

## CHAPTER II

### THEORY

#### 2.1 Common Types of Copolymers

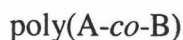
Polymer made from only one kind of monomeric unit, or mer, were normally considered. Many kinds of polymers can contain two kinds of mers. These can be combined in various ways to obtain interesting and often highly useful materials. Some of the basic copolymer nomenclature is presented in Table 2.1.1. If three mers- A, B, and C-are considered, some of the possible copolymers are also named in Table 2.1.1. The connectives in copolymer nomenclature will be defined as below [Sperling,2001].

**Table 2.1.1 Some copolymer terminology [Ward et al,1993]**

Type	Connective	Example
<i>Short Sequences</i>		
Unspecified	-co-	poly(A-co-B)
Statistical	-stat-	poly(A-stat-B)
Random	-ran-	poly(A-ran-B)
Alternating	-alt-	poly(A-alt-B)
Periodic	-per-	poly(A-per-B-per-C)
<i>Long Sequences</i>		
Block	-block-	poly A-block-poly B
Graft	-graft-	poly A-graft-poly B
Star	-star-	star-poly A
Blend	-blend-	poly A-block-poly B
Starblock	-star-...- block-	star-poly A-block-poly B
<i>Networks</i>		
Cross-linked	-cross-	cross-poly A
Interpenetrating	-inter-	cross-poly A-inter- cross-poly B
AB-crosslinked	-cross-	poly A-cross-poly B

### 2.1.1 Unspecified Copolymers

An unspecified sequence arrangement of different monomeric units in a polymer is represented by



Thus an unspecified copolymer of styrene and methyl methacrylate is named

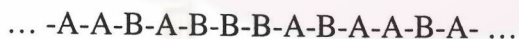


In the old reference literature, *-co-* was used to indicate a random copolymer, where the mer were added in random order, or perhaps addition preference was dictated by thermo dynamic or spatial considerations. These are now distinguished from one another [Malcolm,1999].

### 2.1.2 Statistical Copolymers

Statistical copolymers are copolymers in which the sequential distribution of the monomeric units obeys known statistical laws. The term *-stat-* embraces a large proportion of those copolymers that are prepared by simultaneous polymerization of two or more monomers in admixture. Thus the term *-stat-* is now preferred over *-co-* for most usage.

The arrangement of mers in a statistical copolymer of A and B might appear as follows:



The statistical arrangement of mers A and B is indicated by



### 2.1.3 Random Copolymers

A random copolymer is a statistical copolymer in which the probability of finding a given monomeric unit at any given site in the chain is independent of the nature of the neighboring units at the position. Stated mathematically, the probability of finding a sequence ...ABC... of monomeric units A, B, C, ...,  $P(\dots ABC \dots)$  is

$$P(\dots ABC \dots) = P(A) \cdot P(B) \cdot P(C) \dots = \prod_i P(i), \quad i = A, B, C \dots$$

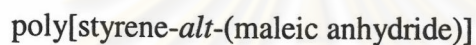
Where  $P(A)$ ,  $P(B)$ ,  $P(C)$ , and so on, are the unconditional probabilities of the occurrence of the various monomeric units.

#### 2.1.4 Alternating Copolymers

In the discussion above, various degrees of randomness were assumed. An alternating copolymer is just the opposite, comprising two species of monomeric units distributed in alternating sequence:



Alternating copolymerization is caused either by A or B being unable to add itself, or the rate of addition of the other monomer being much faster than the addition of itself. An important example of an alternating copolymer is

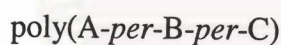


#### 2.1.5 Periodic Copolymers

The alternating copolymer is the simplest case of a periodic copolymer. For three mers,



the structure is indicated by



#### 2.1.6 Block Copolymers

A block copolymer contains a linear arrangement of blocks, a block being defined as a portion of a polymer molecule in which the monomeric units have at least one constitutional or configurational feature absent from the adjacent portions. A block copolymer of A and B may be written



Note that the blocks are linked end on end. Since the individual blocks are usually long enough to be considered polymers in their own right, the polymer is named



An especially important block copolymer is the triblock copolymer of styrene and butadiene,  $\text{polystyrene-}i>\text{block}\text{-polybutadiene-}i>\text{block}\text{-polystyrene}$



In the older literature, *-b-* was used for *-block-*, and *-g-* was used for *-graft-* (below). Only the first poly was indicated. Structure was then written

polystyrene-*b*-polybutadiene-*b*-polystyrene

### 2.1.7 Graft Copolymers

A graft copolymer comprises a backbone species, poly A, and a side-Chain species, poly B. The side chains comprises units of mer that differ from those comprising the backbone chain. If the two mers are the same, the polymer is said to be branched. The name of a graft copolymers of A and B is written in this order:

poly A-*graft*-poly B

although many of the block co polymers reported in the literature are actually highly blocked, some of the most important “graft copolymers” described in the literature have been shown to be only partly grafted, with much homopolymer being present. To some extent, then, the term graft copolymer may also mean, “polymer B synthesized in the immediate presence of polymer A”. Only by a reading of the context can the two meanings be distinguished.

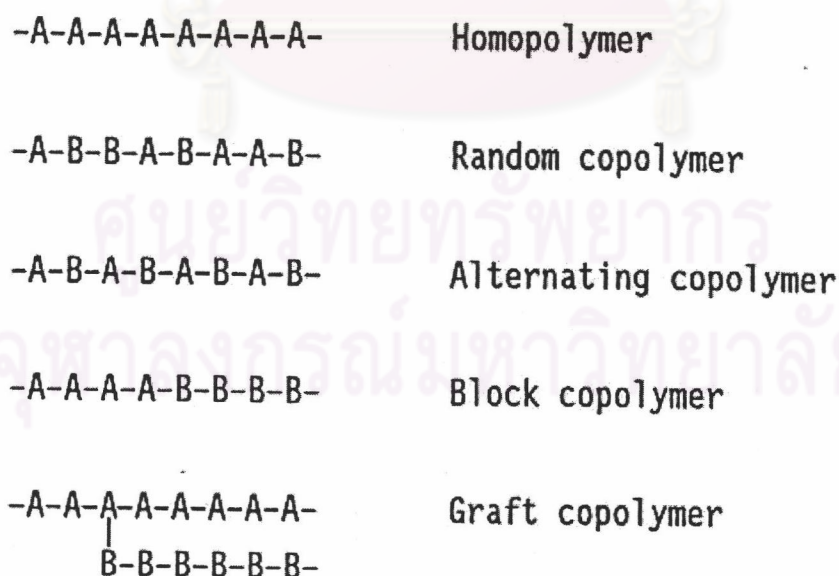


Figure 2.1.1 Homopolymer and Copolymer [Cowie,1991]



### 2.1.8 AB-Cross-linked Copolymer

The polymers of section 2.1.7 are soluble, at least in the ideal case. A continuously grafted copolymer has polymer B grafted at both ends, or at various points along the structure to polymer a, and hence it is a network and not soluble. See structure(f) in Figure 2.1.3, which is sometimes called a continuously grafted copolymer.

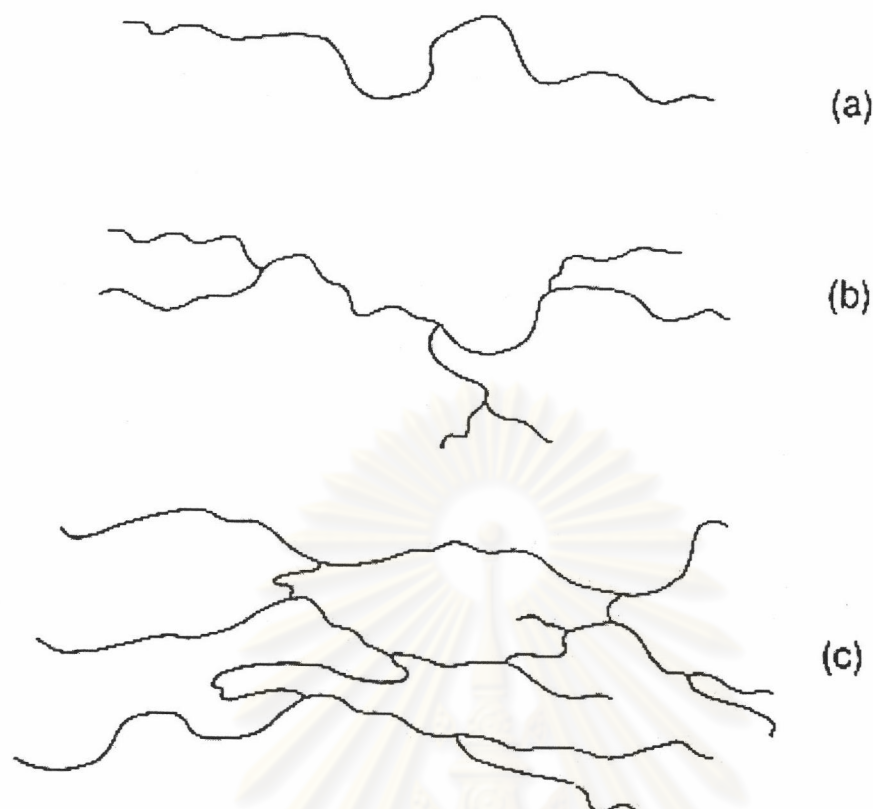
### 2.1.9 Interpenetrating Polymer Networks

This is an intimate combination of two polymers in network form. At least one of the polymers is polymerized and/or cross-linked in the immediate presence of the other. While ideally the polymers should interpenetrate on the molecular level, actual interpenetration may be limited owing to phase separation.

### 2.1.10 Other Polymer-Polymer Combinations

According to new nomenclature, a polymer blend is accorded the connective *-blend-*. Many of these blends are prepared by highly sophisticated methods and are actually on a parallel with blocks, grafts, and interpenetrating polymer networks.

Block copolymer may also be arranged in various star arrangements. In this case polymer A radiates from a central point, with a number of arms to be specified. Then polymer B may be attached to the end of each arm, that mentioned before.



**Figure 2.1.2** Structure of the polymer a) linear b) branched c) network

**Table 2.1.2** Specialized nomenclature terms [Magoshi et al,1996]

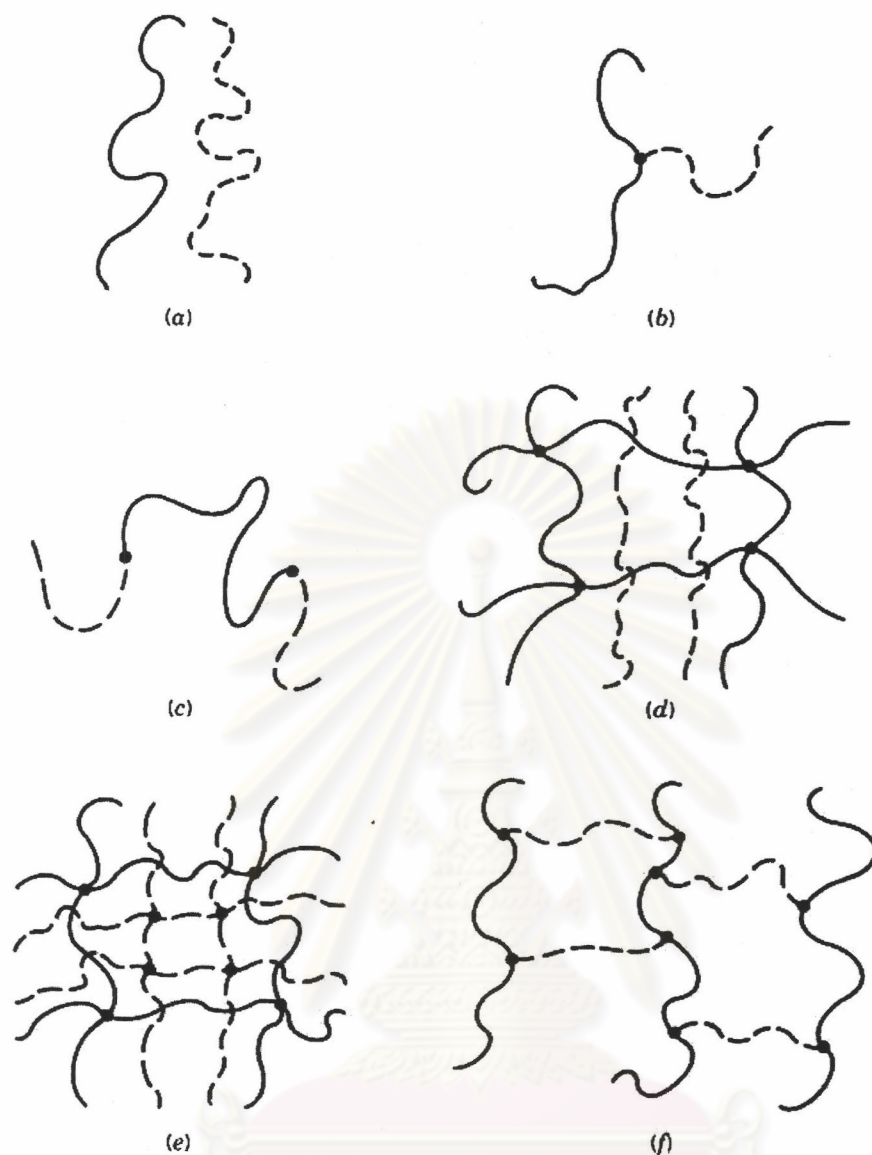
<i>Link</i>	Covalent chemical bond between two monomeric units, or between two chains.
<i>Chain</i>	Linear polymer formed by covalent linking of monomeric units.
<i>Backbone</i>	Used in graft copolymer nomenclature to describe the chain onto which the graft is formed.
<i>Side chain</i>	Grafted chain in a graft copolymer.
<i>Cross-link</i>	Structure bonding two or more chains together.
<i>Network</i>	Three-dimensional polymer structure, where ( ideally ) all the chains are connected through cross-links.
<i>Multicomponent polymer, multipolymer, and multi component molecule</i>	General terms describing intimate solutions, blends, or bonded combinations of two or more polymers.

**Table 2.1.2** Specialized nomenclature terms (continued)

<i>Copolymer</i>	Polymers that are derived from more than one species of monomer.
<i>Block</i>	Portion of a polymer molecule in which the monomeric units have at least one constitutional or configurational feature absent from the adjacent portions.
<i>Block copolymer</i>	Combination of two or more chains of constitutionally or configurationally different features linked in a linear fashion.
<i>Graft copolymer</i>	Combination of two or more chains of constitutionally or configurationally different features, one of which serves as a backbone main chain, and at least one of which is bonded at some point(s) along the backbone and constitutes a side chain.
<i>Polymer blend</i>	Intimate combination of two or more polymer chains of constitutionally or configurationally different features, which are not bonded to each other.
<i>Conterminous</i>	At both ends or at points along the chain.
<i>AB-cross-linked copolymer</i>	Polymer chain that is linked at both ends to the same or to constitutionally or configurationally different chain or chains; a polymer cross-linked by a second species of polymer.
<i>Interpenetrating polymer network</i>	Intimate combination of two polymers both in network form, at least one of which is synthesized and/or cross-linked in the immediate presence of the other.
<i>Semi-interpenetrating Polymer network<sup>a</sup></i>	Combination of two polymers, one cross-linked and one linear, at least one of which was synthesized and/or cross-linked in the immediate presence of the other.
<i>Star polymer</i>	Three or more chains linked at one end through a central moiety.
<i>Star block copolymer</i>	Three or more chains of different constitutional or configurational feature linked at one end through a central moiety.

<sup>a</sup>Also called a pseudo-interpenetrating polymer network. See D. Klempner, K. C. Frisch, and H. L. Frisch, *J. Elastoplastics*, 5, 196 [1973]





**Figure 2.1.3** Six basic modes of linking two or more polymer are identified [Kahovec et al,1997]. (a) A polymer blend, constituted by a mixture of mutual solution of two or more polymers, not chemically bonded together. (b) A graft copolymer, constituted by a backbone of polymer I with covalently bonded side chains of polymer II. (c) A block copolymer, constituted by linking two polymers end on end by covalent bonds. (d) A semi-inter penetrating polymer network constituted by an entangled combination of two polymers, one of which is crosslinked, that are not bonded to each other. (e) An interpenetrating polymer network, abbreviated IPN, is an entangled combination of two cross-linked polymers that are not bonded to each other. (f) AB-cross-linked copolymer, constituted by having the polymer II species linked, at both ends, onto polymer I. The ends may be grafted to different chains or the same chain. The total product is a network composed of two different polymers.

## 2.2 Techniques of free radical polymerization

Free radical polymerization can be accomplished in bulk, suspension, solution, or emulsion. Ionic and other nonradical polymerizations are usually confined to solution techniques. Each of the methods has advantages and disadvantages, as outlined in Table 2.2.1 In addition, work has also been done on solid- and gas-phase polymerization of vinyl monomers. Because polymers are not volatile, the term gas-phase polymerization mean, in effect, bulk polymerization in which monomer vapors diffuse to the polymerization site.

**Table 2.2.1** Free Radical Polymerization Techniques [Sperling,2001]

<i>Method</i>	<i>Advantages</i>	<i>Disadvantages</i>
Bulk	Simple; no contaminants added	Reaction exotherm difficult to control; high viscosity
Suspension	Heat readily dispersed; low viscosity; polymer obtained in granular form and may be used directly	Washing and/or drying required; agglomeration may occur; contamination by stabilizer
Solution	Heat readily dispersed; low viscosity; may be used directly as solution	Added cost of solvent; solvent difficult to remove; possible chain transfer with solvent; possible environmental pollution
Emulsion	Heat readily dispersed; low viscosity; high molecular weight obtainable; may be used directly as emulsion; works on tacky polymer	Contamination by emulsifier and other ingredients; chain transfer agents often needed to control molecular weight distribution; washing and drying necessary for bulk polymer

### 2.2.1 Bulk

Bulk polymerization is simplest from the standpoint of formulation and equipment, but it is also the most difficult to control, particularly when the polymerization reaction is very exothermic. This, coupled with problems of heat transfer as the monomer-polymer solution increases in viscosity, limits the use of bulk methods in commercial production, although more efficient bulk processes have been developed in recent years.

In cases where polymer is insoluble in its monomer, polymer precipitates and the viscosity of the medium does not change appreciably. Problems still arise, however, as a result of free radicals (detectable by Electron Spin Resonance Spectroscopy) being occluded in the polymer droplet, which can lead to *autoacceleration*, that is, a rapid increase in the polymerization rate. In some instances, particularly with diene monomers, this occlusion effect may lead to formation of insoluble crosslinked polymer nodules, a phenomenon referred to as popcorn polymerization. The crosslinked nodules are usually of light weight and occupy considerably more volume than the monomers from which they are derived, which may cause fouling and even fracture of the polymerization apparatus.

The major commercial uses of bulk vinyl polymerization are in casting formulations and low-molecular-weight polymers for use as adhesives, plasticizers, tackifiers, and lubricant additives.

### 2.2.2 Suspension

Suspension polymerization involves mechanically dispersing monomer in noncompatible liquid, usually water, and polymerizing the resultant monomer droplets by use of a monomer soluble initiator. Monomer is kept in suspension by continuous agitation and the use of *stabilizers* such as poly(vinyl alcohol) or methyl cellulose. If the process carefully controlled, polymer is obtained in the form of granular beads, which are easy to handle and can be isolated by filtration or by spraying into a heated chamber (*spray drying*). A major advantage is that heat transfer is very efficient and the reaction is therefore easily controlled. Suspension polymerization cannot be used for tacky polymers such as elastomers because of the tendency for agglomeration of polymer particles. From the standpoint of kinetics and mechanism, suspension polymerization is identical to bulk polymerization.

Suspension methods are utilized in preparing a number of granular polymers, including polystyrene, poly(vinyl chloride), and poly(methyl methacrylate).



### 2.2.3 Solution

Like suspension, solution polymerization allows efficient heat transfer. Solvent must be chosen carefully, otherwise chain transfer reactions may severely limit the molecular weight. Apart from the environmental concerns associated with organic solvents, a major problem in solution polymerization is that it is often difficult to remove solvent completely from finished polymer. As a result there is considerable interest in using supercritical carbon dioxide as a polymerization solvent. Advantages are that carbondioxide is nontoxic, inexpensive, and easily removed and recycled from the polymer.

### 2.2.4 Emulsion

Developed at Goodyear Tire and Rubber Company in the 1920s, emulsion polymerization resembles suspension polymerization in that water is used as a dispersing medium and heat transfer is very efficient; but there the similarity ends. Monomer is dispersed in the aqueous phase by an emulsifying agent such as soap or detergent. Initiator radicals, usually of the redox type, are generated in the aqueous phase and diffuse into soap micelles swollen with monomer molecules. As monomer is used up in the polymerization reaction, more monomer migrates into the micelles to continue the reaction. Termination of polymerization occurs by radical combination when a new radical diffuses into the micelle. Because only one radical is present in the micelle prior to termination, extremely high molecular weights polymer are obtainable, generally too high to be of practical value unless compounds called *chain transfer agents* are added to control the degree of polymerization. The overall process is complex, with reaction kinetics differing significantly from that of bulk or solution processes.

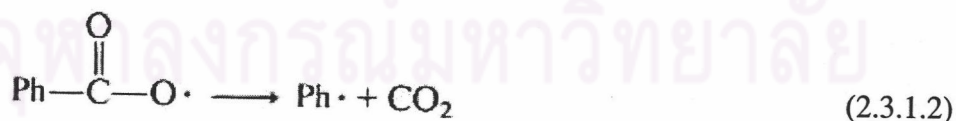
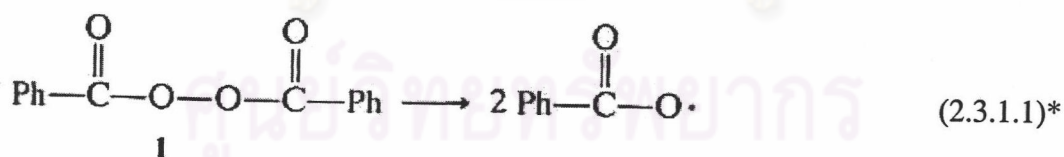
Emulsion polymerization is widely used in industry for large-scale preparations, and is particularly useful for manufacturing water-based (latex) paints or adhesives in which the emulsified product is used directly. Emulsion polymerization is also suitable for preparing tacky polymers because the very small particles are stable and resist agglomeration.

## 2.3. Free Radical Initiators

Certain monomers, notably styrene and methyl methacrylate and some strained-ring cycloalkenes, undergo polymerization on heating in the absence of any added free radical initiator. Most monomers, however, require some kind of initiator. A large number of free radical initiators are available; they may be classified into four major types: peroxides and hydroperoxide, azo compounds, redox initiators, and certain compounds that form radicals under the influence of light (photoinitiators). High energy radiation ( $\alpha$ - and  $\beta$ -particles,  $\gamma$ - and x-rays) can also promote free radical polymerization.

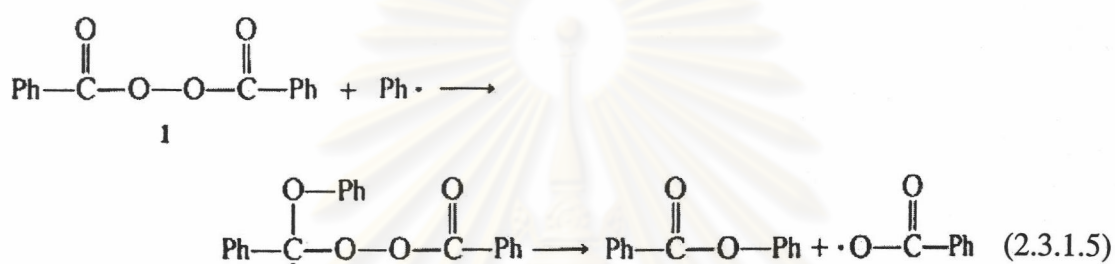
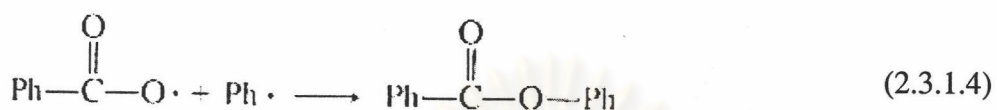
### 2.3.1 Peroxides and Hydroperoxides

Of the various types of initiators, peroxides (ROOR) and hydroperoxides (ROOH) are most widely used. They are thermally unstable and decompose into radicals at a temperature and rate dependent on structure. The most commonly used peroxide is benzoyl peroxide(1), which undergoes thermal homolysis to form benzoyl radicals (reaction 2.3.1.1)\*. The benzoyloxy radicals may undergo a variety of reactions besides adding to monomer, including recombination (reverse of 2.3.1.1), decomposition to phenyl radicals and carbon dioxide (2.3.1.2),

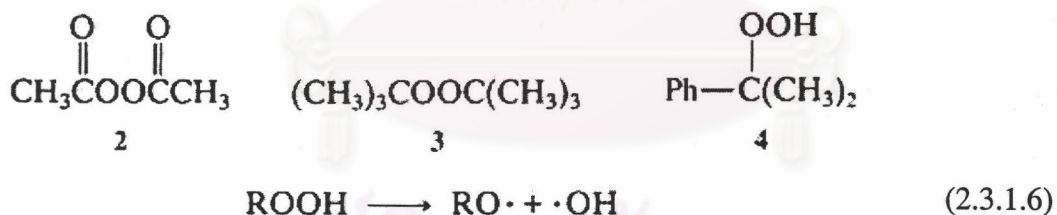


(\* Ph = phenyl. For radical structure such as the benzoyloxy radical, only the unpaired electron is shown. A more complete representation would include lone pair electrons and contributing resonance structures.)

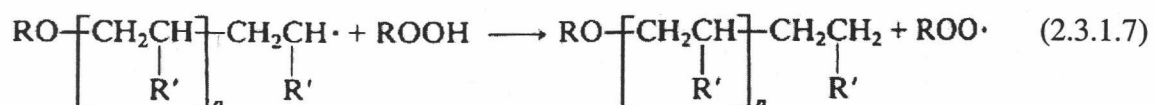
and radical combination (2.3.1.3 and 2.3.1.4). These secondary reactions occur because of the confining effect of solvent molecules (the cage effect), and as a result, the concentration of initiator radicals is depleted. Induced decomposition (2.3.1.5) is another "wastage" reaction.



Two other common initiators are diacetyl peroxide (2) and di-*t*-butyl peroxide (3). Hydroperoxides such as cumyl hydroperoxide (4) decompose to form alkoxy and hydroxyl radicals (2.3.1.6).



Because hydroperoxides contain an active hydrogen atom, induced decomposition occurs readily, for example, by a chain-end radical (2.3.1.7). Peroxy radicals may also combine with subsequent formation of oxygen (2.3.1.8).

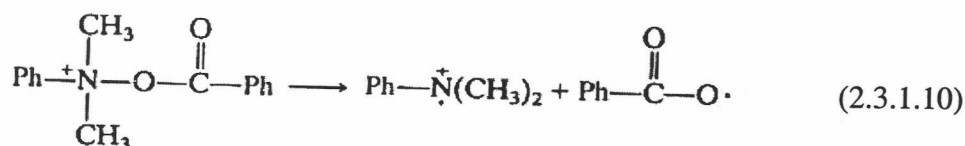
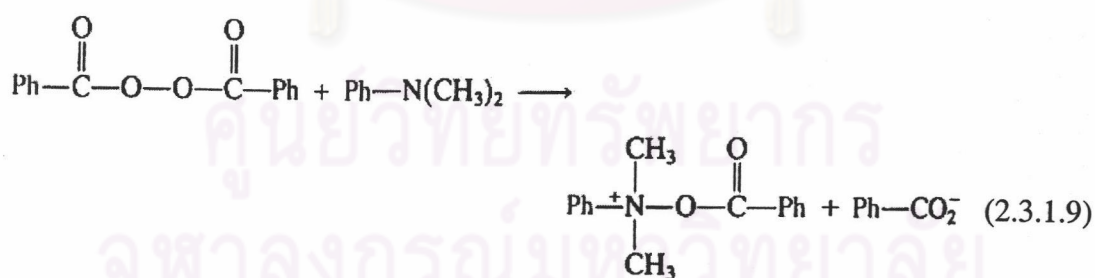






The extent to which side reactions occur depends on the structure of the peroxide, the stability of initially formed radicals, and the reactivity of the monomer. Ideally, a peroxide initiator should be relatively stable at room temperature but should decompose rapidly enough at polymer-processing temperatures to ensure a practical reaction rate. Benzoyl peroxide (half-life 30 minutes at 100 °C) has the advantage that benzoyloxy radicals are stable enough that they tend to react with more reactive monomer molecules before eliminating carbon dioxide, thus reducing initiator wastage. Acetoxy radicals formed from (2), on the other hand, are much less stable, and initiator wastage occurs more readily. More stable than benzoyloxy radicals are *t*-butoxy radicals, which are almost entirely captured by monomer; however, the decomposition temperature is relatively high (half-life 10 hours at 126 °C).

Decomposition of peroxides can frequently be induced at lower temperatures by the addition of *promoters*. For example, addition of N,N-dimethylaniline to benzoyl peroxide caused the latter to decompose rapidly at room temperature. Kinetics studied indicate that the decomposition involves formation of an unstable ionic intermediate (2.3.1.9) that reacts further to give benzoyloxy radical and radical cation (2.3.1.10). The radical cation apparently undergoes reactions other than addition to monomer, since polymers formed by this method contain no nitrogen.



## 2.4. Polymer Blends

A polymer blend is a mixture of at least two polymers or copolymers [Utracki, 1990]. The first polymer blend performed is not exactly known, but the first patent of polymer blend which was a blend between natural rubber and gutta percha was done in 1846 whereas the first patent on thermoplastic polymer blends, which was a blend of polyvinyl chloride (PVC) and acrylonitrile rubber (NBR), was performed in 1942 [Utrachi, 1990]. The main purpose of blending polymers is to design new properties of polymeric material that different from those of the pure polymers with out synthesizing a new polymer. The results of blending have many benefits such as no requiring more money, time and efforts than synthesizing the new polymer.

### 2.4.1 The Preparation of the Blends

There are many ways to prepare the new polymer blends such as using heat, by using solvent or by mixing via reaction, etc.

#### 2.4.1.1 Melt Mixing

Melt mixing of thermoplastics polymer is performed by mixing the polymers in the molten state under shear in the mixing equipment. This method of choice for the preparation of polymer blends in a commercial scale because of its simplicity, speed of mixing and the advantage of being free from foreign components (e.g. solvents) in the result blends. A number of devices are available for laboratory-scale mixing such as brabender mixer, electrically heated two-roll mill, extruder, rotational rheometer.

The primary disadvantage of this method is that both components must be in the molten state. It means that the temperature should not be high to cause degradation. The secondary, melt mixing is difficult to mix in some pairs of polymers due to difference in the melt viscosity of the components. Beside, the cost of the equipment is another disadvantage of melt mixing. Finally, This method only works well with large amounts of material, e.g. at least 50 grams is required for even laboratory-size mixing equipment. If mixing of quantities of less than 1 g is required, melt mixing is usually not feasible.

### 2.4.1.2 Solvent Casting

This method is done by dissolving polymers into a suitable solvent. Solution of polymer blend is then cast on a glass plate into thin films and the removal of solvent from films is performed by evaporating at ambient or elevated temperature. Solvent casting is the simplest mixing method available and is widely practiced in academic studies. Finally, this method is suitable and easy for very small quantities of experimental polymers.

The most severe problem with solvent casting is the influence of the solvent and the casting history on the resulting product. In spite of the fact that the most of the solvent can be removed from a cast film, the nature of the film depends strongly on the solvent and the conditions used during casting. Casting is best done in thin films, normally not exceeding 0.1 mm in thickness [Thongyai,1990], with slow solvent removal to avoid concentration and temperature gradients during the removal of solvent.

To remove traces of solvent from the casting polymer films, the condition of high temperature is invariably needed, and protection of the polymer in case of degradation is essential. Flowing inert gas or vacuums are typically used. In the vacuums conditions, the vapor pressure can be reduced and thus allows the solvents to evaporate more easily. However, too fast evaporation rate of solvent will result in the bubble in the final films produced.

### 2.4.1.3 Freeze Drying

In the freeze drying process, a solution of the two polymers is quenched down to a very low temperature and solvent is frozen. Solvent is then removed from the frozen solution by sublimation at a very low temperature and pressure. Dilute solutions must be used and the solution volume must be kept low for good heat transfer.

An advantage of this method is that resulting blend will be independent of the solvent, if the solution is single phase before freezing and the freezing occurs rapidly. However there are many limitations of this method. Freezing drying seems to



work best with solvents having high symmetry, i.e. benzene, dioxane, naphthalene, etc. The powdery form of the blend after solvent removal is usually not very useful and further shaping must be performed. Freeze drying does require a good vacuum system for low-boiling solvents and it is not a fast blending method.

#### **2.4.1.4 Emulsions**

The handling of polymers as emulsion has as many advantages as the use of solvent casting. Films can be cast; mixing requires neither expensive equipment nor high temperature. However, emulsions of polymers are not always available or easy to make. While emulsion polymerization is highly advanced, it is not applicable to all monomers.

#### **2.4.1.5 Mixing via Reaction**

Co-crosslinking and interpenetrating polymer networks (IPN) formation are specially methods for forming blends. The idea of these methods is to force a degree of miscibility by reactions between the polymers. Other methods involve the polymerization of a monomer in the presence of a polymer and the introduction of groups onto the polymer chain.

### **2.5 Polymer Morphology**

Generally, there are two morphologies of polymers, amorphous and crystalline. The former is a physical state characterized by almost complete lack of order among the molecules. The crystalline refers to the situation where polymer molecules are oriented or aligned. Because polymers for all practical purposes never achieve 100 % crystallinity, it is more practical to categorize their morphologies as amorphous and semicrystalline.

#### **2.5.1 The Amorphous State**

Some polymers do not crystallize at all. Therefore they remain in an amorphous state throughout the solidification. The amorphous state is characteristic of those polymers in the solid state that, for reasons of structure, exhibit no tendency toward crystallinity. In the amorphous state, the polymer resembles as a glass.

### 2.5.2 Glass Transition Temperature

One of the most important characteristics of the amorphous state is the behavior of a polymer during its transition from solid to liquid. If an amorphous glass is heated, the kinetic energy of the molecules increases. Motion is still restricted, however, to short-range vibrations and rotations so long as the polymer retains its glasslike structure. As temperature is increased further, there comes a point where a decided change takes place, the polymer loses its glasslike properties and assumes those more commonly identified with a rubber. The temperature at which this takes place is called the glass transition temperature. If heating is continued, the polymer will eventually lose its elastomeric properties and melt to a flowable liquid. The glass transition temperature is defined as the temperature at which the polymer softens because of the onset of long-range coordinated molecular motion. The amorphous parts of semicrystalline polymers also experience glass transition at a certain  $T_g$ .

### 2.5.3 The Crystalline Polymer

Polymers crystallized in the bulk state are never totally crystalline, a consequence of their long chain nature and subsequent entanglements. The melting temperature ( $T_m$ ) of the polymer, is always higher than the glass transition temperature,  $T_g$ . Thus the polymer may be either hard and rigid or flexible. For example, ordinary polyethylene that has a  $T_g$  of about  $-80\text{ }^\circ\text{C}$  and a melting temperature of about  $+139\text{ }^\circ\text{C}$ . At room temperature it forms a leathery product as a result. Factors that control the  $T_m$  include polarity, hydrogen bonding and packing capability.

## 2.6 Melting Phenomena

The melting of polymers may be observed by any of several experiments. For linear or branched polymer, the melting causes the samples to become liquid and flows. First of all, simple liquid behavior may not be immediately apparent because of the polymer has high viscosity. If the polymer is cross-linked, it may not flow at all. It must also be noted that amorphous polymers soften at their glass transition

temperature, which is emphatically not a melting temperature. If the sample does not contain colorants, it is usually hazy in the crystalline state because of the difference in refractive index between the amorphous and crystalline portions. On melting, the sample becomes clear or more transparent.

## 2.7 Thermal Properties

The existence of a polymeric system as a rigid glassy liquid, a mobile liquid, a microcrystalline solid or a liquid crystalline mesophase depends on the temperature and the chemical structure of the polymer. Changes from a microcrystalline state to a liquid crystalline or isotropic liquid state take place at the equilibrium melting temperature.

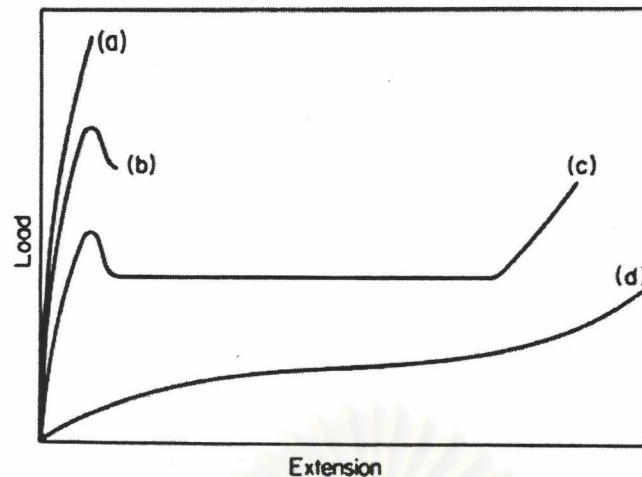
In various kind of the polymers, the melting points refer to the melting of crystal form with the highest  $T_m$ . Changes from one form to another at easily attained temperatures and pressures can be reversible or involve melting of one form and crystallization of the other.

## 2.8 Polymer Toughening

### 2.8.1 Definition of tough and brittle behaviour in polymers

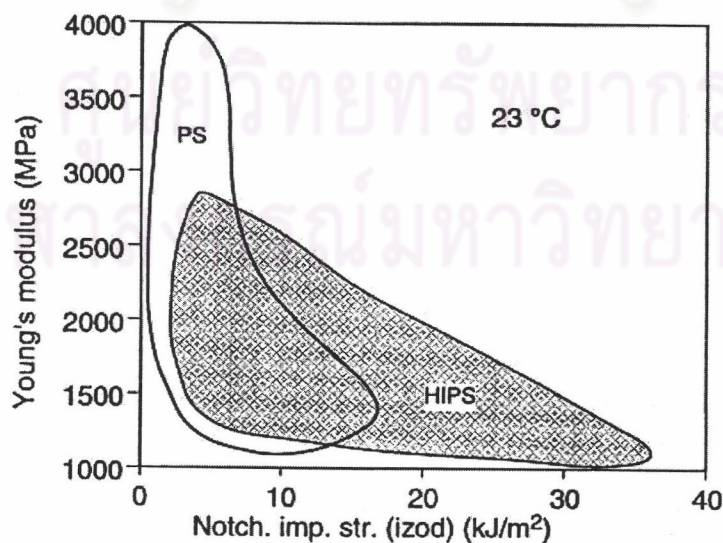
The mechanical properties of polymers are greatly affected by temperature and strain rate, and the load-elongation curve at a constant strain rate changes with increasing temperature as shown schematically (not necessarily to scale) in Figure 2.8.1. At low temperatures the load rises approximately linearly with increasing elongation up to the breaking-point when the polymer fractures in a brittle manner [Ward et al ,1993].





**Figure 2.8.1.1** Load-extension curves for a typical polymer tested at four temperatures showing different regions of mechanical behaviour. (a) Brittle fracture, (b) ductile failure, (c) necking and cold-drawing and (d) homogeneous deformation (quasi-rubber-like behaviour)

At higher temperatures a yield point is observed and the load falls before failure, sometimes with the appearance of a neck: i.e. ductile failure, but still at quite low strains (typically 10-20%). At still higher temperatures, under certain conditions, strain hardening occurs, the neck stabilizes and cold-drawing ensues. The extensions in this case are generally very large, up to 1000%. Finally, at even higher temperatures, homogeneous deformation is observed, with a very large extension at break. In an amorphous polymer this rubber-like behaviour occurs above the glass transition temperature so the stress levels are very low.



**Figure 2.8.1.2** Young's modulus (MPa) of HIPS and PS

For polymers the situation is clearly more complicated than that for the brittle-ductile transition in metals, as there are in general four regions of behaviour and not two. It is of considerable value to discuss the factors which influence the brittle-ductile transition, and then to consider further factors which are involved in the observation of necking and cold-drawing.

Ductile and brittle behaviour are most simply defined from the stress-strain curve. Brittle behaviour is designated when the specimen fails at its maximum load, at comparatively low strains (say  $< 10\%$ ), whereas ductile behaviour shows a peak load followed by failure at a lower stress (Figure 2.8.1(a) and (b))

The distinction between brittle and ductile failure is also manifested in two other ways: (1) the energy dissipated in fracture, and (2) the nature of the fracture surface. The energy dissipated is an important consideration for practical applications, and forms the basis of the Charpy and Izod impact tests. At the testing speeds under which the practical impact tests are conducted it is difficult to determine the stress-strain curve, so that impact strengths are customarily quoted in terms of the fracture energy for a standard specimen.

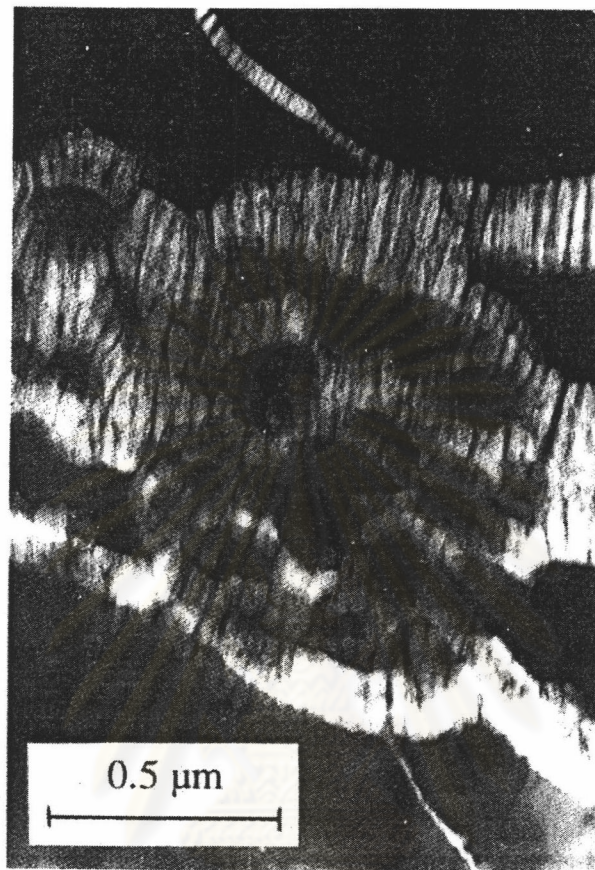
The appearance of the fracture surface can also be an indication of the distinction between brittle and ductile failure, although the present state of knowledge concerning the crack propagation is not sufficiently extensive to make this distinction more than empirical.

### 2.8.2 Crazeing

A craze is initiated when an applied tensile stress causes microvoids to nucleate at points of high stress concentrations in the polymer created by scratches, flaws, cracks, dust particles, molecular heterogeneities, etc. The microvoids develop in a plane perpendicular to the maximum principal stress but do not coalesce to form a true crack since they become stabilised by fibrils of plastically deformed, oriented polymeric material spanning the craze. The resulting localised yielded region therefore consists of an interpenetrating system of voids and polymer fibrils and is known as a craze. Unlike a crack, it is capable of transmitting loads across its faces. However, when cracks do initiate and grow they do so by means of the breakdown of the fibrillar structure in a craze. This typically results in slow cavity expansion



followed by crack extension through the craze, and finally crack propagation preceded by a craze or crazes at the crack tip through the remainder of the material.



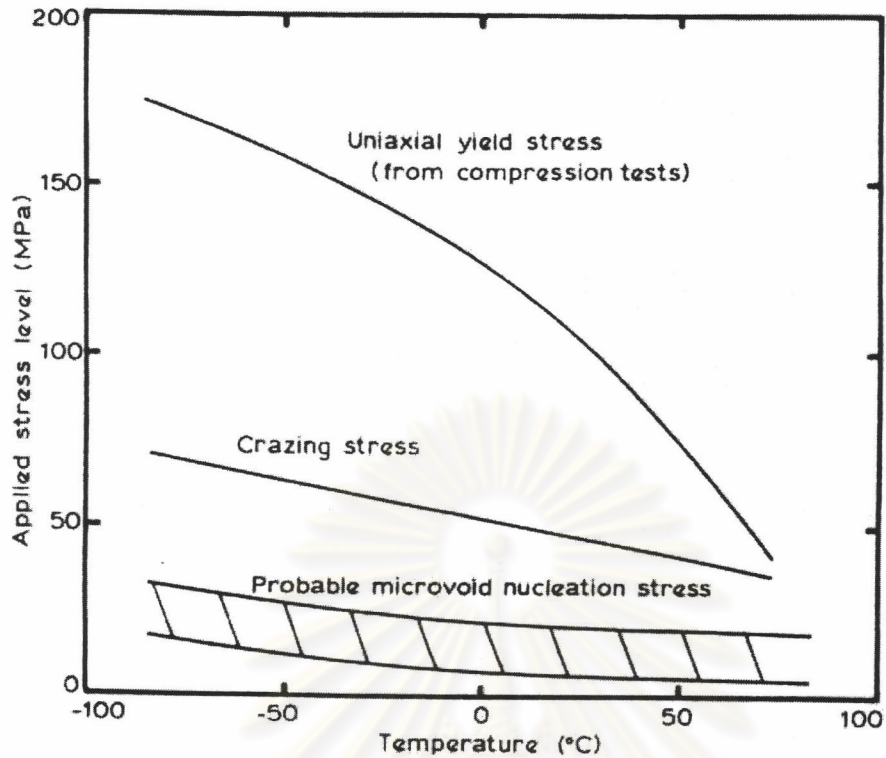
**Figure 2.8.2.1** Crazing of HIPS

The importance of crazing is that it is frequently a precursor to brittle fracture. This is because, although considerable plastic deformation and local energy adsorption are involved in craze initiation, growth and breakdown, this micromechanism is often highly localised and confined to a very small volume of the material. However, it should be recognised that if stable crazes can be initiated in a comparatively large volume of the polymer, i.e. a multiple deformation mechanism, then such multiple crazing may lead to a tough, and possibly even a ductile, material response in connection with polymers tested under plane-stress conditions at elevated temperatures near the  $T_g$  but, more importantly, multiple crazing is a major mechanism in some tough multiphase polymers.



Crazing, like the formation of shear bands or zones, involves localised or inhomogeneous plastic deformation of the material-which arises from strain softening. However, whereas shear yielding occurs essentially at constant volume, crazing is a cavitation process and hence occurs with an increase in volume. Craze initiation therefore usually requires the presence of a dilatational component to the stress tensor and may be inhibited by applying hydrostatic pressure but enhanced by the presence of triaxial tensile stresses. The latter stress state exists ahead of flaws in relatively thick specimens in plane strain. Also, under such conditions crazing is additionally favoured since the applied tensile stress necessary for shear yielding is high, due to the constraint, whilst the cavitation involved in crazing relieves the plane strain constraint and so enables the material to undergo plastic deformation more readily. Thus, the presence of sharp cracks or defects in thick specimens, or in thick sections of manufactured components, will favour craze initiation leading to a brittle fracture, as opposed to a bulk shear yielding mechanism leading to ductile failure.

As mentioned above, the importance of crazing is that crazes may initiate, grow and break down to give cracks at stresses below those necessary to cause bulk shear yielding and so lead to brittle fracture requiring only a relatively low value of fracture energy,  $G_{Ic}$ , or stress-intensity factor,  $K_{Ic}$ . The various stress levels for polystyrene as a function of temperature are illustrated in Fig. 2.8.2.2 As may be seen, both the crazing stress and the yield stress rise with decreasing temperature but the latter parameter rises more rapidly and, except at high temperatures, is usually considerably greater than the crazing stress. Thus, except at high temperatures near the glass transition temperature ( $-90^{\circ}\text{C}$ ), crazing which results in a brittle fracture mode will be the dominant micromechanism. Apart from low temperatures, high strain-rates, aggressive liquid environments and, as discussed above, a plane-strain stress state, also favour a brittle crazing mechanism. At temperatures near the  $T_g$ , the stresses necessary for shear yielding and crazing are relatively low and approach one another and hence both extensive shear yielding and crazing leading to a ductile fracture mode may be observed, as was mentioned above.



**Fig. 2.8.2.2** Relationship between yield stress, crazing stress and microvoid nucleation stress in polystyrene

Unfortunately, the initiation, growth and breakdown of isolated crazes not only result in most of the glassy thermoplastic polymers behaving in a brittle manner but is often the dominant micro mechanism when many polymers which are generally thought of as being tough ductile materials are subjected to the test conditions listed above. Thus, a ductile/brittle transition may be induced which obviously has important consequences for the design- or materials engineer.

In the following sections general features of the microstructure and micromechanics of crazes will be considered first. Aspects of the fracture process involving craze initiation, growth and breakdown and the influence of polymer structure will then be discussed.



### 2.8.3 Cavitation

A toughening mechanism developed and proposed independently by [Kinloch et al,1983] and by [Pearson and Yee,1983] is now generally recognized as the most consistent in terms of the experimental data and observations generated in recent years. Based on the concept of both rubber particle cavitation and matrix shear yielding, it is of interest to discuss this mechanism in some detail.

Many investigations have demonstrated a positive correlation between toughness and the extent of plastic deformation found on fracture surfaces. Such a simple correlation has therefore suggested a mechanism based on yielding and plastic shear flow of the matrix as the primary source of energy absorption in rubber modified epoxies. Since greatly enhanced plastic deformation in the matrix has usually been found to accompany the incorporation of rubber particles, it is clearly necessary to focus attention initially on the particles and in particular the stress distribution which exists around them when located in the vicinity of a stressed crack tip.

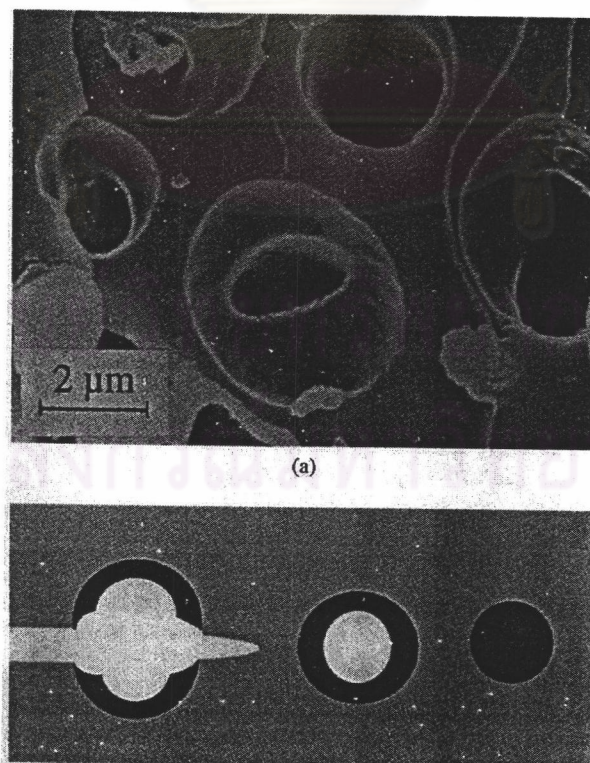
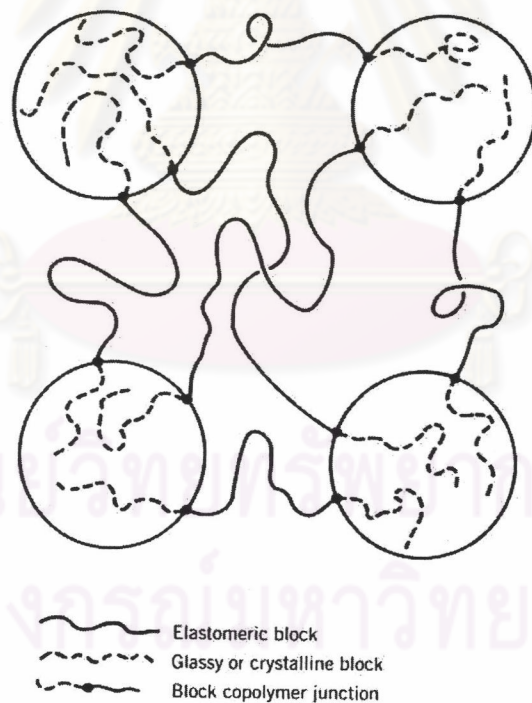


Figure 2.8.3.1 Cavitation Phenomena in Rubber



First considered this effect by studying the case of an isolated spherical particle embedded in an isotropic elastic matrix which is subjected to a uniform uniaxial tensile stress remote from the particle [Goodier, 1933]. He found that, for a rubbery particle possessing a considerably lower shear modulus than the matrix, a maximum stress concentration of 1.9 occurred in the equatorial regions of the particle. Allowing for further factors such as particle-particle interaction, which would inevitably occur in practical systems, together with a triaxial as opposed to a uniaxial stress state, which particles would inevitably be subjected to, a stress concentration factor of approximately 1.6 would exist

Now the interactions between a triaxial stress field at the tip of a loaded crack and the triaxiality associated with rubber particles experiencing the presence of the crack tip stress field could be envisaged as resulting in the initiation of two important processes.



**Figure 2.8.3.2** Polymer junction interphase

Initially, the development of a triaxial stress would gradually promote dilation of the matrix [Collyer,1994]. This, together with triaxial stresses inherent in the rubber particles owing to differential thermal contraction effects resulting from the initial cure process, would provide the conditions necessary for cavitation of the rubber particles. It is this cavitation process, rather than crazing of the epoxy matrix, which can be considered responsible for the stress whitening effects frequently observed with rubber modified epoxies.

In addition, the increasing presence of stress concentrations around the rubber particles during loading would promote both initiation and growth of shear yield deformation zones in the matrix. Owing to the large number of particles which would clearly exist, the degree of yielding generated would be substantially greater than would otherwise have occurred in an unmodified epoxy. However, since the particles would also act as sites for yield termination, yielding would remain localized in the vicinity of the crack tip.

It is reasonable to assume that both the cavitation and shear yielding processes would occur during the early stages of load application. In addition, once initiated, rubber particle cavitation would greatly enhance further shear yielding in the matrix. This would be partly attributable to an increased stress concentration which would inevitably accompany void formation. In addition, however, void formation would considerably reduce the level of constraint on the matrix adjacent to voided particles. This would essentially relieve the degree of triaxiality experienced by the matrix in the interparticle regions, and in turn lower yield stress and thus promote further extensive shear yielding. Crack tip blunting would, as a result, increase extensively resulting in the increased development of the plastic zone at the crack tip. Thus toughness would be considerably enhanced, as indeed has frequently been found in practice.