

# CHAPTER 3

## Theories

### 3.1 Polymer Blends

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 have 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.

#### *3.1.1 The Blends Preparations*

There are many ways to mix each polymer together, such as by using heat (melt-mixing), by using solvent (solution casting, freeze drying) or by in situ reaction, etc.

##### 3.1.1.1 Melt Mixing

Melt mixing of thermoplastics polymer is performed by mixing the polymers in the molten state under shear in various mixing equipment. 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. solvents) 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.

#### 3.1.1.2 Solvent Casting

This method group is performed by dissolving polymers in some 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. Solvent casting is the simplest mixing method available and is widely practiced in academic studies, usually when the experiments need a very small quantities of polymers.

The most severe problem with solvent casting is the influence of the solvent on the resulted product especially the shift of phase diagram. 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 types of solvents and the casting conditions. The best way to cast the thin films, whose thickness is normally not exceeding 0.1 mm, [Thongyai, 1990] is to gradually increase the temperature during the removal of solvent.

To remove traces of solvents from the casting polymer films, the condition of high temperature is invariably needed, and protection of the polymer in case of degradation is essential. The inert gas or lower down the pressure (vacuums) is

typically used. In the vacuum 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.

### 3.1.1.3 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.

An advantage of this method is that the resulted blend will be independent of the solvent, if the single phase solution is freezed rapidly enough. However, there are many limitations of this method. Freeze drying method 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. While not complex, freeze drying does require a good vacuum system for low-boiling solvents and it is not a fast blending method. After solvent removal, the blend is in the powdery form, which usually needs further shaping. The advantage of this method is the simplicity. However, this method needs a good fume trap, vacuum line for the sublimation solvent and it takes times to complete the sublimation process.

#### 3.1.1.4 Emulsions

The advantages of the emulsion polymer mixing are the easy handling 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 advantage technique and not always applicable to all monomers.

#### 3.4.1.5 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 polymers chains. Other methods involve the polymerization of a monomer in the presence of a polymer and the introduction of interface graft co-polymer onto the polymer chains.

### **3.2 Rheology**

The developments of the chemical industry at the beginning of this century, followed by the advents of large-scale synthetic polymer productions resulted in a host of new materials with “strange” flow behavior. In 1920, the studies of such materials prompted a new chemistry professor at Lehigh University, Eugene Bingham, to coin a new word, *rheology*. Thus rheology means the study of flow and deformation. In principle then, rheology includes everything dealing with flow behavior : aeronautics, hydraulics,

fluid dynamics and even solid mechanics. However, in practice rheology has usually been restricted to the study of the fundamental relations, called *constitutive relations*, between force and deformation in materials. The rheologist focuses on material behaviors, using every simple deformation and also explains to more complex behaviors.

### 3.2.1 Important terms about rheology

Shear stress ( $\tau, \sigma$ ), is a force per unit area (showed in Figure 3-1) in unit of Pascal, Pa (S.I unit) or dyne/cm<sup>2</sup> (English unit), ( $F/X_0^2$ ).

Shear strain ( $\gamma, \epsilon$ ) is the relative deformation in shear in dimensionless form ( $dX/X_0$ ).

Shear rate ( $\dot{\gamma}$ ) is the change of shear strain per unit time, in the unit of sec<sup>-1</sup> ( $V/X_0$ ).

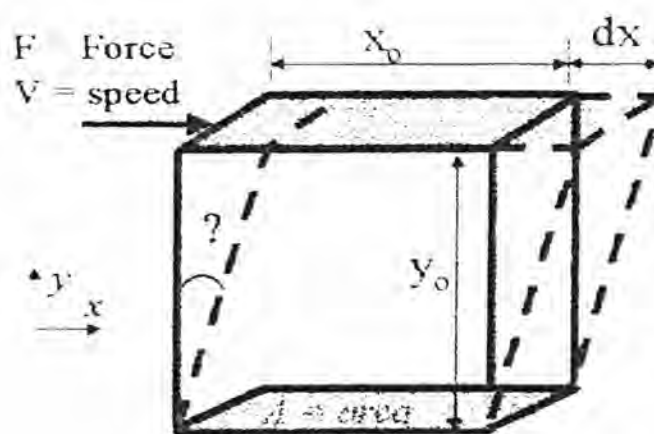


Figure 3-1 Schematic definition of stress-strain [Ferry, 1980]

### 3.2.2 Range of rheological material behaviors

Rheological behaviors of materials were classified between two classical categories, elastic solid (elasticity) and viscous liquid (viscosity).

#### 3.2.2.1 Elasticity

This classical theory is explained by Robert Hooke. Hooke's law described the mechanical behavior of an ideal solid, relating the stress ( $\sigma$ ) as always directly proportional to strain in small deformation ( $\epsilon$ ), the proportionality factor called the "Elastic Modulus"; thus

$$\sigma = E\epsilon \quad (3-1)$$

or

$$\tau = G\gamma \quad (3-2)$$

The modulus, E or G, is a measurement of material's stiffness (i.e., its ability to resist deformation). The linear region in which the modulus does not change when the strain is changed, is called the linear elasticity or hookian region of the material.

Figure 3-2 showed the schematic experiments explained by Hooke's law. The ideal elastic solids acted like a spring. When the materials subject to the different size of forces, the deformations of materials were different according to the force and when stop those force, these materials could be restored to the same memories (same elongation).

Almost all of elastic materials at present can hardly act like the 100% elastic materials. Their behaviors were called Non- Hookian. The relationships of stress ( $\sigma$ ) and strain ( $\epsilon$ ) of Hookian and Non-Hookian materials are shown in Figure 3-3

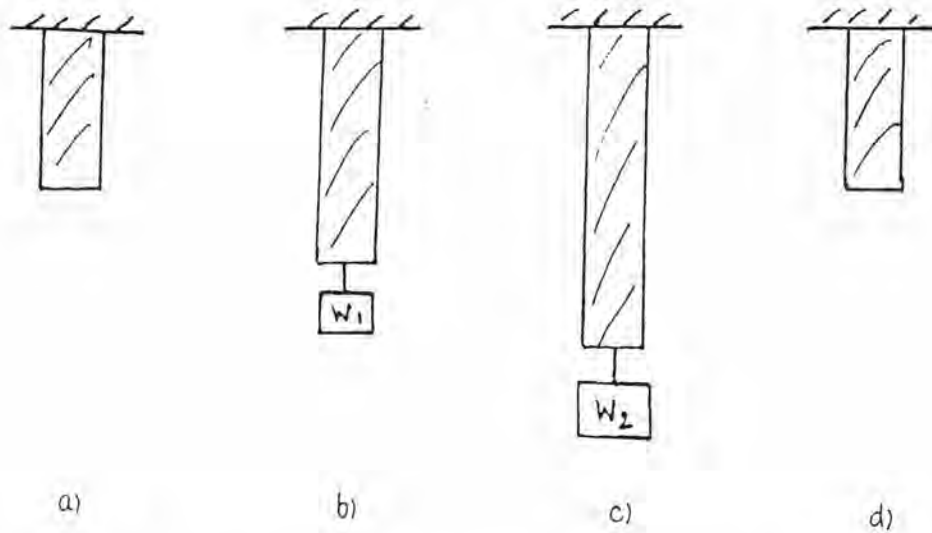


Figure 3-2 Elastic properties of ideal solid from Hooke's law. [S. Damrongsakkul, 1998]  
 (a) in normal condition (b),(c) when applied stress  $\sigma_i = W_i/A$  and (d) when remove the stress

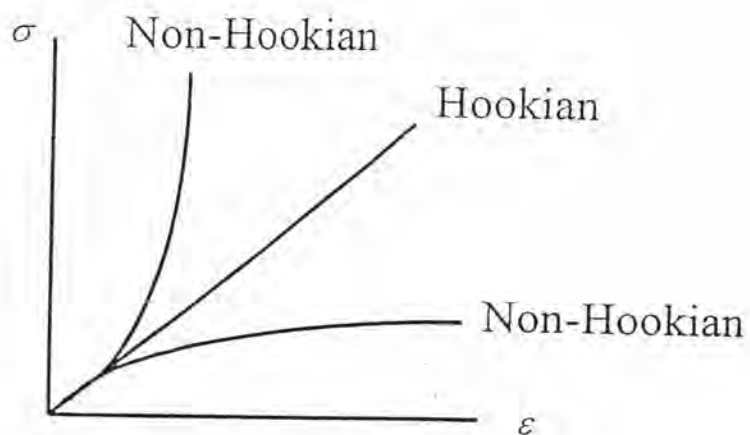


Figure 3-3 Relationship between stress and strain of elastic solid  
 [S. Damrongsakkul, 1998]

### 3.2.2.2 Viscosity

Sir Isaac Newton has developed the a relationship for the basic idea of viscous liquid like Hooke's law. His relationship is the meaning of local stress; "velocity by which the parts of fluid are being separated" In other point of view, the local shear rate means "velocity gradient is the change of velocity with position in the fluid". The proportionality between them is called "the viscosity" or "lack of slipperiness". Thus,

$$\tau = \eta \frac{\partial v}{\partial x} \quad (3-3)$$

or

$$\tau = \eta \gamma \quad (3-4)$$

Figure 3-4 represents the ideal concept for Newton's law. Pushing force into the viscous liquid produced the resistance, which arises from the lack of slipperiness originating in a fluid. In others words, the resistance is proportional to the velocity by which the parts of the fluid are being separated from each other.

We called a Newtonian fluid when the viscosity of fluid is independent of shear rate. Newtonian fluids give linear range in a stress-strain plot and the viscosity does not change when changing the strain rate. In some fluids, which acted differently from Newtonian fluids, the viscosity of these fluids is changed when the shear rate changes. These fluids are called non-Newtonian fluids. Polymer solutions and melts are usually non-Newtonian. Their viscosity decreases when the shear rate increases. This phenomenon is called shear thinning or pseudoplasticity. The opposite phenomenon is



called shear thickening or dilatency, that their viscosity increases when the shear rate increases.

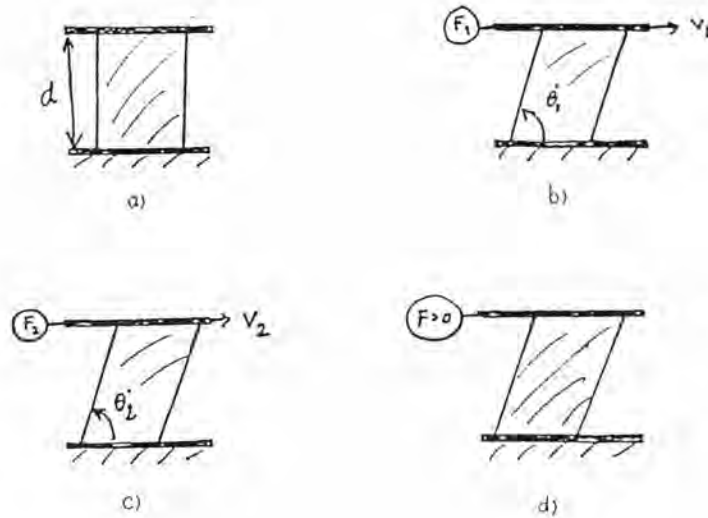


Figure 3-4 Viscous properties of ideal liquid from Newton's law. [S. Damrongsakkul, 1998]

(a) in normal condition (b),(c) when stress applied and (d) when the stress remove

The relationship of stress and strain rate of Newtonian and Non-Newtonian fluids is shown in Figure 3-5

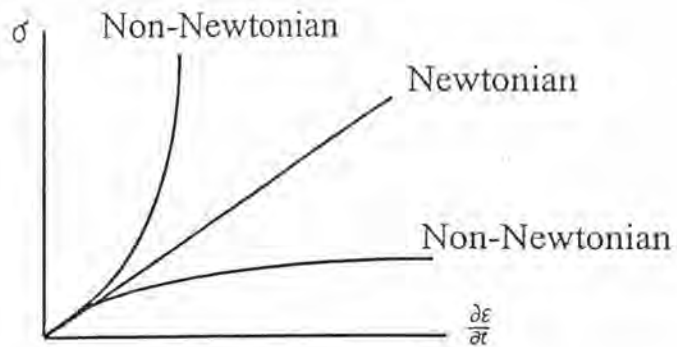


Figure 3-5 Relationship between stress and strain rate of viscous liquid [S. Damrongsakkul, 1998]

Hooke's and Newton's laws are linear laws. They assume direct proportionality between stress and strain, or shear rate, no matter what the stress. Most materials that we work with obey these laws over the limit range of stresses. Beyond this limits range, a material behaves non-linearly.

### *3.2.3 Viscoelasticity and Linear Viscoelastic Definition.*

Viscoelasticity of materials is defined by the response of material to an applied force or displacement by exhibiting either elastic or viscous behavior, or through a combination of these, called *viscoelastic* behavior. Most polymeric materials are viscoelastic, their mechanical properties showing a marked time and temperature - dependence.

Linear Viscoelasticity of materials is classified linearly viscoelastic if, when it is deformed under small strains, the ratio of stress to strain is a function only of frequency (or time) and temperature.

#### 3.2.3.1 Time-Dependence properties

Besides showing both strain and strain rate dependence, many materials exhibit a time-dependent behavior. This is apparent in the recovery behavior of viscoelastic materials when compared to Hookian or Newtonian materials.

A Hookian solid, under a constant stress, deforms immediately to a constant strain, then recovers instantly and completely when the stress is removed. A steel spring behaves like Hookian solid.

A Newtonian fluid deforms continuously while the stress is applied, but it does not recover when the stress is relieved. Water is one of the Newtonian fluids.

A viscoelastic material combines these behaviors, showing a time-dependent but incomplete recovery. Figure 3-6 illustrates their behaviors.

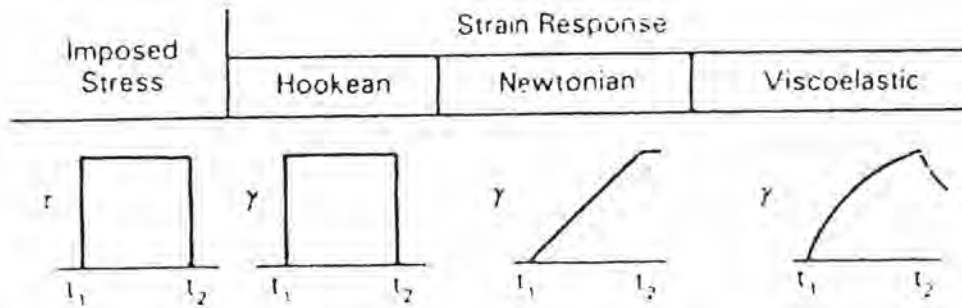


Figure 3-6 Deformation and recovery behaviors of ideal and non-ideal materials subject to a constant stress [S. Damrongsakkul, 1998]

The foregoing exemplifies an important aspect of viscoelastic materials, namely, *creep*. Creep is the change in shape of a material under a constant load or force over time. This property is usually measured in terms of a quantity known as the creep compliance,  $J(t)$ .

Creep measurements are widely used for studying thermoplastic melts and fluid suspensions. Creep measurements on polymer melts provide the zero shear viscosity and molecular weight. In other words, creep measurement on structured fluids provide the yield stress and recovery behavior. Moreover, creep measurements on solids provide vital information about load-bearing capabilities, dimensional stability and resistance to aging.

The phenomenon, which is equally important to creep, is the complementary behavior called *relaxation*. Figure 3-7 presents the relaxation behavior of viscoelastic materials according to Maxwell model. When the material (combined with spring and dash pot in series) is stretched at time  $t = t_0$ , by the amount of  $\Delta L$ , the applied force increases instantly and all deformation goes into the elastic spring element. For time  $t > t_0$ , the dash pot gives way under the internal spring force and the deformation of the spring recovers as the force decreases. The response of the model is a relaxing force with the time. The combination of elastic and viscous interactions in a material are so responsible for the time dependence of a viscoelastic materials.

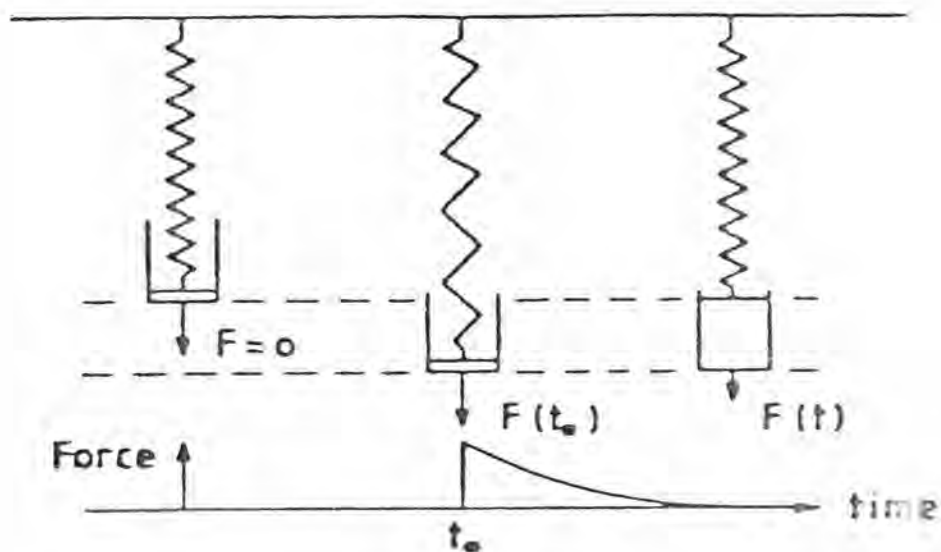


Figure 3-7 Stress relaxation behavior by Maxwell model [S. Damrongsakku] 1998]

### 3.2.3.2 Temperature Effects.

Polymer physical properties change systematically with temperature. These changes are also related to such properties as molecular weight (MW), molecular weight distribution (MWD), and branching in polymer melts, composition, crystallinity and morphology in solids.

For polymers that form crosslinks, temperature changes alter the polymer's viscosity and reaction rate. The reaction can be sensitively followed by measuring the dynamic viscosity during the reaction.

By studying temperature effects, the increases in the damping (energy dissipation) can be measured and related to different types of molecular motions. This provides the convenient and sensitive means for obtaining the molecular-level understanding of the influences of molecular structure and compositional variations on the material's intrinsic properties, and finally the material performance.

### *3.2.4 Linear Viscoelastic measurements of polymer*

The rheological measurements for evaluating linear viscoelastic behaviors of polymers are classified into two categories, transient and dynamic mechanical tests.

Transient experiments, or step changes in stress or strain experiments, to study the responses of strain or stress as a function of time, are similar to the creep or stress relaxation experiments in previous point.

For dynamic test, the stress or strain is applied continuously in many different forms, such as steady flow and oscillatory flow, to the sample.

Figure 3-8 shows the parallel plate geometry, which is the one of rheometric measuring equipment to study the viscoelastic behavior of material.

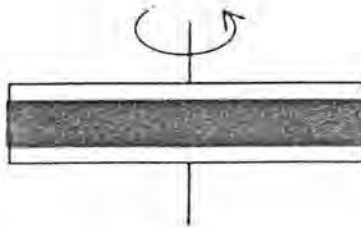


Figure 3-8 The parallel plate geometry

#### 3.2.4.1 Basic concept of steady shear flow experiment

Steady shear flow experiment is a direct way of measuring the apparent viscosity. The simple shear flow is imposed on the testing material by rotating the upper plate while fixing the lower plate. The viscosity can be determined straightforwardly as the ratio of the shear stress ( $\tau$ ) and the shear rate ( $\dot{\gamma}$ ) shown in the equation as :

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (3-5)$$

One of the controlled parameters is the shear rate. The shear stress is directly proportional to the torque,  $M$ , which is directly measured by the transducer. The major difference between using the cone and plate and the parallel plate geometry is the distribution of the shear rate along the diameter of shear cell. In the cone and plate, all material elements are under approximately the same rate of deformation. On the contrary, in the parallel plate, the shear rate varies radially.

### 3.2.4.2 Basic concept of oscillatory shear flow Experiment

The study of linear viscoelastic behavior of polymeric materials is commonly employed by oscillatory shear flow experiment. In oscillatory shear flow, the material is held either in between two parallel plates with the upper plate experiencing a periodic variation in strain ( $\gamma(t)$ ) caused by the oscillation with frequency,  $\Omega$ .

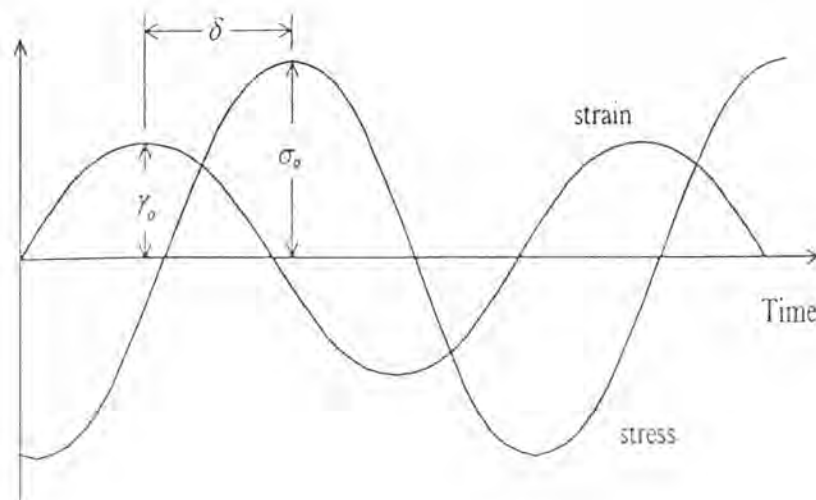


Figure 3-9 The sinusoidal variations of the strain and the stress as a function of frequency

[S. Damrongsakkul, 1998].

The alteration of the strain can be expressed in a sinusoidal form as

$$\gamma(t) = \gamma_0 \sin(\omega t) \quad (3-6)$$

where  $\gamma_0$  is the maximum amplitude. For highly viscous materials like polymer melts in a very small gap, it is appropriate to assume that the velocity profile along the diameter is instantaneously linear (Bird et al, 1977). The rate of strain is subsequently given by,

$$\dot{\gamma}(t) = \frac{\partial \gamma(t)}{\partial t} = \omega \gamma_0 \cos(\omega t) \quad (3-7)$$

The magnitude of the strain must be sufficiently small to ensure that the stress ( $\sigma(t)$ ) is linearly proportional to the imposed strain. In response to the sinusoidal strain, the stress also varies sinusoidally with a phase shift,  $\delta$ :

$$\begin{aligned} \sigma(t) &= \sigma_0 \sin(\omega t + \delta) \\ &= \sigma_0 \cos(\delta) \sin(\omega t) + \sigma_0 \sin(\delta) \cos(\omega t) \end{aligned} \quad (3-8)$$

where  $\sigma_0$  is the amplitude of the stress.



Defining the dynamic functions  $G'$  and  $G''$  as,

$$G' = \frac{\sigma_0}{\gamma_0} \cos(\delta) \quad (3-9)$$

and

$$G'' = \frac{\sigma_0}{\gamma_0} \sin(\delta) \quad (3-10)$$

Equation 3-8 can alternatively be expressed in the form:

$$\sigma(t) = \gamma_0 G' \sin(\omega t) + \gamma_0 G'' \cos(\omega t) \quad (3-11)$$

By comparing the form of the stress written in Equation (3-11) to the strain given in Equation (3-6),  $G'$  is considered as the modulus of the stress component in-phase with the strain reflecting an elastic behavior. It is, thus, called a **Storage Modulus**. On the other hand,  $G''$  is associated with the viscous character of materials and is called a **Loss Modulus** as it appears in the stress component that is 90 out-of-phase of the strain.  $G'$  and  $G''$  can be calculated directly from the amplitude ratio ( $\sigma_0 / \gamma_0$ ) and the phase shift ( $\delta$ ) according to definitions given in Equations (3-9) and (3-10).

In general, the oscillatory shear results are also presented in terms of viscosity related function by defining

$$\eta'(\omega) = \frac{G''(\omega)}{\omega} \quad (3-12)$$

and

$$\eta''(\omega) = \frac{G'(\omega)}{\omega} \quad (3-13)$$

and the complex viscosity,

$$\eta^*(\omega) = \eta'(\omega) - i\eta''(\omega) \quad (3-14)$$

of which the magnitude is given by

$$|\eta^*(\omega)| = \sqrt{\eta'(\omega)^2 + \eta''(\omega)^2} \quad (3-15)$$

$$= \frac{\sqrt{G'(\omega)^2 + G''(\omega)^2}}{\omega} \quad (3-16)$$

### 3.3 Liquid crystal


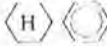
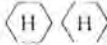
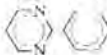
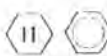
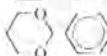



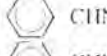
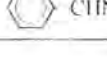
#### 3.3.1 Introduction to the liquid crystal

Liquid crystals were discovered more than a hundred years ago. They are defined as liquid materials, which also have the high degree of anisotropy. One of the important manifestations of LCs is their melting behavior. When heating normal crystalline solids, they change from solid phase directly to isotropic liquids at their crystalline melting point ( $T_m$ ). In liquid crystalline materials, several different mesophases may form after their  $T_m$ , the mesophases will become isotropic at the higher transition temperature or at the clearing temperature. The transition properties of liquid crystals come from the rigid parts of their molecules, which are called mesogens. Mesogens may consist of low molecular compounds. They may be arranged along the main polymer chain or on side branches of the graft molecules.

Many natural materials can exist in the liquid crystal state; for example, DNA, cholesterol or tobacco mosaic virus. Probably the best known synthetic liquid crystals are the liquid crystal displays.

The liquid crystalline state can be discovered as small molecules or polymers and generally requires special chemical structures. The chemical structures are composed of the central core comprising aromatic or cycloaliphatic units joined by rigid links or either polar or flexible alkyl and alkoxy terminal groups. Some typical examples of possible rigid small molecule structures or mesogens that can form liquid crystalline state are shown in Table 3-1.

Table 3-1 the example of mesophase structure [Demas, et. Al., 1998]

Compound	Molar mass, <i>M</i>
$C_{15}H_{15}$  CN	277.4
$C_{15}H_{15}$  CN	283.5
$C_{15}H_{15}$  CN	289.5
$C_{15}H_{15}$  CN	281.4
$C_{11}H_{11}$  CN	255.38
$C_{11}H_{11}$  CN	259.3
$C_{11}H_{11}$  CN	281.4
$C_{13}H_{13}$  $OC_6H_{13}$	340.5
$C_{13}H_{13}$  $OC_9H_{19}$	382.6
$CH_3O$  CHN $C_4H_9$	267.4
$CH_3O$  CHN $C_4H_9$	267.4

The mesophase may exist in a solution state (lyotropic liquid crystals) or in a melting state (thermotropic liquid crystals). The ability of the polymers to form lyotropic or thermotropic liquid crystalline mesophases depends on the chemical structure of the molecules.

The formation of a lyotropic liquid crystalline mesophase can be present alone or in equilibrium with an isotropic liquid phase. At higher polymer concentrations the liquid crystalline mesophase can be present in equilibrium with crystalline solid.

The presence of mesogenic groups is important for the anisotropic formation of liquid crystals in solutions and melts, but the occurrence of liquid crystals also depends on many other factors such as temperature. Liquid crystals form only in a certain temperature range which lies between the melting point, **T<sub>m</sub>** and the upper transition

temperature at which a liquid crystalline phase changes into an isotropic liquid or clearing point,  $T_i$ . This temperature is called the temperature of isotropisation or the solution point. If the material being tested does not crystallize, liquid crystals are formed between the glass transition temperature,  $T_g$ , and the temperature of isotropisation  $T_i$ .

In order to use liquid crystals, it is essential that the range of the mesophase extends over a wide temperature range. However, compounds containing a mesophase, particularly polymers, have a high melting point, and the melting point of crystals is often a limiting factor, since the range of liquid crystalline transition is located in the range of thermal decomposition.

Many kinds of mesophases can be classified by the different ways of the molecular arrangements. The anisotropic region ends at the clearing temperature because of the completely disordering of the molecules. There are many different types of liquid crystals. However, there are three main classifications as recognized by Friedel : nematic, smectic and cholesteric.

### *3.3.2 Structure of Liquid Crystals*

Although there are many different types of liquid crystals, there are three main classifications according to Friedel : nematic, smectic and cholesteric.

#### 3.3.2.1 Nematic structure

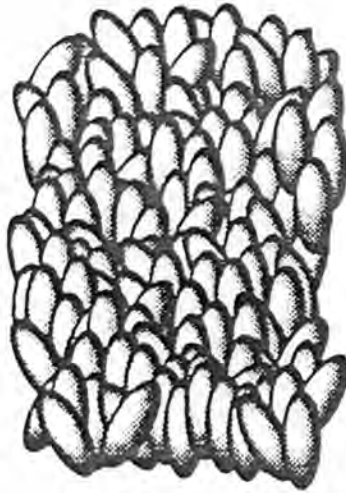
The molecular organization, classified as a nematic mesophase, involves in the irregular alignment in one dimension. Molecules remain parallel to each other in

the nematic structure (Figure 3-10), but the positions of their gravitational centers are disorganized. Molecules of nematic liquid crystals can be oriented in one dimension. Their mobilities can be reduced by the attraction to supporting surfaces. For examples, nematic molecules tend to lie parallel to the rough surface of a glass slide. A bright satin-like texture is observed when nematic liquid crystals are viewed between crossed polaroids. Characteristic dark threads appear at lines of optical discontinuity. These wavering filaments give the mesophase its name, taken from the Greek word *nematos*, meaning fiber.

#### 3.3.2.2 Smectic structure

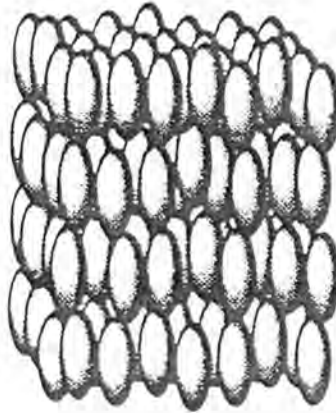
In the smectic structures, long molecules are arranged side by side in layers much like those in soap films. The term smectic (soap-like) derives from the Greek word for grease or slime. The layers are not strictly rigid, but they are flexible. Two dimensional molecular sheets can slide pass each other (Figure3-11). Molecular motion is rather slow, so smectic mesophases are quite viscous.

Optically smectic layers behave like uniaxial, birefringent crystals. The intensity of light transmitted parallel to the molecular layers is greater than that transmitted perpendicularly. The temperature dependence of smectic interval tested by birefringence has slightly small effect to internal order. The smectic mesophase is the most solid-like of all the liquid crystal behaviors.



The Nematic Mesophase  
Orientationally Ordered

Figure 3-10 Nematic Structure [Demas, et. Al., 1998]



The Smectic Mesophase  
Layer Ordering

Figure 3-11 Smectic Structure [Demas, et. Al., 1998]

### 3.3.2.3 Cholesteric or chiral nematic structure

The cholesteric structure is the third type of liquid crystal behaviors. It is so named because many compounds that form this mesophase are the derivatives of cholesterol. A cholesteric structure (Figure 3-12) is the shape of a nematic phase which is periodically wrapped around the axis. When chiral groups are present, the basic structure is helicoidal.

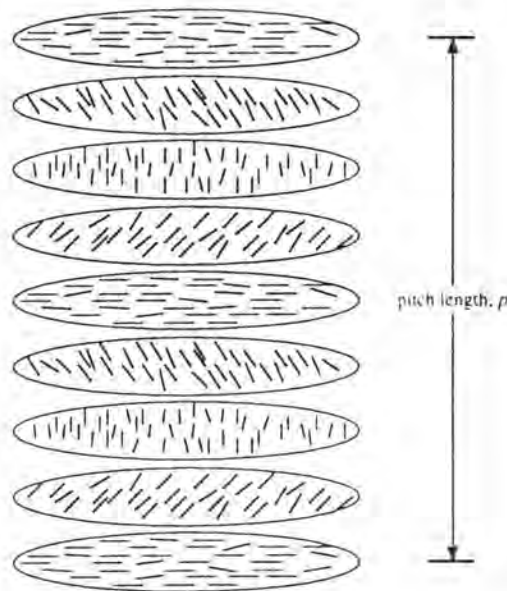


Figure 3-12 Chiral Nematic Structure [Demas, et. Al., 1998]

### *3.3.3 Mesophasic Transition Temperature*

The various liquid crystal phase transitions, that liquid crystals undergo as the temperature increases from the most ordered to the least ordered states, can be shown as Figure 3-13,



crystal  $\rightarrow$  smectic (S)  $\rightarrow$  nematic (N)  $\rightarrow$  isotropic

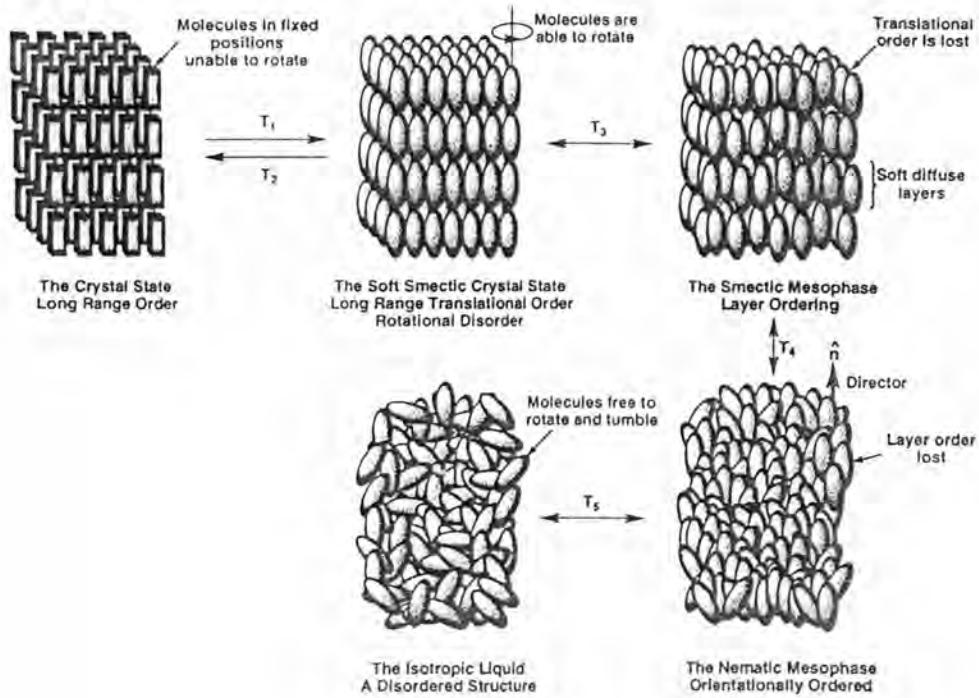


Figure 3-13 Phase Transition of Liquid Crystal [Demas, et. Al., 1998]

The temperature, when liquid crystal changes from crystal to the first liquid crystalline phase, is called "crystalline melting temperature" ( $T_3$ ).

The temperature, when liquid crystal changes from crystal from smectic phase to nematic phase, is call "S  $\rightarrow$  N transition temperature" ( $T_4$ ).

The temperature, when the last (or only) liquid crystalline phase gives way to the isotropic melt or solution, is called "clearing temperature" ( $T_5$ ).

The examples of mesophasic transition temperature of low molar mass liquid crystals used in this study are shown below:

a) CBC33 exhibits a crystalline melting transition at  $153^{\circ}\text{C}$  and the  $S \rightarrow N$  transition temperature at  $223^{\circ}\text{C}$ . CBC33 exhibits the state change from the nematic to isotropic (clearing temperature) at  $327^{\circ}\text{C}$  [Merck, 1996].

$153^{\circ}\text{C}$        $223^{\circ}\text{C}$        $327^{\circ}\text{C}$   
crystal  $\rightarrow$  smectic (S)  $\rightarrow$  nematic (N)  $\rightarrow$  isotropic

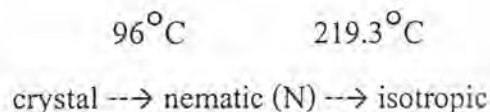
b) CBC53 exhibits a crystalline melting transition at  $64^{\circ}\text{C}$  and the  $S \rightarrow N$  transition temperature at  $260^{\circ}\text{C}$ . CBC53 exhibits the state change from the nematic to isotropic (clearing temperature) at  $317^{\circ}\text{C}$  [Merck, 1996].

$64^{\circ}\text{C}$        $260^{\circ}\text{C}$        $317^{\circ}\text{C}$   
crystal  $\rightarrow$  smectic (S)  $\rightarrow$  nematic (N)  $\rightarrow$  isotropic

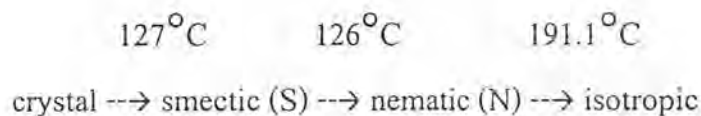
c) HP5N exhibits a crystalline melting transition at  $111^{\circ}\text{C}$  and becomes an isotropic liquid (clearing temperature) at  $226^{\circ}\text{C}$  [Merck, 1996].

$111^{\circ}\text{C}$        $226^{\circ}\text{C}$   
crystal  $\rightarrow$  nematic (N)  $\rightarrow$  isotropic

d) BCH5 exhibits a crystalline melting transition at  $96^{\circ}\text{C}$  and becomes an isotropic liquid (clearing temperature) at  $219.3^{\circ}\text{C}$  [Merck, 1996].



e) HD35 exhibits a crystalline melting transition at  $127^{\circ}\text{C}$  and the S  $\rightarrow$  N transition temperature at  $126^{\circ}\text{C}$ . HD35 exhibits the state change from the nematic to isotropic (clearing temperature) at  $191.1^{\circ}\text{C}$  [Merck, 1996].



### 3.3.4 *Liquid crystal polymer*

The term "liquid crystal" has been used by many scientists to describe supramolecular arrangements in amorphous and semi-crystalline polymers. The liquid crystal polymers are the group of polymers that can exhibit one of the above liquid crystal structures. There are two main ways that anisotropic building blocks can form a polymer. They can either be joined end to end to form a main chain LCP or dangle off the side of a normal polymer chain to form a side chain LCP. Anisotropic aromatic building blocks can be very useful copolymerized with traditional flexible monomers, if these flexible units are placed within the main chain. They can be modified in order to control the melting point and glass transition temperature of the results LCP. Flexible units can also be placed between a normal polymer backbone in the main chain and the liquid crystal group.

The most important LCPs for blending with bulk polymer is the thermotropic main chain LCPs. This group of LCPs exhibits a liquid crystal phases within processing window of the bulk polymer, but which then solidifies on cooling to room temperature.

As with any polymer, the LCP can either crystallize on cooling or still amorphous when quenched under the glass transition temperature. Hence, at room temperature, the structure of the LCP can be the ordered glass structure or a semi-crystalline polymer morphology.

As LCPs are often formed from highly aromatic stiff monomers, it is hardly surprising that they can form very stiff polymers. "KEVLAR" fibers, for example, have a specific modulus considerably in excess of steel fiber. Carbon fibers with moduli up to 700 GPa can be produced from a liquid crystal pitch. The advantage that the liquid crystal brings is the perfect final structure that processing from a naturally ordered fluid which is better than processing a normal chaotic fluid. These highly aromatic LCPs are also very brittle and have very low failure strains, but the fiber can be very strong.

### *3.3.5 Properties characterization of liquid crystal and liquid crystal polymer*

*[Fles, 1995]*

Liquid crystalline compounds are characterized according to the type of mesophase, thermal and thermodynamic properties and distribution of the anisotropic phase. The following methods are most frequently used :

- X-ray diffraction at small and large angles,
- differential dynamic calorimetry,
- rheological methods.

Also important are the methods of light scattering, electron microscopy and electron diffraction, and magnetic resonance.

These methods are used for characterisation of smectic and nematic systems.

#### 3.3.5.1 Microscopy

Characterization of liquid crystals by polarization microscope is the most direct method that exists and it is used whenever possible as the initial phase of testing of a polymer. With microscopy a thin layer of melt is examined on a hot plate under polarized light. The appearance of the melt depends on the structure of the mesophase which often permits immediate identification of the mesophase [Hartshorne, 1974 and Demus, et. al., 1978]

Identification of the structure of a mesophase of low molecular compounds is much simpler than those structures of LCP. The textures of polymers are basically identical to texture of the mesophase of low molecular compounds, but for LCP minutes or even hours are required before the textures of the mesophase can be identified, and during this length of time the polymer frequently degrades.

### 3.3.5.3 Thermal analysis

In addition to the characterization of the mesophase by microscopy and X-ray diffraction, DSC and GA are also very frequently employed. The thermal methods show the regions of the transition temperatures, the heat of the transitions and heat resistance. Numerous research reports have shown that the melting point of polymeric materials normally depends largely on the history of the sample, while the temperature of isotropization is less dependent on the thermal treatment of the sample and has no tendency to cool.

Examination of the mesophase structure by DSC requires considerable expertise and generally comparison with the structure obtained by the use of microscopy and X-ray diffraction.

### 3.3.5.4 Rheological properties

A great number of theoretical and experimental analyses of the rheological properties of low molecular weight thermotropic compounds have been carried out, while the rheological properties of liquid crystals have received very little research. One of the studies often quoted was carried out by Jackson and Kuhfuss [1976]. The apparent viscosity was measured of a copolymer of HBA and PET as a function of the composition of the copolymer. With a low fraction of HBA the viscosity of the melt increases because of the substitution of the flexible ethylene glycol fraction by the rigid HBA units. For approximately the same molecular mass, the viscosity of the copolymer reaches a maximum with a molar ratio of HBA of 30%.

since with a further increase in the fraction of HBA the viscosity would fall to a minimum with about 60% of HBA in the copolymer.

In 1981 Jerman and Baird measured the rheological properties of the same copolymer using the Instron capillary rheometer. They measured the die swell and pressure at the entry to the die. They confirmed the results obtained in an earlier study by Jackson and Kuhfuss, establishing that the viscosity of the copolymer at 50% HBA/PET was two orders lower than the viscosity of the PET at 285<sup>0</sup>C. Wissbrun [1980] noted the very long time of relaxation and the high elasticity of anisotropic melts of aromatic polyesters, and also some other anomalies in connection with the melt flow of liquid crystalline polymers.

### *3.3.6 Application of liquid crystalline polymers [Fles, 1995]*

The most important properties of LCP materials which are essential for their use are related to the orientation of the macromolecules during flow in the mesophase, both in melt and solution. Because of their oriented regions liquid crystalline polymers behave like reinforced materials, and so they are called self reinforcing materials.

The importance of liquid crystalline polymers as materials for special applications was grasped even in the early days of development of aromatic polyamides in the 1960s. However, it was only in the period after 1980 that the development of LCP became one of the most important areas of development in materials science.

The lyotropic method of production of LCPs has up till now been commercially developed only for the production of Kevlar, poly(p-phenylene terephthalamide). By stretching the fibers in the nematic mesophase which is formed in a 20% solution of aramid in concentrated sulphuric acid, high-modulus fibers are obtained whose mechanical properties depend on the method of orientation of the mesophase and the method of extraction of the sulphuric acid. In many patents, after being forced through spinnerets the fibers are introduced directly into a lye solution and after this are oriented by stretching. However, fibers with much superior mechanical properties are obtained by cooling the solution of aramid in sulphuric acid in air and stretching the fibers in the mesophase, after which the sulphuric acid is extracted with additional stretching. The method with air cooling permits the fibers to be obtained while they are still in the form of liquid crystals, so that the orientation can be controlled through the whole section of the fiber. The use of air space permits production with higher solution concentration, at higher temperatures and at a faster rate of stretching. A comparison of tensile moduli and specific moduli of Kevlar and a number of constructional materials is given in Table 3-2.

The use of Kevlar in the period after 1980 began to expand rapidly for the manufacture of nautical ropes, as fiber for reinforcement of thermoplastics and thermosets, as a substitute for metal cord in the production of tyres, and its use was particularly important in the production of bullet-proof clothing. However, more recently a variety of thermotropic fibers which can be produced more easily have been competing with Kevlar.



Table 3-2 The value of the axial tensile moduli (E) and the specific moduli (modulus/Sp. Gr., E/SG) for a series of organic fibers. [Fles, 1995]

Fiber	E (GPa)	E/SG
Kevlar 29	60	42
Kevlar 49	120	83
Kevlar 149	185	128
Spectrala <sup>(a)</sup>	170	175
HBA/PET (Xydar) <sup>(b)</sup>	23	16
HBA/HNA (Vectra) <sup>(c)</sup>	65	46
Carbon fiber	390	215

- (a) High-modulus PE obtained by drawing from gel.
- (b) Copolymer of p-hydroxybenzoic acid and ethylene terephthalate.
- (c) Copolymer of p-hydroxybenzoic acid and hydroxynaphthalene - carboxylic acid.

The invention of Kevlar is one of the most important in the development of LCPs. However, owing to the difficulties in production by the lyotropic method, and because of the fact that this technique is restricted only to the production of one dimensional product (fibers), development nowadays is for the most part concentrated in the sector of thermotropic LCPs. After 1990, many new polymeric materials have appeared on the market which contain a stable mesophase and which are known under the name of self-reinforcing materials

The important characteristic of these materials is that with increase in the liquid-crystalline phase there is a decrease in viscosity of the melt, but simultaneously the mechanical properties are improved. Figure 3-14 shows that with increase in the molar fraction of p-hydroxybenzoic acid (HBA) in the copolymer with terephthalic acid the viscosity increases up to 30% of HEA and then falls to a minimum at 60% of HEA. In this region the proportion of liquid crystals is at a maximum, and the tensile strength is at its highest, while its processibility is greatest [Jackson et. al., 1976].

The data in Figure 3-14 indicate that the melt viscosity of thermotropic polymers is greatly dependent on shear, which shows that the individual regions are oriented in the direction of drawing at low shear rate.

This maybe the reason why during injection moulding and extrusion of fibers in the nematic state the macromolecules are oriented and ordered.

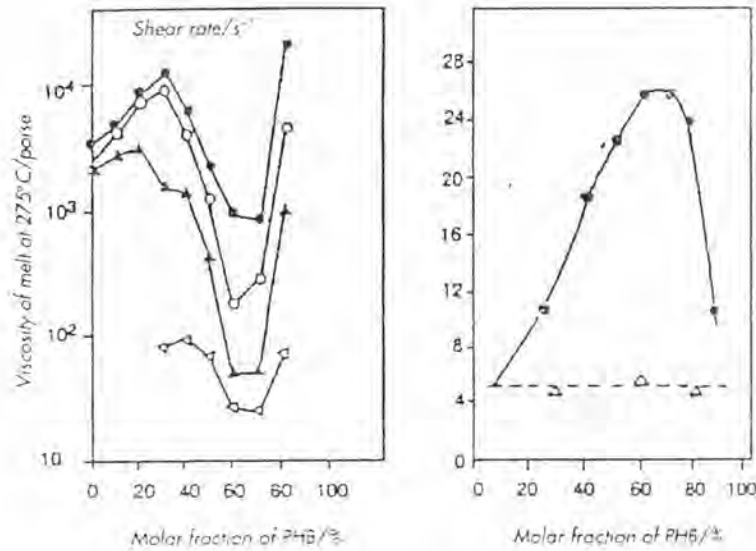


Figure 3-14 Viscosity and tensile strength vs the composition of poly(HBA co ETA)  
The liquid crystallinity appears in the melt at 30mol% of HBA [Jackson, et. Al., 1976]

The first thermotropic LCP was marketed by Dart and Kraft in 1984 under the name Xydar [Us Patent, 1984]. Xydar is a terpolymer of HBA-terephthalic acid-biphenol. Shortly after this a firm, Celanese, brought out block copolymers of HBA and HNA under the name Vectra [US patent 1985]. Both of these LCP materials are characterized by high strength and modulus, in which they are superior to conventional constructional thermoplastics, and have high impact strength and resistance to high temperature. Even at high temperatures LCPs are distinguished by resistance to chemicals, and they have excellent dimensional stability, including low heat extensibility and low moisture absorption. They can be processed by all conventional methods, and are particularly suitable for the manufacture of thin products of complicated shapes. Because of the effect of orientation, the tensile strength of LCP articles increases with decrease in wall thickness. As well as having good dielectric properties, LCPs are resistant to radiation, hydrolysis and atmospheric factors, and resist burning.

LCP materials are employed in many applications where they replace metals and various polymers for special purposes: the electrical industry and electronics, telecommunications, transport, optical fibers, aerospace applications, applications involving corrosive chemicals and the manufacture a household appliances. It is anticipated that during the 1990s the consumer goods market will account for about 73% of these materials, various industrial applications about 8%, the electrical industry and electronics about 5%, telecommunications 5% and the automobile industry about 4%. Although the electrical and electronics industries are not the largest consumers of LCP as regards actual quantity, in terms of the importance and value of use of LCP electronics are still the most important sector. The use of LCPs makes it possible to

print electronic components directly on the surface of a substrate without preliminary forming of the recesses in the electronic elements or inserted. Also, the elements can be pressed onto both sides of the substrate, and the average dimensions of the blocks can be significantly reduced. Requirements of materials for these applications are high strength and dimensional stability, which permit contact of thin-walled connecting elements and a higher rate of automatic bonding. The materials must be resistant to solvents and to combustion, and additionally they must have heat extensibility similar to the elements which are mounted on the board and must be weldable. The material must have good dielectric properties, and low melt viscosity in order to achieve thin parts of mouldings. The plastics materials which meet all of these requirements are various types of liquid crystalline polymers.

Often small amount of LCP considerably improve the properties of constructional materials. For example, only 10% of Xydar improves the processability of a thermoplastic polyimide (TPI). The melt viscosity decreases by 50%, the elastic modulus increases from 3.0 to 4.9 kPa., and the thermal expansion can be reduced so that it is negligible at 35% by mass of the LCP. Blends with LCPs behave like reinforced materials which can be deeply thermoformed.

### **3.4 Tensile Properties [Rosato, 1991]**

The tensile test is the experiment for test relation between stress-strain. It's the most widely use method to characterize the mechanical properties of materials such as plastics, metals and woods. The obtained test results contain the important characteristics of samples, such as elastic properties, yield strength, tensile strength, and toughness, etc.

The ASTM D638 explains the international standard method for conducting tensile test and defines the generally industrial terms. The tensile test according to ASTM D638 is almost performed on the dump-bell specimen; the other, ASTM D882, is also used as a standard procedure for tensile testing of materials in the form of film or thin sheet specimen.

A tensile test involves pulling or stretching a test specimen at a uniform rate of extension and measuring the corresponding load applied. The tensile force is recorded as a function of elongation. Figure 3.15(a) shows a typical plot of tensile force versus tensile elongation. Sometimes such plot is normalized with respect to specimen dimensions as in Figure 3.15(b) [Han, 1992]. Various tensile stress-strain curves are also shown in Figure 3.16. Explanation of the terminology [Rosato, 1991] used in tensile testing is as follows:

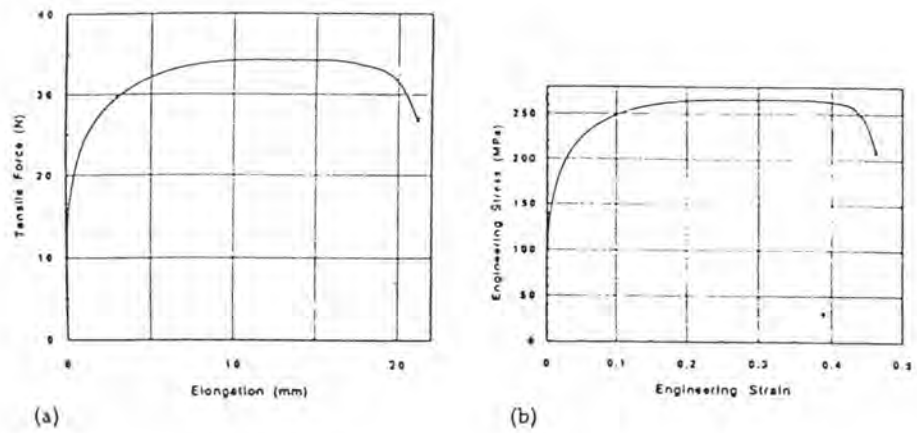


Figure 3-15 (a) Load-elongation curve from a tensile test  
 (b) corresponding engineering stress-strain curve [Han, 1992]

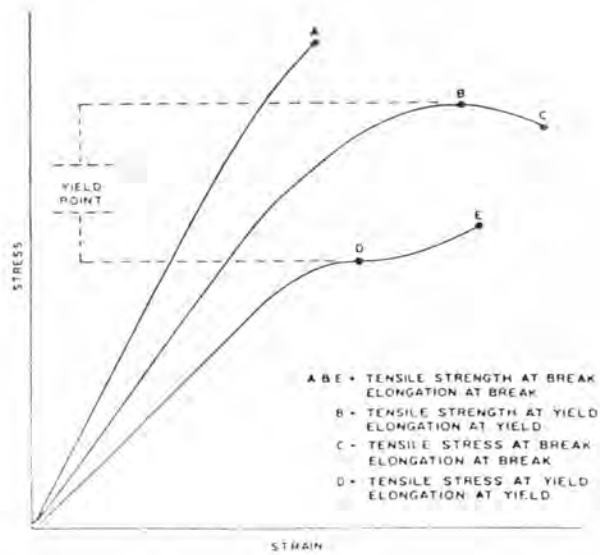


Figure 3-16 Tensile designations according to ASTM D638 [Rosato, 1991]

### *3.4.1 Stress*

Stress is the tensile load applied per unit of the original cross sectional area at a given moment of the specimen. The standard unit measuring in pascal (Pa) or pound per square inch (psi).

### *3.4.2 Strain*

Strain is the ratio of elongation or deformation to the gauge length of the test specimen; that is, the change in length per unit of original length. It is expressed as a dimensionless ratio; mm/mm (in/in). As the strain is increased beyond the material's proportional limit, the specimen's elastic limit is reached.

However, below the elastic limit the material's behavior is elastic; that is, once it is unloaded, its recovery from deformation is essentially complete and instantaneous. Stressing the specimen above its elastic limit results in a degree of permanent set. This non-recoverable stress is call plastic strain. This strain is usually associated with plastics, but it is also seen in other materials.

### *3.4.3 Elongation*

The elongation is expressed as a percentage of length increase of the test specimen. Normally call it as the percentage of elongation

#### *3.4.4 Yield*

The first point on a stress-strain curve which increases in strain occurs without any increase in stress is its yield point of yield strength or tensile strength at yield. The yield strength is generally established by constructing a line to the curve where stress and strain is proportional at a specific offset of strain, usually at 0.2 percent. The stress at this point is the yield strength of materials. The example of the yield strength at 0.2 percent offset is shown in the Figure 3.17.

#### *3.4.5 Proportional limit*

A material's proportional limit is the greatest stress which is the capability of sustaining an applied load without deriving from the proportionality of stress to strain. The proportional limit is shown in Figure 3.17.

#### *3.4.6 Elastic Limit*

The elastic limit of a material is the greatest stress which is the capability of sustaining an applied load without any permanent strain remained, once stress is completely released.

#### *3.4.7 Tensile Strength*

The maximum tensile stress sustained by a specimen during a tension test is its tensile strength, Again it is expressed either in pascal (Pa) or pound per square inch (psi). Tensile strength is shown in Figure 3.17.



### 3.4.8 Modulus of Elasticity

Most materials, including plastics have deformation proportional to their load below the proportional limit. Since stress is proportional to load and strain to deformation, this implies that stress is proportional to strain. Hook's law, developed in 1676, follows that this straight line (in Figure 3.17) of proportionality is calculated as

$$\frac{\text{Stress}}{\text{Strain}} = \text{Constant}$$

The constant is called the modulus of elasticity (E) or Young's modulus, elastic modulus, or just the modulus. This modulus is the slope of the initial portion of the stress-strain curve, normally expressed in terms such as MPa or GPa.

The modulus of elasticity is applied to describe the stiffness or rigidity of a plastic where its stress-strain characteristics depend on such factors as the stress or strain rate, the temperature, and its previous history as a specimen.

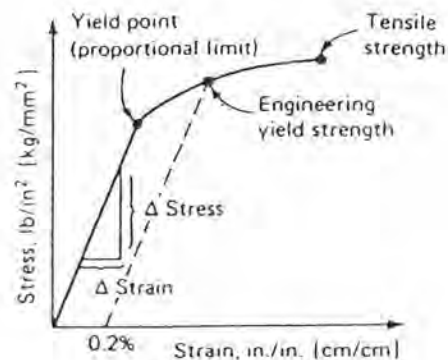


Figure 3-17 An example of the modulus of elasticity determined on the initial straight portion of the stress-strain diagram [Rosato, 1991]

### 3.4.9 Area under the curve

Generally, the area under the stress-strain curve is proportional to the energy required to break the plastic. It is thus sometimes referred as the toughness of plastics (Figure 3.18). However, there are types of behavior of plastics that are hard, strong or tough.

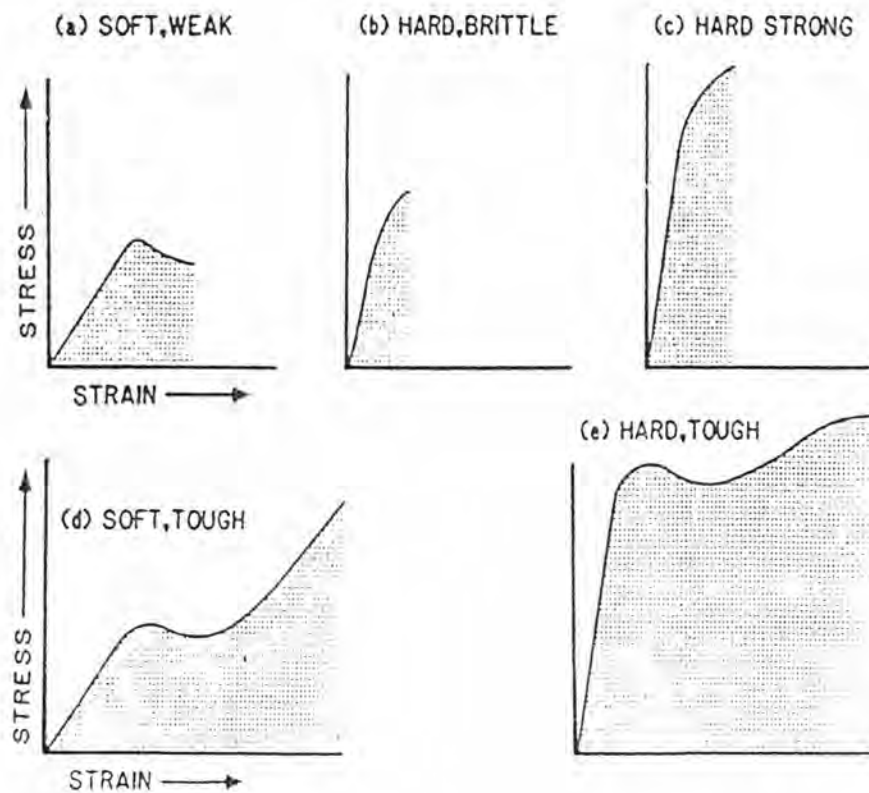


Figure 3-18 Tensile stress-strain curves for different plastics that relate the area under the curve to their toughness or physical properties [Rosato, 1991]

#### *3.4.10 Test rates*

Test rate or cross - head rate is the speed that the movable cross member of a testing machine moves in relation to the fixed cross-member. The speed of tests is typically reported in cm/min, mm/min, or in/min.

An increase in strain rate typically results in an increasing yield point and ultimate strength as shown in Figure 3.19 (a) and (b). For most rigid plastics, the modulus does not change significantly with the strain rate. For softer thermoplastics, the theoretical elastic or initial tangent modulus is usually independent of the strain rate.

The elastic modulus and strength of both rigid and the softer plastics each decrease with an increase of temperature as shown in Figure 3.19 (c). While in many respects the effects of temperature change are similar to those resulting from the strain rate change but the effects of temperature change are relatively much greater.

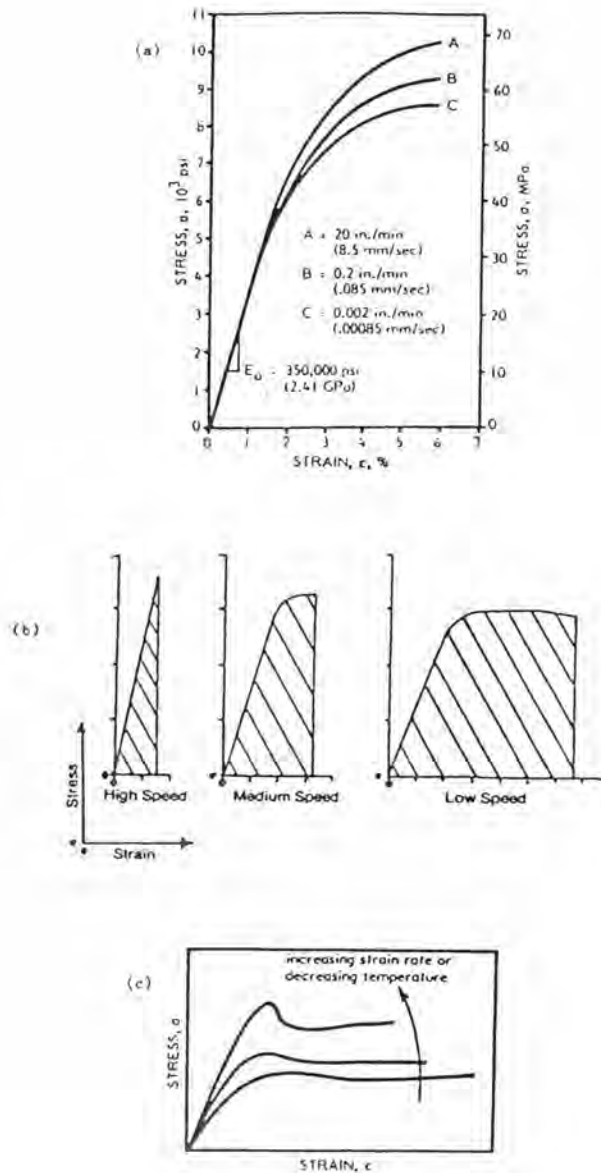


Figure 3-19 Examples of the influent of different test rates and temperatures on basic stress-strain behavior of plastics [Rosato, 1991]

(a) different testing rates as shown for polycarbonate

(b) effects of tensile speeds on the shapes of stress-strain diagram

a simplified version of the effects on curves of changes in test rates and temperature

### 3.5 Differential Scanning Calorimeter (DSC)

The DSC instrument can detect the heat that is absorbed or emitted from the samples as they are heated or cooled at a constant rate. The amount of sample required are about 5-20 mg. The schematic diagram of the DSC that was used in this experiment, can be seen in Figure 3-20

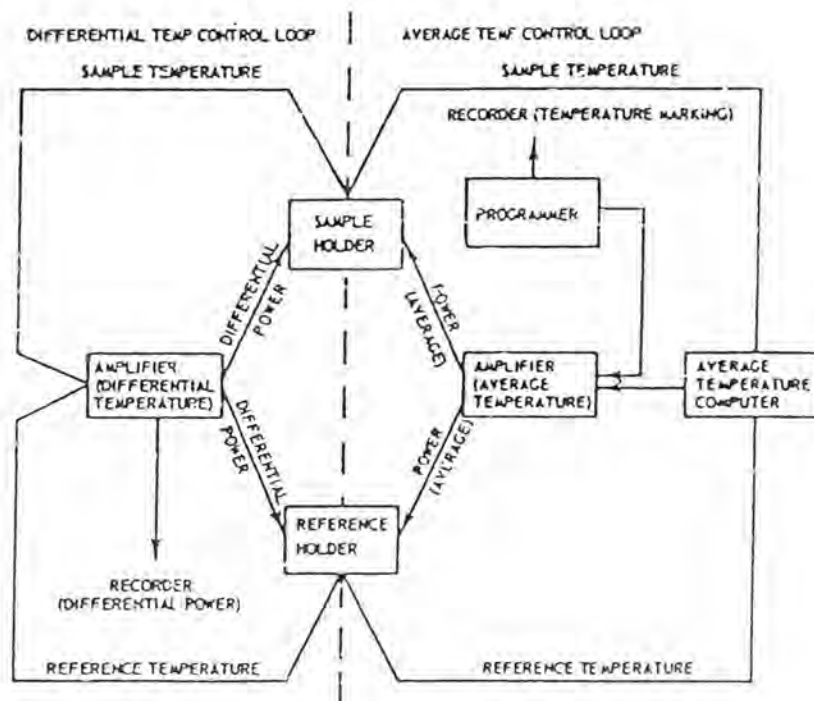


Figure 3-20 Schematic Diagram of the DSC [S. Thongyai, 1994]

As shown in Figure 3-20, a sample and a reference were heated up (or cooled down) at a rate controlled by the programmer and the feed back temperature. The differential power is the power that compensates the sample in order to maintain the same temperature as the reference. The temperature and the differential power used were

detected and reported as a DSC curve. A typical specific heat curve obtained in this way is shown in Figure 3-21.

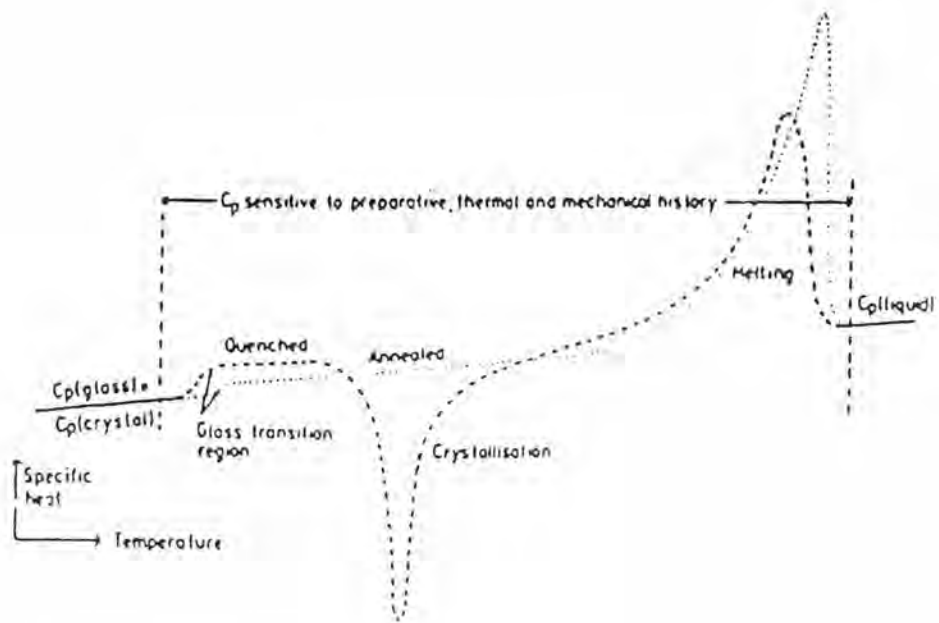


Figure 3-21 Typical specific heat curve [S. Thongyai, 1994].

As shown in Figure 3-21, the glass transition temperature ( $T_g$ ) is indicated by a step change in specific heat, while the crystalline melting point temperature ( $T_m$ ) and the crystallisation temperature ( $T_c$ ) are obtained from the position of the relevant peaks. The  $T_m$  peak is the endothermic peak, while the  $T_c$  peak is the exothermic peak. The values of  $T_m$  and  $T_c$  depend strongly on the thermal history and preparation of the blend, while  $T_g$  is effectively less dependent on thermal history.