CHAPTER III

THEORIES

The basic theories about this work were mentioned such as Ziegler-Natta catalytic system, type of copolymer, and reinforcement of polymer.

3.1 Ziegler-Natta catalysts

Ziegler-Natta catalysts, the important classes of mixtures of chemical compounds, are remarkable for their ability to affect the polymerization of olefins to produce polymers of high molecular weights and highly ordered (stereoregular) structures. These catalysts were originated in the 1950s by, the German chemist, Karl Ziegler for the polymerization of ethylene at atmospheric pressure.

The Ziegler-Natta catalysts are complexes formed by reaction of a transition metal compound (halide, alkoxide alkyl or aryl derivative) of group IV-VIII transition metals with a metal compound (alkyl or alkyl halide) of group I-III base metal. The former component is usually called the catalyst and the latter called the cocatalyst. There are a very large number of patents involving every combination of pure or mixed metal alkyls with transition metal compounds. Each patent claims particular advantages. In practice, only a few group I-III metal alkyls are effective. Aluminum alkyls (such as $AlEt_3$, $Al\text{-}i\text{-}Bu_3$, $AlEt_2Cl$, $AlEtCl_2$ and $AlEt_2OR$) have been overwhelmingly preferred [22]. Also, transition metals compounds containing titanium (Ti), vanadium (V), and chromium (Cr) and, in special cases, molybdenum (Mo), cobalt (Co), rhodium (Rh) and nickel (Ni) are primarily used.
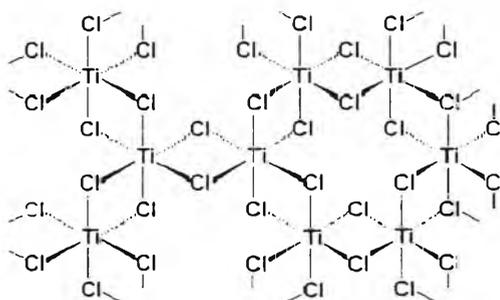

Figure 3.1 Crystal of $\alpha\text{-}TiCl_3$

$$TiCl_3 \quad and \quad Al(C_2H_5)_2Cl \longrightarrow$$

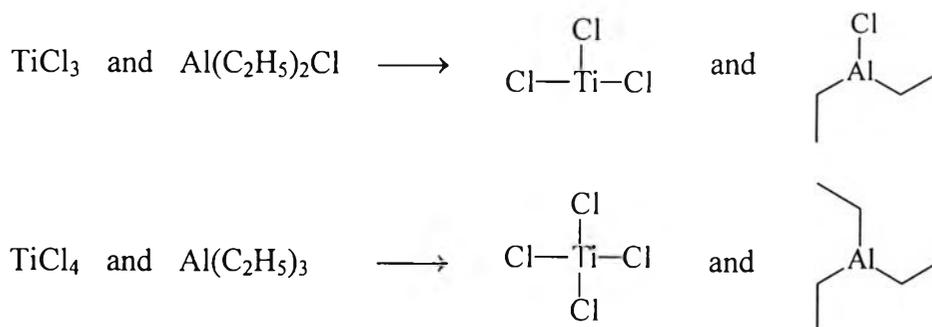$$TiCl_4 \quad and \quad Al(C_2H_5)_3 \longrightarrow$$

Figure 3.2 Ziegler-Natta catalyst/cocatalyst systems

For a short period after discovered Ziegler-Natta catalysts, it was found that election donors could greatly affect the kinetic of the catalyst and the stereo chemical behavior of the products. This component can either be incorporated into the catalyst during its synthesis (internal donor) or can be added to the polymerization reactor with the catalyst during the polymerization (external donor). Electron donor compounds, such as amines, ethers and esters, have the potential of complexing and reacting with the components of the catalyst or the active centers. They have been used in controlled amounts in many Ziegler-Natta catalytic systems as a third component to increase catalyst activity and/or stereo selectivity [23].

Heterogeneous Ziegler-Natta catalyst systems have been a great success in commercial production of linear polyethylene and isotactic polypropylene and higher α-olefin polymers. A representative of heterogeneous catalyst is the $MgCl_2$ supported titanium tetrachloride system. The catalyst system consists of heterogeneous catalyst component, $MgCl_2$/Lewis base/$TiCl_4$ ternary mixture, and cocatalyst component, metal alkyl. The interaction between the catalyst and cocatalyst leads to initiation of polymerization.

Both homogeneous and heterogeneous catalysts have been extensively investigated and proved useful in α-olefin polymerization. In the past, the heterogeneous systems offered better stereospecific addition for the preparation of isotactic structure.

Today, Ziegler-Natta catalysts are used worldwide to produce the following classes of polymers from alpha olefins:

- High density polyethylene (HDPE)

- Linear low density polyethylene (LLDPE)

- Ultra-high molecular weight polyethylene (UHMWPE)

- Polypropylene (PP) homopolymer, and copolymers

- Thermoplastic polyolefins (TPO's)

- Ethylene propylene diene monomer polymers (EPDM)

- Polybutene (PB)

3.2 Copolymers [24]

3.2.1 Common types of copolymers

Polymer made from only one kind of monomeric unit, or monomer, was normally considered. Many kinds of polymers can contain two kinds of monomers. 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 3.1. If two mers-A, and B are considered, some of the possible copolymers are also named in Table 3.1. The connectives in copolymer nomenclature will be defined as below.

Table 3.1 Some copolymer terminology

Type	Connective	Example
Short Sequences		
Unspecified	*-co-*	poly(A-*co*-B)
Random	*-ran-*	poly(A-*ran*-B)
Alternating	*-alt-*	poly(A-*alt*-B)
Long Sequences		
Block	*-block-*	poly A-*block*-poly B or poly(A-*b*-B)
Graft	*-graft-*	poly A-*graft*-poly B or poly(A-*g*-B)

3.2.1.1 Unspecified copolymers

An unspecified sequence arrangement of different monomeric units in a polymer is represented by poly(A-*co*-B)

3.2.1.2 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 $\cdots$ABC$\cdots$ of monomeric units A, B, C... so P($\cdots$ABC$\cdots$) is

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

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

3.2.1.3 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

3.2.1.4 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 in Figure 3.3.

3.2.1.5 Graft copolymers

A graft copolymer comprises a backbone species, poly A, and a side-Chain species. poly B. The side chains comprise units of monomer that differ from those comprising the backbone chain. If the two monomers are the same, the polymer is said to be branched.
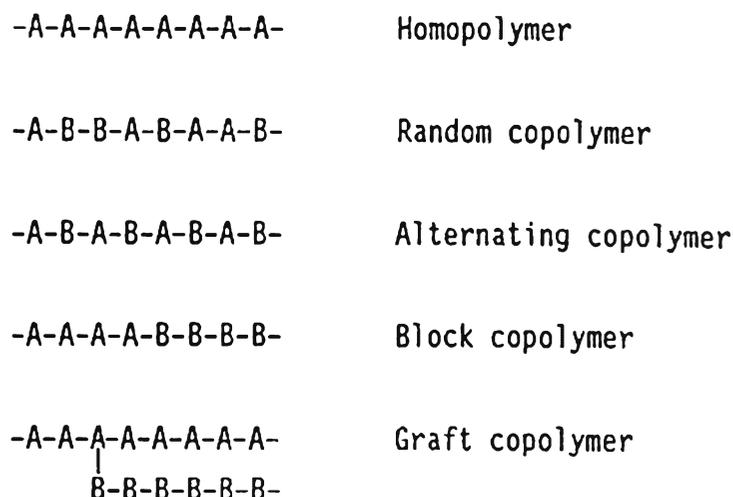
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-A-A-A-A-A-A-A-A-          Homopolymer


-A-B-B-A-B-A-A-B-          Random copolymer


-A-B-A-B-A-B-A-B-          Alternating copolymer


-A-A-A-A-B-B-B-B-          Block copolymer


-A-A-A-A-A-A-A-A-          Graft copolymer
      |
     B-B-B-B-B-B-
```

Figure 3.3 General type of polymer

3.2.2 Block copolymer

Block copolymers are useful in many applications where a number of different polymers are connected together to yield a material with hybrid properties. The block copolymer, a kind of polymer alloy, behaves as a rubber at ambient conditions, but can be moulded at high temperatures due to the presence of the glassy domains that act as physical cross links.

A block copolymer molecule contains two or more polymer chains attached at their ends. Linear block copolymers comprise two or more polymer chains in sequence, whereas a star block copolymer comprises more than two linear block copolymers attached at a common branch point. Polymers containing at least three homopolymers attached at a common branching point have been termed mixed arm block copolymers, although they can also be viewed as multigraft copolymers. Primarily di- and tri- block copolymers can be shown in Figure 3.5.
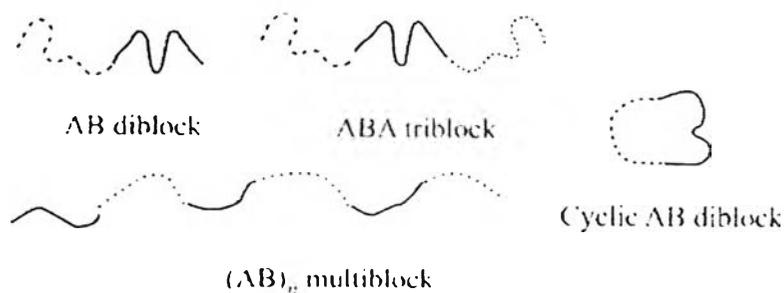

AB diblock   ABA triblock

Cyclic AB diblock

(AB)ₙ multiblock

Figure 3.4 Type of block co polymer

3.3 Polypropylene (PP) [25]

Professor Giulio Natta produced the first polypropylene resin in Spain in 1954. Natta utilized catalysts developed for the polyethylene industry and applied the technology to propylene gas. The first commercial production began in 1957. The polymerization of propylene, recovered from crack gas streams in olefin plants and oil refineries, is carried out with catalyst. Polypropylene is a thermoplastic polymer, used in a wide variety of applications, including food packaging, textiles, laboratory equipment, and polymer banknotes.
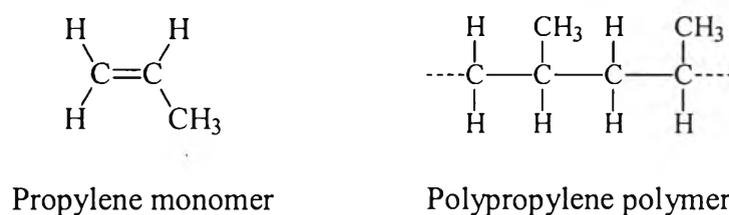

Propylene monomer   Polypropylene polymer

Figure 3.5 Propylene monomer and Polypropylene polymer

An important concept in understanding the link between the structure of polypropylene and its properties is tacticity. The relative orientation of each methyl group (CH_3 in the figure 3.7) relative to the methyl groups on neighboring monomers has a strong effect on the finished polymer's ability to form crystals, because each methyl group takes up space and constrains backbone bending. Polypropylene can be made in three typical stereo-configurations (tacticity): isotactic, syndiotactic and atactic. Isotactic PP, in which all methyl groups are on the same side of chain, results from polymerization of only one isomeric configuration from propylene monomer. Syndiotactic PP is defined by methyl groups arranged alternatively on either side of chain. Atactic PP is formed with a sterically random sequence of methyl groups. The crystallizability of isotactic propylene makes it the sole from with properties of commercial interest.
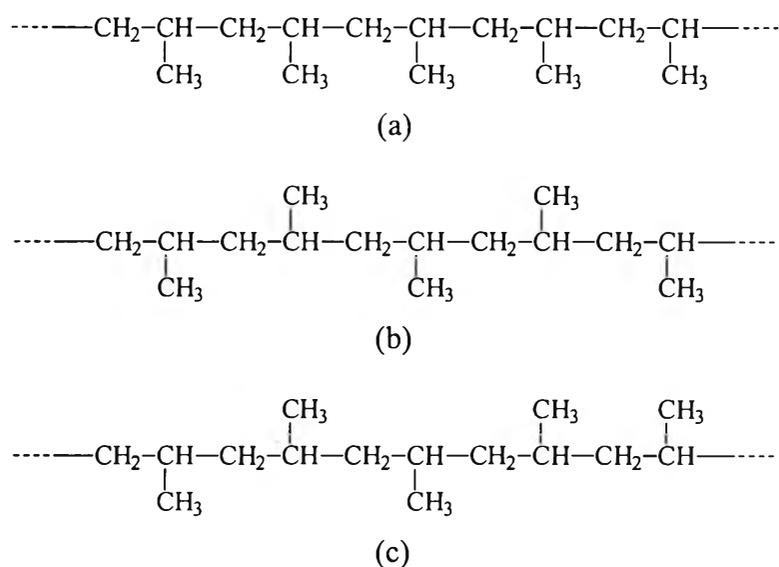
$$\cdots\cdots\text{—CH}_2\text{-CH—CH}_2\text{-CH—CH}_2\text{-CH—CH}_2\text{-CH—CH}_2\text{-CH—}\cdots\cdots$$
$$\qquad\quad\underset{\text{CH}_3}{|}\qquad\underset{\text{CH}_3}{|}\qquad\underset{\text{CH}_3}{|}\qquad\underset{\text{CH}_3}{|}\qquad\underset{\text{CH}_3}{|}$$

(a)

$$\qquad\qquad\quad\overset{\text{CH}_3}{|}\qquad\qquad\qquad\overset{\text{CH}_3}{|}$$
$$\cdots\cdots\text{—CH}_2\text{-CH—CH}_2\text{-CH—CH}_2\text{-CH—CH}_2\text{-CH—CH}_2\text{-CH—}\cdots\cdots$$
$$\qquad\quad\underset{\text{CH}_3}{|}\qquad\qquad\underset{\text{CH}_3}{|}\qquad\qquad\underset{\text{CH}_3}{|}$$

(b)

$$\qquad\qquad\overset{\text{CH}_3}{|}\qquad\qquad\qquad\overset{\text{CH}_3}{|}\quad\overset{\text{CH}_3}{|}$$
$$\cdots\cdots\text{—CH}_2\text{-CH—CH}_2\text{-CH—CH}_2\text{-CH—CH}_2\text{-CH—CH}_2\text{-CH—}\cdots\cdots$$
$$\qquad\underset{\text{CH}_3}{|}\qquad\qquad\underset{\text{CH}_3}{|}$$

(c)

Figure 3.6 Tacticities of polypropylene (a) isotactic propylene, (b) syndiotactic

polypropylene, and (c) atactic polypropylene

Some typical properties and mechanical properties of 1100RC Polypropylene resin are reported below:

Melt flow index	20	g/10min
Flexural modulus	1500	MPa
Glass transition temperature (T_g)	-10	°C
Melting temperature (T_m)	170	°C
Crystallization temperature (T_c)	100	°C
Molecular weight (Mw)	246,900	
Molecuiar weight distribution (MWD)	2.6	

3.4 Ethylene-Propylene rubbers (EPR) [26]

Ethylene-propylene rubber, poly(ethylene-co-propylene) or EPR, is a random copolymer of ethylene and propylene. This is rubbery noncrystalline materials that have rubbery behavior. Commercial ethylene-propylene rubbers (EP or EPR) generally contain about 35% propylene although rubbery properties are shown by copolymers with a different content of propylene. At present time, exclusively Ziegler-type processes prepare this material.
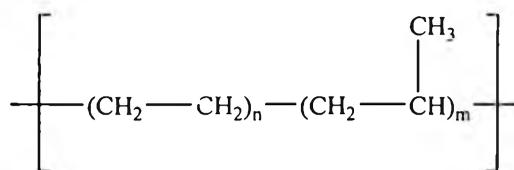
$$\left[-\!\!\!-(CH_2\!-\!\!-CH_2)_n\!-\!\!(CH_2\!-\!\!\!\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{CH})_m\!-\!\!\!-\right]$$

Figure 3.7 Repeating unit of ethylene propylene random copolymer

Ethylene-propylene rubbers are valuable for their excellent resistance to heat, oxidation, ozone and weather aging due to their stable, saturated polymer backbone structure. Commonly, EPR used for toughening of other polymers.

3.5 Thermoplastic elastomers [26]

Thermoplastic elastomers are materials that combine the properties of thermoplastic and rubber-like behavior. Properties of thermoplastic elastomers can be controlled by varying the ratio of the monomers and the lengths of the hard and soft segments. Block techniques create long-chain molecules that have various sequences, or blocks, of hard and soft segments.

Five types of commercially important thermoplastic elastomers have been developed, including the following:

1. Styrenic thermoplastic elastomers
2. Polyester thermoplastic elastomers
3. Polyurethane thermoplastic elastomers
4. Polyamide thermoplastic elastomers
5. Polyolefin thermoplastic elastomers

Polyolefin thermoplastic elastomers or Polypropylene/EP copolymer blends are general blends of propylene with up to 65% ethylene-propylene rubber. In these blends the rubber is present as finely dispersed particles in a polypropylene matrix. Blends of PP with EPR provide the means of modifying the crystallinity or rigid component, thus adjusting the properties, as well as the economy. The PP/EPR blend show excellent process ability. Polyolefin thermoplastic elastomers have good mechanical properties and excellent resistance to oxygen, ozone and polar solvents. The major use of polyolefin thermoplastic elastomers is in automotive field.

3.6 Polymer blend [27]

Polymer blends are the mixtures of at least two or more polymers. The mixing of two or more existing polymers may obtain the new properties of the blend. By using these techniques the designed properties can be explored without synthesizing the new polymer which has the designed properties. The results of blending polymers have many advantages, for example, lower cost than synthesizing the desired properties of new polymer. The new properties can be under control.

3.6.1 Melt mixing

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

The advantages of this method are the most similar to the industrial practice. The commercial compounding or adding additives into base polymers are applied by melt mixing. So the investigations of polymer blends by melt mixing method are the most practical methods in industrial applications.

3.6.2 Solvent casting

This method group is performed by dissolving polymers in the same solvent. The solution is then cast on a glass plate into thin films and the removal of solvent from the films is performed by evaporating the solvent out at ambient or elevated temperature.

3.6.3 Freeze drying

In the freeze drying processes, the solution of the two polymers is quenched down immediately to a very low temperature and the solution is frozen. Solvent is then removed from the frozen solution by sublimation at a very low temperature. Dilute solutions must be used and the solution volume must have as large surface area as possible for good heat transfer.

3.6.4 Emulsions

The advantages of the emulsion polymer mixing methods are the easy handing and all the other advantages as the solvent casting. The mixing or casting of the film requires neither expensive equipment nor high temperature. However, emulsions of polymers are an advance technique and not always applicable to all monomers.

3.6.5 Reactive blend

Co-crosslinking and interpenetrating polymer networks (IPN) formations are the special methods for forming blends. The idea of these methods is to enforce degree of miscibility by reactions between the polymer chains. Other methods involve the polymerization of a monomer in the presence of a polymer and the introduction of interface graft copolymer onto the polymer chains.

3.7 Reinforced polymer

3.7.1 Reinforcement [28]

Thermoplastic composites with various fillers and reinforcements are well established for a variety of applications. The incorporation of these materials into thermoplastic matrices results in improved mechanical and thermal properties.

The roles of the matrix, reinforcement, and interface in composites are well defined. The matrix is responsible for transferring the load from the matrix to the reinforcement, for distributing the stress among the reinforcement elements, for protecting the reinforcement from environmental attack, and for positioning the reinforcing material. Meanwhile, the task of the reinforcement is to carry the load, due

to its higher stiffness and strength compared with that of the matrix. The interface, (for two dimensions) or the interphase (for three dimensions) is a negligible or finite thin layer with its own properties, and its role is stress transfer from the matrix to the reinforcement [29]. The blended polymer, usually present as a fine dispersion in the matrix, is aimed at improving the toughness of the composites, or more exactly, to achieving the desired balance between stiffness and toughness.

The mechanical performance of reinforced thermoplastic blends is affected by the following factors

1. blend composition and morphology
2. type and amount of the reinforcement
3. interface or interphase between matrix and reinforcement
4. processing methods and conditions, and
5. testing conditions.

3.7.2 Toughened polymer [25]

The process of increasing resistance to failure under mechanical stress is called toughening. Toughness is the energy absorbed by the material during deformation before failure. Depending on the type of application and the test involved there are two ways of defining toughness.

3.7.2.1 Toughened PP

The technology of rubber toughening, which involves blending small amounts of rubber with rigid polymers in order to increase their fracture resistance, has been used commercially since the late 1940s and has played a major part in the growth of the polymer industry. Manufacturers of both thermoplastics and thermosets now offer rubber-toughened grades of almost every type of rigid polymer, including glassy thermoplastics, semicrystalline thermoplastics, and thermosetting resins.

It is of particular interested for many applications to produce PP with a better toughness at lower temperatures. To improve the toughness, various modifier particles with different physical properties can be added to the PP matrix.

The matrix material plays an important role in filled polymer systems. If the polymer matrix has high ductility, it can increase the toughness of the composite. Usually PP itself has poor impact properties, especially at low temperatures. The impact properties of PP can be improved through the use of block copolymers of polypropylene, addition of elastomers, or with copolymerization with ethylene. The most commonly used and most effective impact modifiers for PP are ethylene/propylene copolymers (EPM) or ethylene/propylene/diene terpolymer (EPDM). Blends with 10-40% elastomers, which dispersed in the polymer matrix, are called "impact polypropylenes".

The toughness of filled polymers can be improved in several ways:

1. Increase the matrix toughness

2. Optimize the interface (or interphase) between the filler and the matrix through the use of coupling agents, compatibilizer, and sizes

3. Optimize the filler-related properties such as filler content, particle size, and dispersion

4. Aspect ratio and orientation distributions also play a role in toughness of composites containing more fibrous materials.

3.7.2.2   *Mechanism of toughened PP*

The function of the modifier particles is to act as concentrators and to initiate plastic deformation processes (shear yielding) of the matrix strands between the particles. An important precondition is void formation or cavitation within the particles or at the interface. Up to now, there is some controversy regarding the detailed role of the size of modifier particles, the interparticle distance, and others.

Summarize in a three-stage mechanism of toughened PP, described in more detail in:

1. *Stress concentration.* Under external stress, stress concentrations or stresses additionally increased by superposition of local stress fields are built up between the modifier particles. In places of a maximum shear stress component, weak shear bands form between the particles.

2. *Void formation.* Owing to stress concentrations higher hydrostatic stresses are built up inside the particles, causing particles to crack and form microvoids to from inside, yielding a higher local stress concentration between the particles.

3. *Induced shear deformation.* The high local stress concentration initiates shear process in the matrix bridges between the particles/voids. Shear deformation proceeds at numerous adjacent matrix bridges simultaneously, thus taking place in fairly large polymeric volumes. This is the deformation step during which energy is mainly absorbed (main contribution toughness).

Numerous commercial PP/EPR blends are on the market. Reinforced and filled grades are also available. They have been used in automotive industry, in appliances, hardware and plumping, medical tubing etc.
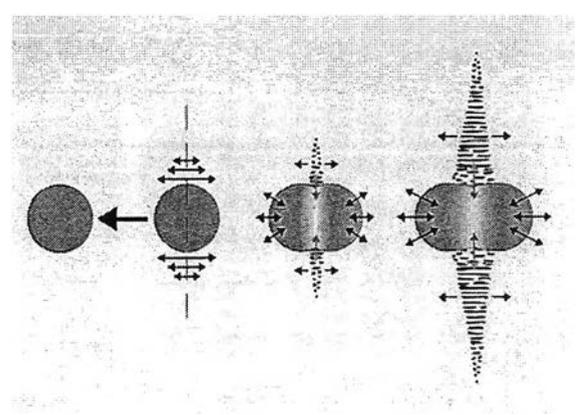
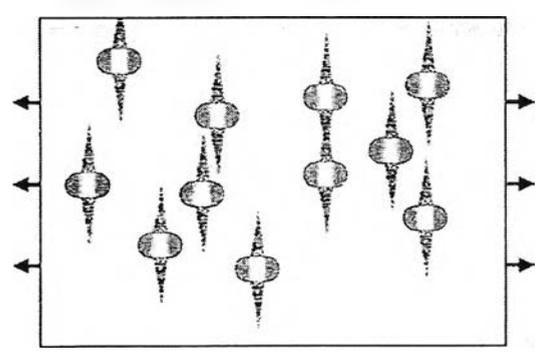**Figure 3.8** Development of crazing with progressive deformation of rubber particles

Figure 3.9 Craze mechanisms in the polymer matrix

3.8 Mechanical properties [30]

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.

3.8.1 Stress-Strain curve

The basic understanding of stress-strain behavior of polymer is of utmost importance to design engineers. One such typical stress-strain diagram is illustrated in Figure 3.10.
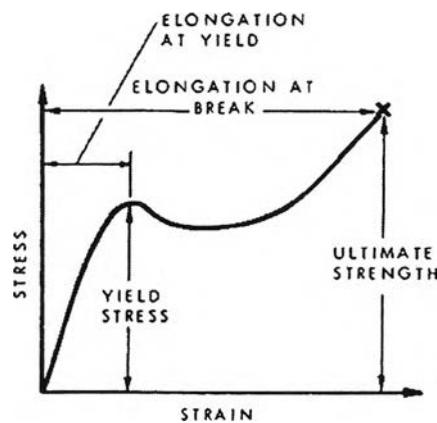

Figure 3.10 Generalized tensile stress-strain curve for polymeric materials

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.

3.8.1.1 Stress

The force applied to produce deformation in a unit area of a test specimen called stress. Stress is a ratio of applied load to the original cross-sectional area.

$$\text{Stress} = \frac{\text{load}}{\text{area of original cross section}} \qquad (3\text{-}1)$$

3.8.1.2 Elongation

The increase in the length of a test specimen produced by a tensile load (Δl) is called Elongation.

3.8.1.3 Strain

The ratio of the elongation to the gauge length of the test specimen change in length per unit of the original length ($\Delta l/l_0$) is called strain.

$$\text{Strain} = \frac{\text{instantaneous gage length}}{\text{original gage length}} = \frac{\text{elongation}}{\text{original gage length}} \quad (3\text{-}2)$$

3.8.1.4 Yield point

The first point on the stress-strain curve at which an increase in strain occurs without the increase in stress is called Yield point.

3.8.1.5 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.

$$\text{Tensile strength at yield} = \frac{\text{Maximum load recorded}}{\text{Cross section area}} \quad (3\text{-}3)$$

3.8.1.6 Modulus of elasticity

The ratio of stress to corresponding strain below the proportional limit of the material is called Modulus of elasticity. This is also known as Young's modulus.

$$\text{Tensile modulus} = \frac{\text{Difference in stress}}{\text{Difference in corressponding strian}} \quad (3\text{-}4)$$

$$= \text{Slope of stress-strain curve in elastic range}$$

3.8.1.7 Ultimate strength

The maximum unit stress a material will withstand when subjected to an applied load in compression, tension, or shear is called ultimate strength. In other words, it can be called as break point, the point which at a material breaks or ruptures.

3.8.1.8 Toughness

The extent to which a material absorbs energy with out fracture is called toughness. The area under a stress-strain diagram is also a measure of toughness of material.
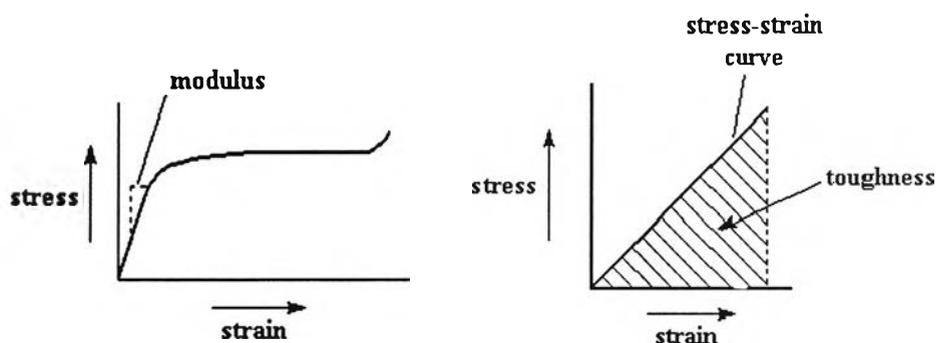

Figure 3.11 Modulus of elasticity and Toughness of materials

3.8.2 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 3.12 illustrates typical tensile stress-strain curve for several type of polymer. The area under curve is considered as the toughness. Table 3.2 lists characteristic features of stress-strain curve as they relate to the polymer properties.
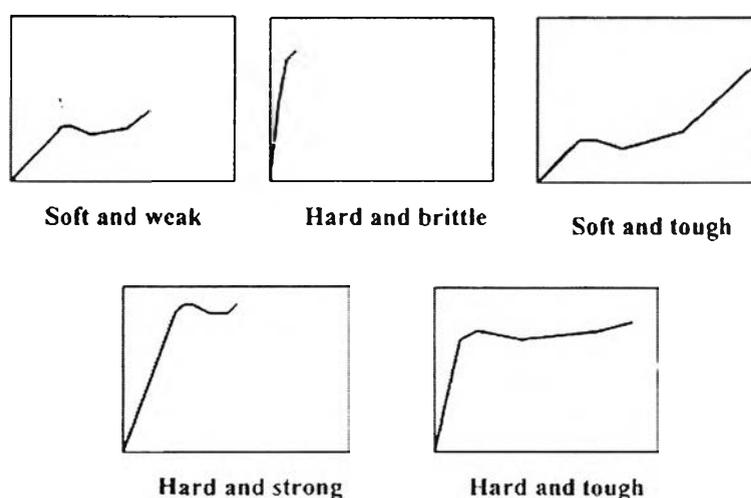

Soft and weak   Hard and brittle   Soft and tough

Hard and strong   Hard and tough

Figure 3.12 Type of stress-strain curve

Table 3.2 Characteristic features of stress-strain curve on 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

3.9 Dynamic mechanical properties [31,32]

3.9.1 Introduction to dynamic mechanical analysis

Dynamic mechanical analysis (DMA) is becoming more and more commonly seen in the analytical laboratory as a tool rather than a research curiosity. This technique is still treated with reluctance and unease, probably due its importation from the field of rheology. DMA is a technique that does not require a lot of specialized training to use for material characterization. It supplies information about major transition as well as secondary and tertiary transitions not readily identifiable by other methods. It also allows characterization of bulk properties directly affecting material performance. DMA can be simply described as applying an oscillating force to a sample and analyzing the material's response to that force (Figure 3.13).
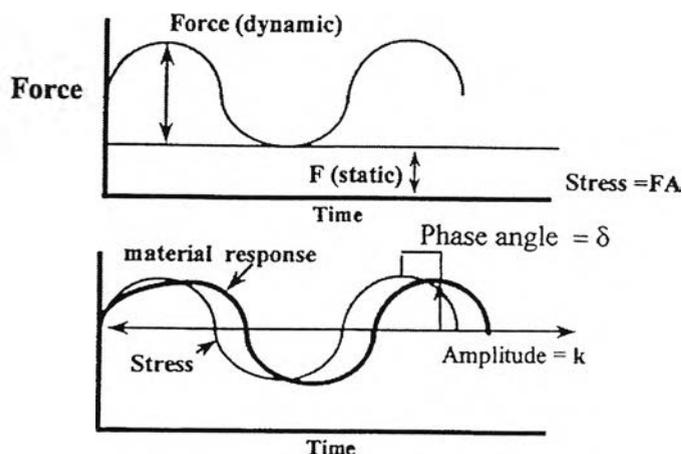
Figure 3.13 Oscillating a sample

The applied force is called stress (σ). When subjected to a stress, a material will exhibit a deformation or strain (ε). From mechanical tensile testing at a fixed temperature, slope of the curve gives the relationship of the stress to strain and is a measure of the material's stiffness, the modulus. The modulus measured in DMA is, however, not exactly the same as the Young's modulus of the classic stress-strain curve. Young's modulus is the slope of a stress-strain curve in the initial linear region. In DMA, a complex modulus (E^*), an elastic modulus (E'), and an imaginary (loss) modulus (E'') are calculated from the material response to the sine wave. These different moduli allow better characterization of the material, because we can now examine the ability of the material to return or store energy (E'), to its ability to lose energy (E''), and the ratio of these effects (tan δ), which is called damping.

3.9.2 Applying a dynamic stress to a sample

The situation is most easily analyzed when an oscillating sinusoidal is applied to specimen at particular frequency. If applied stress varies as a function of time according to

$$\sigma = \sigma_0 \sin \omega t \qquad (3\text{-}5)$$

where σ is the stress at time t, σ_0 is the maximum stress, ω is the frequency of oscillation (angular frequency), and t is the time. The strain obeying Hook's law would vary in a similar manner as

$$\varepsilon = \varepsilon_0 \sin \omega t \qquad (3\text{-}6)$$

However, for viscoelastic material the strain lags somewhat behind the stress. This can be considered as a damping process and the result is that when a stress defined by Equation 3-1 is applied to the sample the strain varies in a similar sinusoidal manner, but out of phase with the applied stress. Thus, the variation of stress and strain with time can be given by expressions of the type

$$\varepsilon = \varepsilon_0 \sin \omega t \qquad (3\text{-}7)$$

$$\sigma = \sigma_0 \sin(\omega t + \delta) \qquad (3\text{-}8)$$

where δ is the phase angle or phase lag. The equation for stress can be expanded to give

$$\sigma = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta \qquad (3\text{-}9)$$

The stress can therefore be considered as being resolved into two components; one of $\sigma_0\cos\delta$ which is in phase with the strain and another $\sigma_0\sin\delta$ which $\pi/2$ out of phase with strain. Hence it is possible to define two dynamic moduli; E' which is in phase with the strain and E" which $\pi/2$ out of phase with strain. Since E' = $(\sigma_0/\varepsilon_0)\cos\delta$ and E" = $\sigma_0/\varepsilon_0)\sin\delta$, Equation 3-9 becomes

$$\sigma = \varepsilon_0 E' \sin \omega t + \varepsilon_0 E'' \cos \omega t \qquad (3\text{-}10)$$

The phase angle δ is then given by

$$\tan \delta = E''/E' \qquad (3\text{-}11)$$

A complex notation is often favoured for the representation of the dynamic mechanical properties of viscoelastic material. The stress and strain are given as

$$\varepsilon = \varepsilon_0 \exp i\omega t \quad \text{and} \quad \sigma = \sigma_0 \exp i(\omega t + \delta) \qquad (3\text{-}12)$$

The overall complex modulus E* = σ/ε is then given by

$$E^* = \frac{\sigma_0}{\varepsilon_0} \exp i\delta = \frac{\sigma_0}{\varepsilon_0} (\cos \delta + i \sin \delta) \qquad (3\text{-}13)$$

From the definitions of E' and E" it follows that

$$E^* = E' + iE'' \qquad (3\text{-}14)$$

3.9.3 Time-Temperature Scans

One of most common uses of the DMA for a thermal analysis is the measurement of the various transitions in a polymer. DMA temperature scanning techniques investigate the relaxation processes of a polymer. In this topic, we will look at how time and temperature can be used in the study the properties of polymers. Starting with a polymer at very low temperature and oscillate it at a set frequency while increasing the temperature, performing a temperature scan (Figure 3.14).
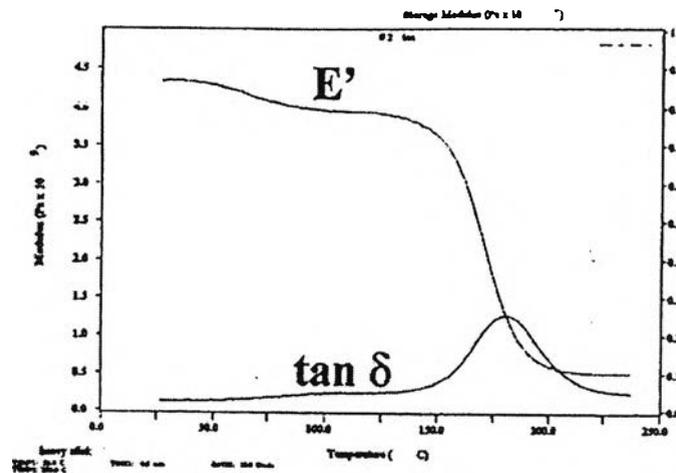
Figure 3.14 Time-temperature studies in vary temperature of DMA

3.9.3.1 Transition in polymer

The thermal transitions of polymers can be described in terms of either free volume change or relaxation times. Changes in free volume, v^f, can be monitored as a volumetric change in the polymer; by the absorption or release of heat associated with that change; the loss of stiffness; increase flow; or by a change in relaxation time.

The free volume of a polymer, v^f, is known to be related to viscoelasticity, aging, penetration by solvents, and impact properties. The free volume defined as the space for molecule to have the internal movement, it is schematically shown in Figure 3.15a. A simple approach to looking at free volume is the crankshaft mechanism, where the molecule is imagined as a series of jointed segments. From this model, we can simply describe the various transitions seen in the polymer. The crankshaft model treats the molecule as a collection of mobile segments that have some degree of the free movement. This is a very simplistic approach, yet very useful for explaining behavior. As the free volume of the chain segment increases, its ability to move in various directions also increases (Figure 3.15b). This increased mobility in either side chains or small groups of adjacent backbone atoms result in a greater compliance (low modulus) of the molecule.
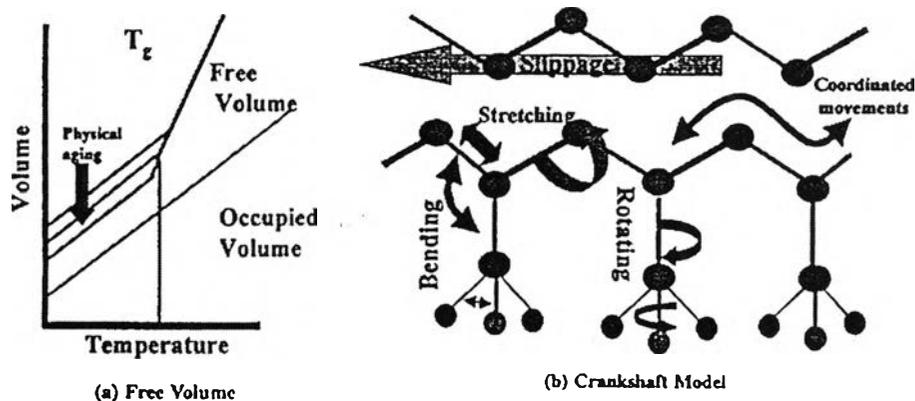
(a) Free Volume

(b) Crankshaft Model

Figure 3.15 Free volumes in polymer (a) The relationship of free volume to transition

(b) A schematic example of free volume and crankshaft model
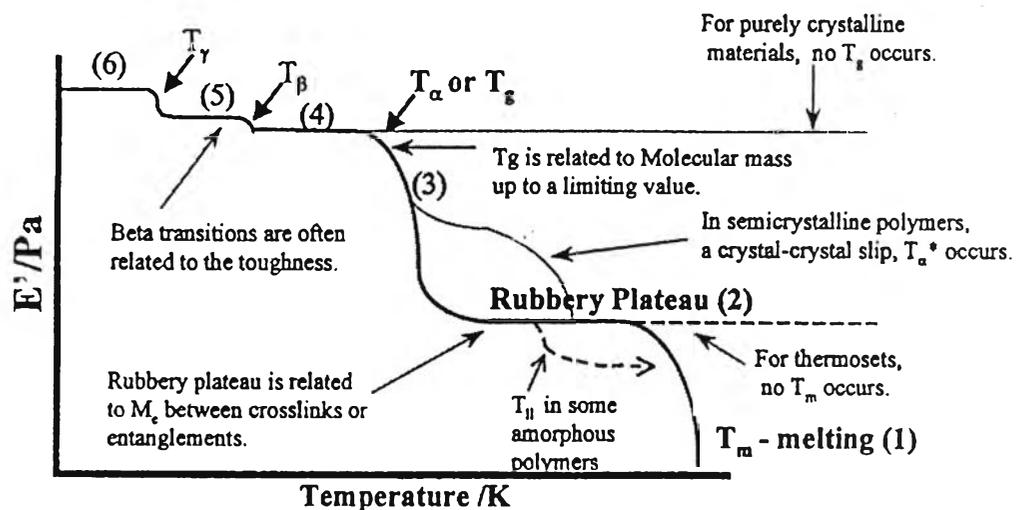
3.9.3.1.1 Sub-T_g Transitions

When temperatures move from very low condition, where the molecule is tightly compressed, pass first through the solid state transitions. This process is shown in Figure 3.16 (6). As the material warms and expands, the free volume increases so that localized bond movements (bending and stretching) and side chain movements can occur. This is the gamma transition, T_γ, which may also involve associations with water. As the temperature and the free volume continue to increase, the whole side chains and localized groups of four to eight backbone atoms begin to have enough space to move and the material starts to develop some toughness. This transition, called the beta transition, T_β, is not as clearly defined as we are describing here (Figure 3.16 (5)). Often it is the T_g of a secondary component in a blend or of a specific block in a block copolymer. However, a correlation with toughness is seen empirically. The area of sub-T_g or higher order transitions has been heavily studied, as these transitions have been associated with mechanical properties.

3.9.3.1.2 The glass transition (T_g or T_α)

As heating continues, the free volume continues to increase with increasing temperature, we reach the T_g or glass transition temperature. The large segments of the chain start moving. This transition is also called the alpha transition, T_α (Figure 3.16 (4)). One classical description of this region is that the amorphous

regions have begun to melt. Since the T_g only occurs in amorphous material, in a 100% crystalline material we would see not a T_g. The T_g represents a major transition for many polymer, as physical properties changes drastically as the material goes from a hard glassy to a rubbery state. It defines one end of the temperature range over which the polymer can be used, often called the operating range of the polymer, and examples of this range are shown in Figure 3.17.

(6)	(5)	(4)	(3)	(2)	(1)
local motions	bend and stretch	side groups	gradual main chain	large scale chain	chain slippage

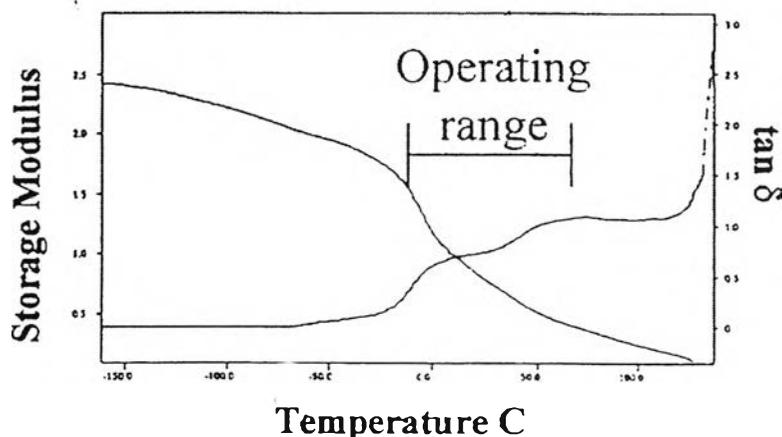Figure 3.16 Idealized temperature scan of a polymer

Figure 3.17 Operating range by DMA of Polypropylene

3.9.3.1.3 The rubbery plateau, T_α^* and T_{ll}

Continued heating bring us to the T_α^* and T_{ll} (Figure 3.16 (3)). For alpha star transition, T_α^*, the former occurs in crystalline or semicrystalline polymer and is a slippage of the crystallites past each other. In amorphous polymers, we stead see the T_{ll}, a liquid-liquid transition associated with increased chain mobility and segment-segment association. The latter is a movement of coordinated segments in the amorphous phase that relates to reduced viscosity. These two transitions are not accepted by everyone, and their existence is still a matter of some disagreement.

3.9.3.1.4 The terminal region

Finally, we reach the melt (Figure 3.16 (2)) where large-scale chain slippage occurs and the free volume has increased so that the chains slide can move past each other and the material flows. This is the melting temperature, T_m. For a cured thermoset, nothing happens after the T_g until the sample begins to burn and degrade because the cross-links prevent the chains from slipping past each other.

3.9.3.2 Time-based studies

The other part of time-temperature effects is studying how a material responds when held at constant temperature for set periods of time. This is most commonly seen in curing and post-curing studies. However, there are several applications where a sample will be held at a set temperature under oscillatory stress for long periods of time. However, this is not a common use of the DMA, and it is more common to hold material under constant dynamic stress at a set temperature under some sort of special conditions. This condition can simply be elevated temperature where degradation occurs or it can be a special environment, like UV light, solvents, humidity, or corrosive gases. These conditions are normally chosen to accelerate the degradation or changes seen in the final use of the material.