elongation, which is just the length the polymer sample is after it is stretched (L), divided by the original length of the sample (I), and then multiplied by 100.

2.5.1.4 Yield point

The first point on the stress-strain curve at which an increase in strain occurs without the increase in stress (Point D) in Figure 2.4 is called yield point.

2.5.1.5 Yield strength

The stress at which a material exhibits a specified limiting deviation from proportionality of stress to strain is called yield strength. This stress will be at yield point.

2.5.1.6 Proportional limit

The greatest stress at which a material is capable of sustaining the applied load without any deviation from proportionality of stress to strain is called proportional limit. Below this limiting value of stress, the ratio of stress to strain is constant, and the material is said to obey Hook's Law (stress is proportional to strain).

2.5.1.7 Modulus of elasticity

The ratio of stress to corresponding strain below the proportional limit of the material is called modulus of elasticity.

2.5.1.8 Break point

The point at which a material breaks or ruptures in tension due to plastic deformation is called break point. The stress-strain diagram illustrated in Figure 2.4 is typical of that obtained in tension for a constant rate of loading. However, the curves can be obtained from other loading conditions such as compression or shear.

The behavior of polymer below the proportional limit (Point C in Figure 2.4) is elastic in nature and therefore the deformations are recoverable. At

Point B, the deformations are relatively small and have been associated with the bending and stretching of the interatomic bonds between atoms of polymer molecules as shown in Figure 2.5(a). At Point C in Figure 2.4, the deformation is similar to a straightening out of a coiled portion of the molecular chain (Figure 2.5(b)). There is no intermolecular slippage and the deformations can be recovered ultimately. The extensions that occur beyond the yield point of the polymer are not recoverable (Figure 2.5(c)).

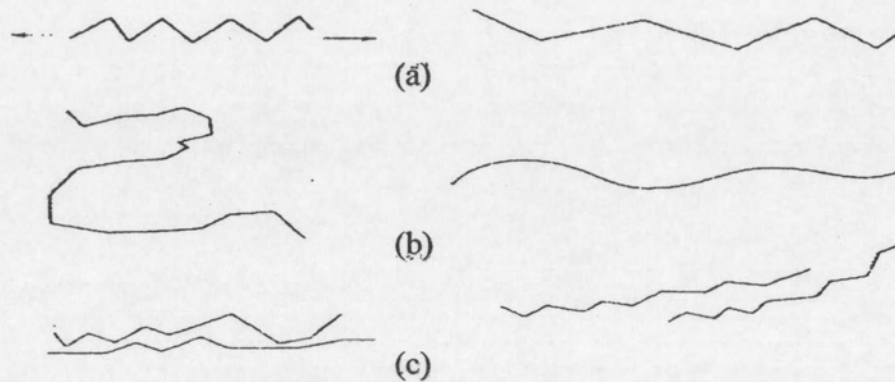


Figure 2.5 Extension types (a) bond bending (b) uncoiling (c) slippage

2.5.2 Type of stress-strain curve

The polymeric material can be broadly classified in term of their softness, brittleness, hardness, and toughness. The tensile stress-strain diagram serves as a basic for such a classification. Figure 2.6 illustrates typical tensile stress-strain curve for several type of polymer. The area under curve is considered as the toughness. Table 2.3 lists characteristic features of stress-strain curve as they relate to the polymer properties.

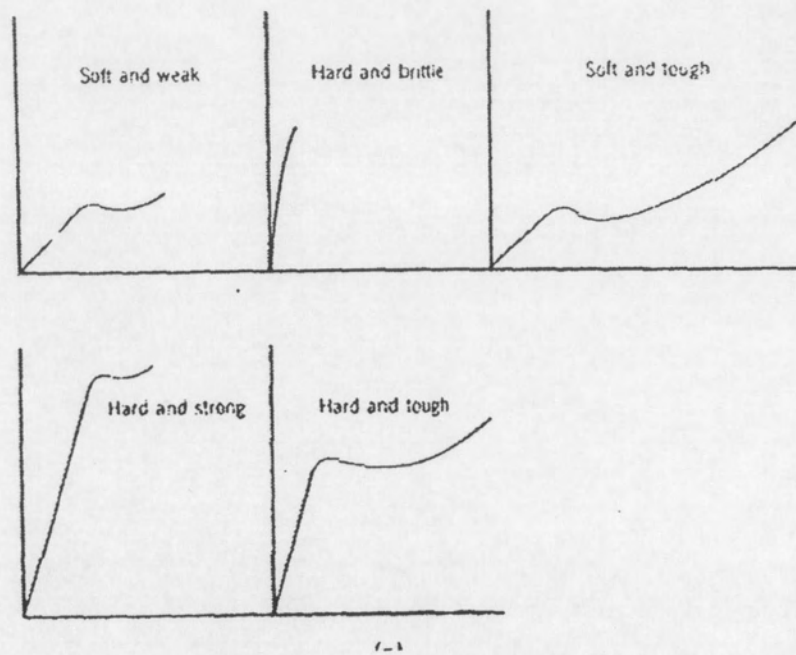


Figure 2.6 Types of stress-strain curve

Table 2.3 Characteristic features of stress-strain curve as they relate to the polymer properties.

Description of polymer	Modulus	Yield stress	Ultimate strength	Elongation at break
Soft , weak	Low	Low	Low	Moderate
Soft , tough	Low	Low	Yield stress	High
Hard , brittle	High	None	Moderate	Low
Hard , strong	High	High	High	Moderate
Hard , tough	High	High	High	High

2.5.3 Tensile tests

The tensile test supplies three descriptive facts about a material. These are the stress at which observable plastic deformation or “yielding” begins; the ultimate tensile strength or maximum intensity of load that can be carried in tension; and the percent elongation or strain (the amount the material will stretch) and the accompanying percent reduction of the cross-sectional area caused by stretching. The rupture or fracture point can also be determined.

2.5.3.1 Tensile strength

Tensile strength	=	Force (load)/Cross section area
Tensile strength at yield	=	Maximum load recorded/Cross section area
	=	Tensile stress at yield point
Tensile strength at break	=	Load recorded at break/Cross section area
	=	Tensile stress at break point

2.5.3.2 Tensile modulus and elongation

Tensile modulus	=	Difference in stress/Difference in strain
	=	Slope of stress-strain curve in elastic range
Elongation at yield	=	Strain at yield x Original length
Percent elongation at yield	=	Elongation at yield x 100
Elongation at break	=	Strain at break x Original length
Percent elongation at break	=	Elongation at break x 100