



CHAPTER III

THEORY

3.1 Syndiotactic Polystyrene

Syndiotactic polystyrene (sPS) is a semicrystalline polymer synthesized from styrene monomer using a single-site catalyst, such as metallocene. First synthesized in 1985 by Idemitsu Kosan Co. Ltd. (Tokyo, Japan), the material has been under joint production and processing development by Idemitsu and Dow Plastics (Midland, MI) since 1988.

Because of its semicrystalline nature, sPS products exhibit performance attributes that are significantly different from those of amorphous styrenic materials. These properties include a high melting point, good chemical and moisture resistance, and a high degree of dimensional stability.

sPS can be differentiated from conventional styrenic polymers on the basis of molecular structure. Atactic, or general-purpose, polystyrene is produced with random stereochemistry, resulting in nonspecific placements of the cyclic aromatic portions of the molecules. In contrast, isotactic and syndiotactic polystyrene are made using stereo-specific catalysis techniques that result in highly ordered molecular structures.

Some typical properties and mechanical properties of SPS are reported below; some reported values, e.g. the melting temperature, can differ slightly between polymers synthesized with different catalysts, owing to the different content of steric effects [16].

Density	1050 kg/m ³
Glass transition temperature (T_g)	~100°C [17]
Melting temperature (T_m)	270°C [18]
Izod impact strength (notched)	2 kJ/m ² (ASTM D 256-A)
Tensile strength	41 Mpa (ASTM D 638)
Tensile modulus	3.4 GPA (ASTM D 638)

Elongation at break	1% (ASTM D 638)
Flexural modulus	3 GPa (ASTM D 790-1)
Flexural strength	75 GPa (ASTM D 790-1)
Dielectric constant, 23°C, 1 MHz	2.6 (IEC 250)

Whereas atactic polystyrene is an amorphous polymer with a T_g of 100°C, syndiotactic polystyrene is semicrystalline with a T_g similar to atactic polystyrene but has its T_m in the range of 255-275°C. The crystallization rate of syndiotactic polystyrene is comparable to that of poly(ethylene terephthalate). sPS exhibits a polymorphic crystalline behavior, which affected the blend properties.

3.2 Polymer Tacticity

Stereoregularity arises because of the order in the spatial structures of polymer chains. If the backbone of a polymer chain is drawn in a flat zigzag form on the plane of the paper, the patterns can be shown in Figure 3.2.1. and easily envisaged in the case of monosubstituted vinyl units. It should be noted that in (a) all the substituent R groups lie uniformly on the same side of the zigzag plane. Natta called this structure isotactic. In (b) the substituent R groups occupy positions alternatively above and below the backbone plane. Such a structure is termed syndiotactic. In (c) there is no regular arrangement of the substituent R groups and this structure is called atactic.

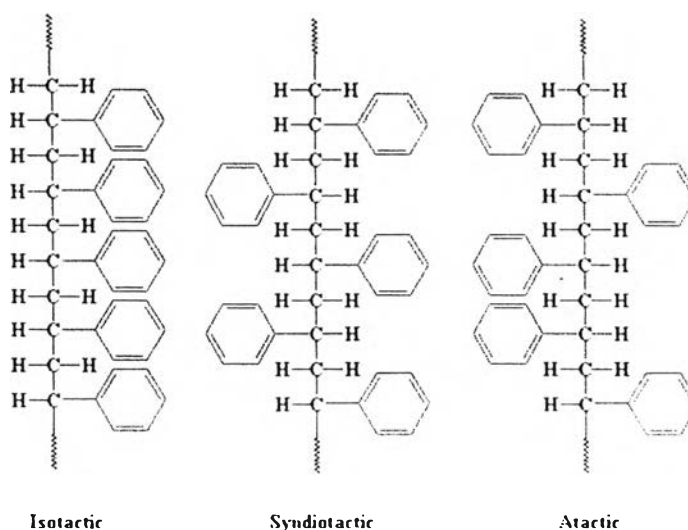


Figure 3.2.1 Types of olefin polymer tacticity[19]

The regularity or lack of regularity in polymers affects their properties by way of large differences in their abilities to crystallize. Atactic polymers are amorphous (noncrystalline), soft (tacky) material with little or no physical strength. The corresponding isotactic and syndiotactic polymers are usually obtained as crystalline materials. The ordered structure is capable of packing into a crystal lattice, while the unordered structures are not. Crystallinity leads to high physical strength and increased solvent and chemical resistance as well as increased the differences in other properties that depend on crystallinity.

3.3 Polymer Morphology

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

3.3.1 The Amorphous State

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

We can imagine the amorphous state of polymers like a bowl of cooked spaghetti. The major difference between the solid and liquid amorphous states is that with the former, molecular motion is restricted to very short – range vibrations and rotations, whereas in the molten state there is considerable segmental motion or conformational freedom arising from rotation about chemical bonds. The molten state has been like on a molecular scale to a can of worms, all intertwined and wriggling about, except that the average worm would be extremely long relative to its cross-

sectional area. When amorphous polymers achieve a certain degree of rotational freedom, it can be deformed. If there is sufficient freedom, the polymer flows when the molecules begin to move past one another. At low temperatures amorphous polymers are glassy, hard and brittle. As temperature is raised, they go through the glass – rubber transition characterized by the glass transition temperature T_g .

3.3.2 Glass Transition Temperature, T_g

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

The importance of the glass transition temperature cannot be overemphasized. It is one of the fundamental characteristics as it relates to polymer properties and processing. The transition is accompanied by more long – range molecular motion, greater rotational freedom and consequently more segmental motion of the chains. It is estimated that between 20 and 50 chain atoms are involved in this segmental movement at the T_g . Clearly for this increased motion to take place, the space between the atoms (the free volume) must increase, which gives rise to an increase in the specific volume. The temperature at which this change in specific volume takes place, usually observed by dilatometry (volume measurement), may be used as a measure of T_g . Other changes of a macroscopic nature occur at the glass transition. There is an enthalpy change, which may be measured by calorimetry. The modulus, or stiffness,

decreases appreciably, the decrease readily detected by mechanical measurements. Refractive index and thermal conductivity have also been changed.

3.3.3 The Crystalline Polymer

Polymers crystallized in the bulk state are never totally crystalline, because of a consequence of their long-chain nature and subsequent entanglements. The melting temperature of the polymer, T_m , is always higher than the glass transition temperature, T_g . Thus the polymer may be either hard and rigid or flexible. For example, polypropylene which has a glass transition temperature of about $-5\text{ }^\circ\text{C}$ and a melting temperature of about $175\text{ }^\circ\text{C}$. At room temperature it forms a leathery product as a result. Factors that control the T_m include polarity, hydrogen bonding and packing capability.

The development of crystallinity in polymers depends on the regularity of structure in the polymer, the tacticity of the polymer. The different possible spatial arrangements are called the tacticity of the polymer. If the R groups on successive pseudo-chiral carbons all have the same configuration, the polymer is called isotactic. When the pseudo-chiral centers alternate in configuration from one repeating unit to the next, the polymer is called syndiotactic. If the pseudo-chiral centers do not have any particular order, but in fact are statistical arrangements, the polymer is said to be atactic.

Thus isotactic and syndiotactic structure are both crystallizable, because of their regularity along the chain but their unit cells and melting temperatures are not the same. On the other hand, atactic polymers are usually completely amorphous unless the side group is small or so polar as to permit some crystallinity.

3.4 Melting Phenomena

The melting of polymers may be observed by any of several experiments. For linear or branched polymer, the melting causes the samples to become liquid and flows. First of all, simple liquid behavior may not be immediately apparent because of the polymer has high viscosity. If the polymer is cross-linked, it may not flow at all. It must also be noted that amorphous polymers soften at their glass transition temperature, which is emphatically not a melting temperature. If the sample does not contain colorants, it is usually hazy in the crystalline state because of the difference in refractive index between the amorphous and crystalline portions. On melting, the sample becomes clear or more transparent.

3.5 Thermal Properties

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

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

3.6 Polymer Blends [20]

Polymer blends are the mixtures of at least two polymers or copolymers. The blending of two or more existing polymers may obtain the new properties that without synthesizing the new polymers. In the plastic industry, polymer blends are more advantageous than the synthesis of new polymers because of their lower production cost.

There are many methods to blend polymers together such as by using heat (melt mixing), solvent (solution casting, freeze-drying) or others.

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. The 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 equipment of are available for laboratory scale mixing such as internal mixer, electrically heated two roll mill, extruder and 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. Solvent casting is the simplest mixing method available and is widely practiced in academic studies, usually when the experiments need 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 the phase diagram. In spite of the fact that most of the solvent can be removed from a cast film, the nature of the film depends strongly on the types of solvents and casting conditions.

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 (vacuum) are 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 formation of bubble in the final films produced.

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 and pressure. Dilute solutions must be used and the solution volume must have as large surface area as possible for good heat and mass 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, 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 point 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.

3.6.4 Emulsions

The advantages of the emulsion polymer mixing 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 other polymer and the introduction of interface graft copolymer onto the polymer chains.

3.7 Ultimate Mechanical Properties

The material selection for a variety of applications is quite often based on mechanical properties such as tensile strength, modulus, elongation, and impact strength [21]. These values are normally derived from the technical literature provided by material suppliers.

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 3.7.1.

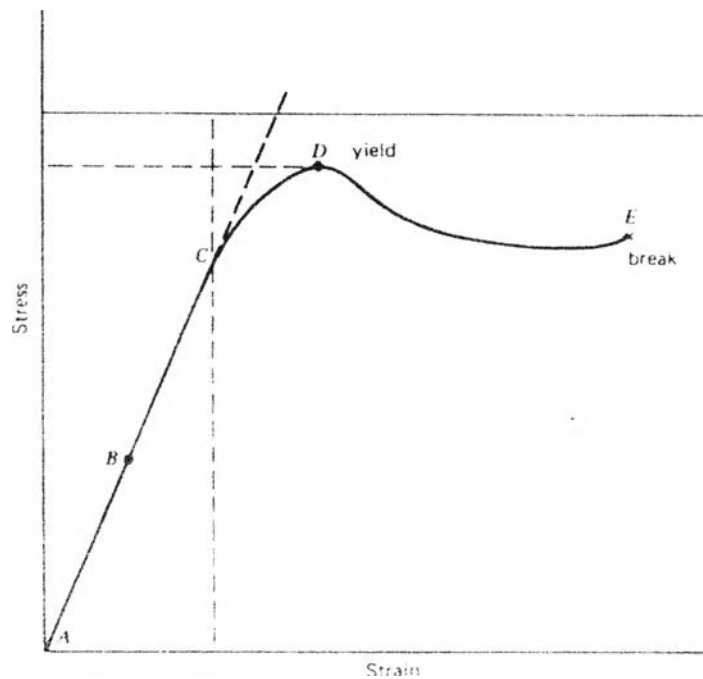


Figure 3.7.1 A typical stress-strain curve

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

3.7.1 Stress-Strain Diagram

3.7.1.1 Stress

The force applied to produce deformation in a unit area of a test specimen. Stress is a ratio of applied load to the original cross-sectional area. Force can be exerted externally on a body in two particular ways. Gravity and inertia can be thought of as body forces. The other types are surface forces, which act only on surface of the body, but their effect is transmitted inside the body through the atomic and molecular bonds. In mechanical properties, we are mainly interested in the effect of applying surfaces forces such as stress or pressure [22].

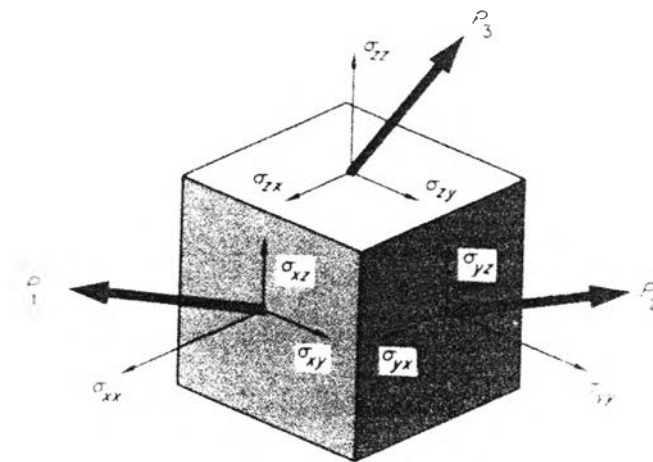


Figure 3.7.2 The component of stress

3.7.1.2 Strain

When forces are applied to a material, the atoms change position in response to the force and this change is known as strain. It is defined as ratio of the elongation to the gauge length of the test specimen, or simply stated, change in length per unit of the original length ($\Delta l/l$).

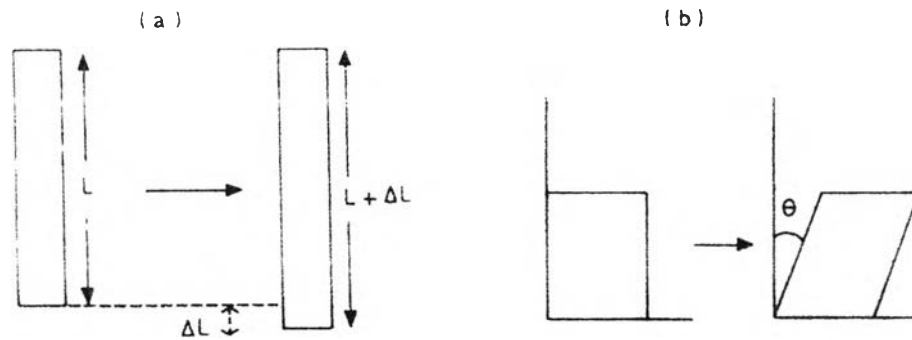


Figure 3.7.3 Illustration of (a) extensional strain (b) simple shear strain

3.7.1.3 Elongation

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

3.7.1.4 Yield Point

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

3.7.1.5 Yield Strength

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

3.7.1.6 Proportional Limit

The greatest stress at which a material is capable of sustaining the applied load without any deviation from proportionality of stress to strain.

3.7.1.7 Modulus of Elasticity

The ratio of stress to corresponding strain below the proportional limit of the material.

3.7.1.8 Break Point

The point which at a material breaks or ruptures in tension.

The stress-strain diagram illustrated in Figure 3.7.1 is typical of that obtained in tension for a constant rate of loading. However, the curves can be obtained from other loading conditions such as compression or shear.

The behavior of polymer below the proportional limit (Point C in Figure 3.7.1) is elastic in nature and therefore the deformations are recoverable. At Point B, the deformation are relatively small and have been associated with the bending and stretching of the interatomic bonds between atoms of polymer molecules as shown in Figure 3.7.4(a). At Point C in Figure 3.7.1, the deformation is similar to a straightening out of a coiled portion of the molecular chain [Figure 3.7.4(b)]. There is no intermolecular slippage and the deformations can be recovered ultimately. The extensions that occur beyond the yield point of the polymer are not recoverable [Figure 3.7.4(c)].

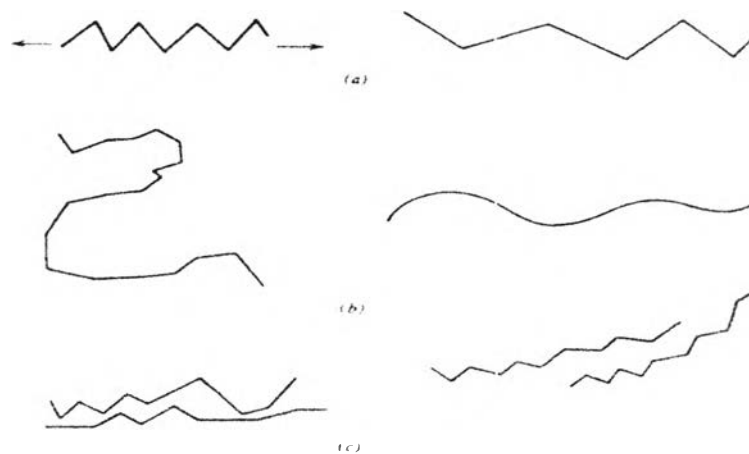


Figure 3.7.4 Extension types (a) bond bending (b) uncoiling (c) slippage

3.7.2 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 3.7.5 illustrates typical tensile stress-strain curve for several type of polymer. The area under curve is considered as the toughness. Table 3.8.1 lists characteristic features of stress-strain curve as they relate to the polymer properties.

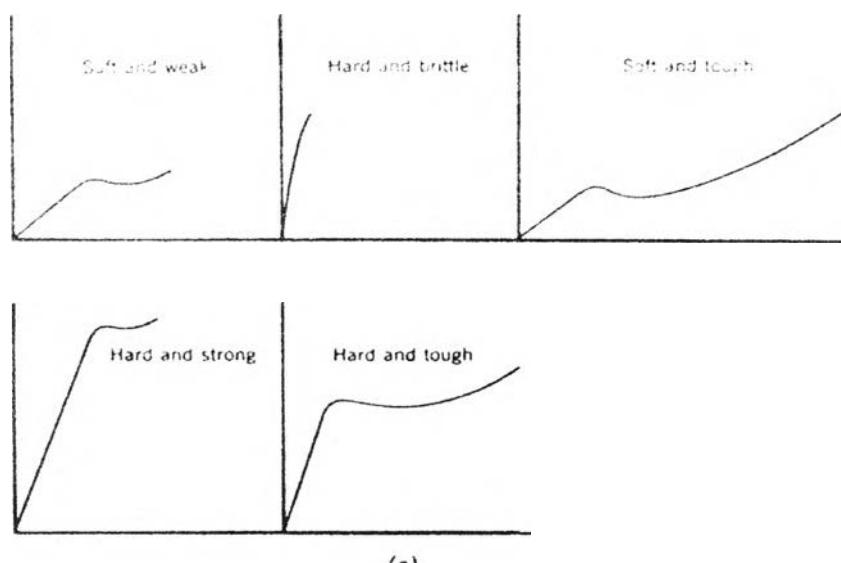


Figure 3.7.5 Types of stress-strain curve

Table 3.7.1 Characteristic features of stress-strain curve as they relate to the polymer properties.

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

3.7.3 Tensile Tests

Tensile elongation and tensile modulus measurements are among the most important indication of strength in a polymer and are the most widely specified properties of polymer. Tensile test is normally a measurement of ability of a polymer to withstand forces that tend to pull it apart and to determine to what extent the polymer stretches before breaking. Tensile modulus, an indication of the relative stiffness of a polymer, can be determined from stress-strain diagram.

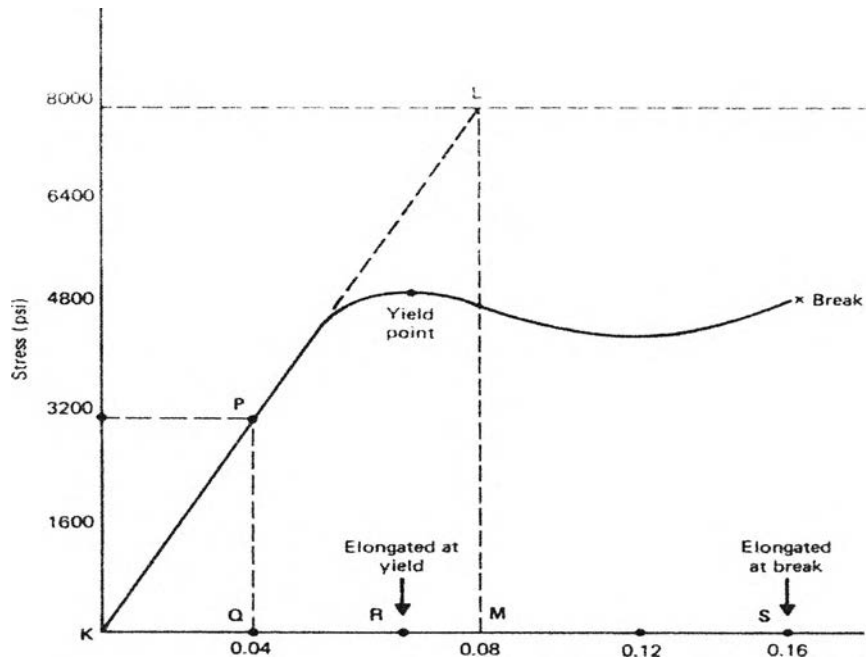


Figure 3.7.6 Diagram illustrating stress-strain curve form which modulus and elongation values are derived

3.7.3.1 Tensile strength

Tensile strength = Force (load)/Cross section area

Tensile strength at yield = Maximum load recorded/Cross section area
= Tensile stress at yield point

Tensile strength at break = Load recorded at break/Cross section area
= Tensile stress at break point

3.7.3.2 Tensile modulus and elongation

Tensile modulus = Difference in stress/Difference in strain
= Slope of stress-strain curve in elastic range

Elongation at yield = Strain at yield x Original length

Percent elongation at yield = Elongation at yield x 100

Elongation at break = Strain at break x Original length

Percent elongation at break = Elongation at break x 100

3.8 Dynamic Mechanical Analysis [23]

3.8.1 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 unuse, probably due its importation from the field of rheology. Rheology, the study of the deformation and flow of materials, has a reputation of requiring a fair degree of mathematical sophistication. Although many rheologists may disagree with this assessment, most chemists have neither the time nor the inclination to delve through enough literature to become fluent. Neither do they have an interest in developing the constituent equations that are a large part of the literature. However, 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.

Depending on whom you talk to, the same technique may be called dynamic mechanical analysis (DMA), forced oscillatory measurements, dynamic mechanical thermal analysis (DMTA), dynamic thermomechanical analysis, and even dynamic rheology. This is a function of the development of early instruments by different specialties (engineering, chemistry, polymer physics) and for different markets. In addition, the names of early manufacturers are often used to refer to the technique, the same way that “Kleenex” has come to mean “tissues”. In next topic, DMA will be used to describe the technique of applying an oscillatory or pulsing force to a sample.

3.8.2 Basic principles

DMA can be simply described as applying an oscillating force to a sample and analyzing the material’s response to that force (Figure 3.8.1). This is a simplification, and we will discuss it in next topic in greater detail. From this, one calculates properties like the tendency to flow (called viscosity) from the phase lag and the

stiffness (modulus) from the sample recovery. These properties are often described as the ability to lose energy as heat (damping) and the ability to recover from deformation (elasticity). One way to describe what we are studying is the relaxation of the polymer chains. Another way would be to discuss the changes in the free volume of the polymer that occur. Both descriptions allow one to visualize and describe the changes in the sample.

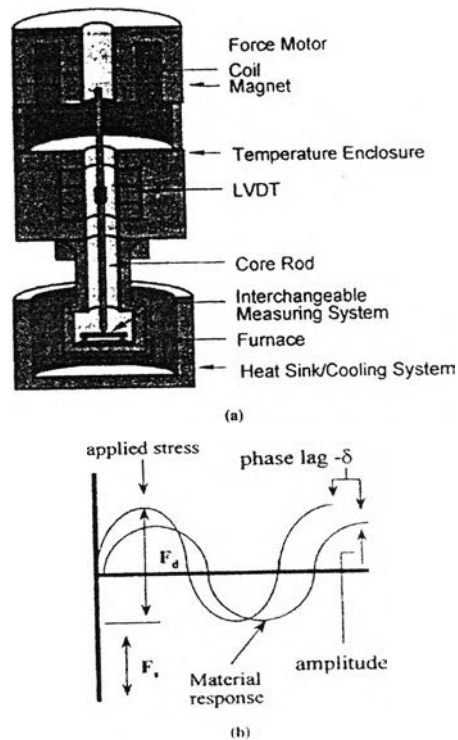


Figure 3.8.1 How a DMA works

The applied force is called stress and is denoted by the Greek letter, σ . When subjected to a stress, a material will exhibit a deformation or strain, γ . Most of us working with materials are used to seeing stress-strain curves as shown Figure 3.8.2. These data have traditionally been obtained from mechanical tensile testing at a fixed temperature. The slope of the line gives the relationship of the stress to strain and is a measure of the material's stiffness, the modulus. The modulus is dependent on the temperature and the applied stress. The modulus indicates how well a material will work in specific application in the real world. For example, if the polymer is heated so that it passes through its glass transition and changes from glassy to rubbery, the modulus will often drop several decades (a decade is an order of magnitude). This drop in stiffness can lead to serious problems if it occurs at a temperature different

from expected. One advantage of DMA is that we can obtain a modulus each time a sine wave is applied, allowing us to sweep across a temperature or frequency range. So if we were to run an experiment at 1 Hz or 1 cycle/second, we would be able to record a modulus value every second. This can be done while varying temperature at some rate, such as 10 °C/min, so that the temperature change per cycle is not significant. We can then with a DMA record the modulus as a function of temperature over a 200 °C range in 20 minutes. Similarly, we can scan a wide frequency or shear rate range of 0.01 to 100 Hz in less than 2 hours. In the traditional approach, we would have to run the experiment at each temperature or strain rate to get the same data. For mapping modulus or viscosity as a function of temperature, this would require heating the sample to a temperature, equilibrating, performing the experiment, loading a new sample, and repeating at a new temperature. To collect the same 200 °C range this way would require several days of work.

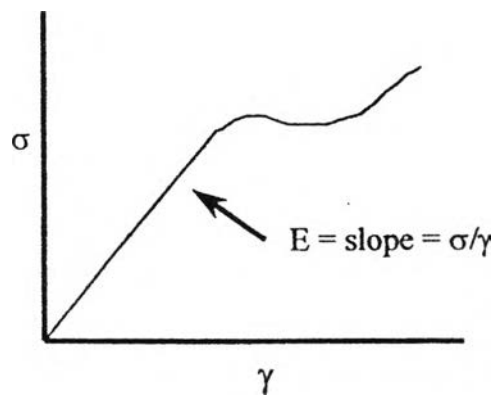


Figure 3.8.2 Stress-strain curves relate force to deformation

The modulus measured in DMA is, however, not exactly the same as the Young's modulus of the classic stress-strain curve (Figure 3.8.3). 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 ($\tan \delta$), which is called damping.

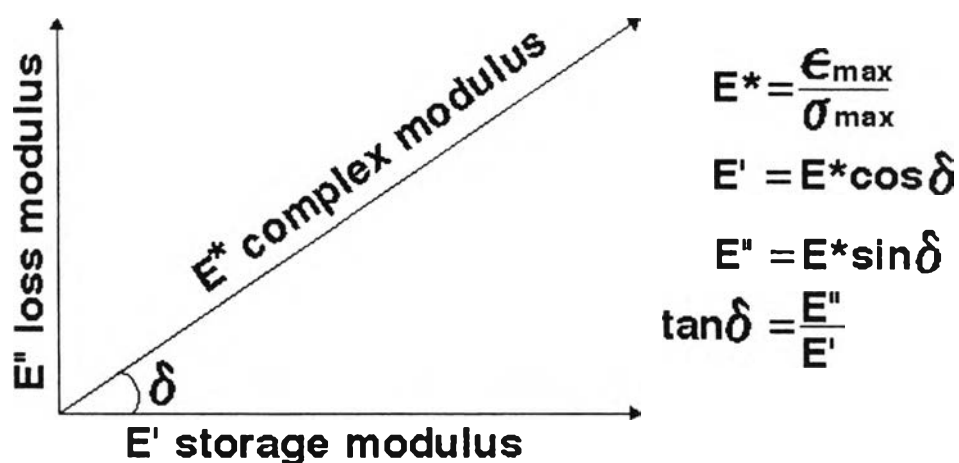


Figure 3.8.3 DMA relationships

3.8.3 Applying a dynamic stress to a sample

If we take a sample at constant load and start sinusoidally oscillating the applied stress (Figure 3.8.4), the sample will deform sinusoidally. This will be reproducible if we keep the material within its linear viscoelastic region. For any one point on the curve, we can determine the stress applied as

$$\sigma = \sigma_0 \sin \omega t \quad 3.8.1$$

where σ is the stress at time t , σ_0 is the maximum stress, ω is the frequency of oscillation, and t is the time. The resulting strain wave shape will depend on how much viscous behavior the sample has as well as how much elastic behavior. In addition, we can write a term for the rate of stress by taking the derivative of the above equation in term of time:

$$d\sigma/dt = \omega \sigma_0 \cos \omega t \quad 3.8.2$$

We can look at the two extremes of the material behavior, elastic and viscous, to give us the limiting extremes that will sum to give us the strain wave. Let's start by treating the material as each of the two extremes. The material at the spring-like or

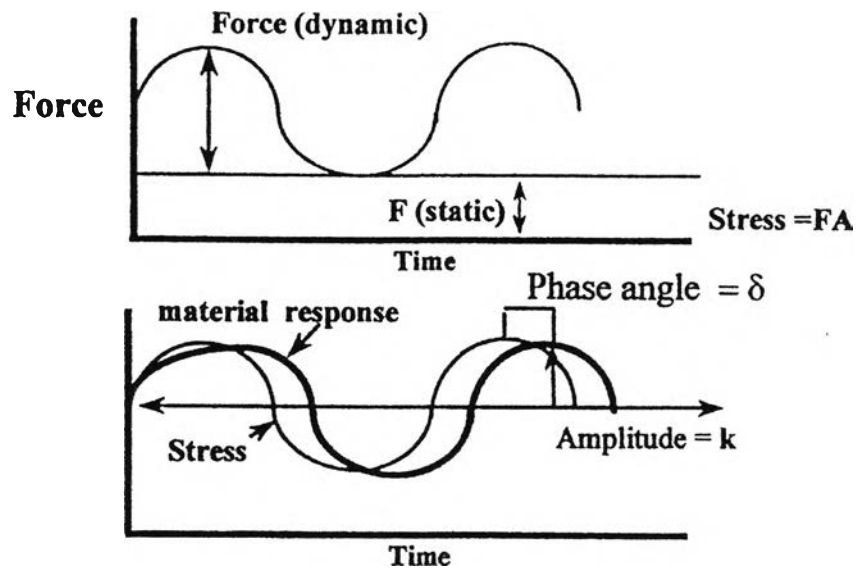


Figure 3.8.4 Oscillating a sample

Hookean limit will respond elastically with the oscillating stress. The strain at any time can be written as

$$\varepsilon(t) = (\sigma_0/E) \sin(\omega t) \quad 3.8.3$$

where $\varepsilon(t)$ is the strain at any time t , E is the modulus, σ_0 is the maximum stress at the peak of the sine wave, and ω is the frequency. Since in the linear region and are linearly related by E , we can also write that

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t) \quad 3.8.4$$

where ε_0 is the strain at the maximum stress. This curve, shown in Figure 3.8.5a, has no phase lag (or no time difference from the stress curve), and is called the in-phase portion of the curve.

The viscous limit was expressed as the stress being proportional to the strain rate, which is the first derivative of the strain. So if we take the dashpot we discussed before, we can write a term for the viscous response in terms of strain rate as

$$\varepsilon(t) = \eta \, d\sigma/dt = \eta\omega\sigma_0 \cos(\omega t) \quad 3.8.5$$

or

$$\varepsilon(t) = \eta \omega \sigma_0 \sin(\omega t + \pi/2) \quad 3.8.6$$

where the terms are as above and η is the viscosity. We can also replace terms as above to write this as

$$\varepsilon(t) = \omega \varepsilon_0 \cos(\omega t) = \omega \varepsilon_0 \sin(\omega t + \pi/2) \quad 3.8.7$$

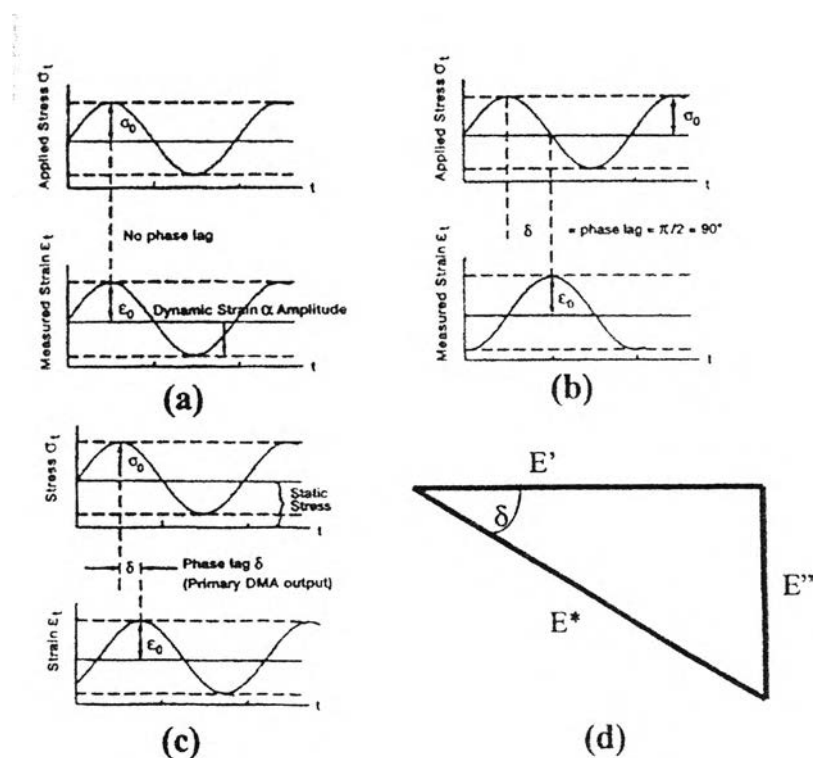


Figure 3.8.5 Material response (a) In-phase response (b) Out-phase response (c) Viscoelastic material fall in between these two lines (d) Relationship between the phase angle, E' , E'' and E^*

This curve is shown in Figure 3.8.5b. Now, let's take the behavior of the material that lies between these two limits. That curve is shown in Figure 3.8.5c and is intermediate between the above cases. The difference between the applied stress and the resultant strain is an angle, δ , and this must be added to equations. So the elastic response at any time can be written as:

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t + \delta) \quad 3.8.8$$

From this we can go back to our old trigonometry book and written this as:

$$\varepsilon(t) = \varepsilon_0 [\sin(\omega t)\cos\delta + \sin\delta\cos(\omega t)] \quad 3.8.9$$

We can now break this equation, corresponding to the curve in Figure 3.8.5c, into the in-phase and out-of-phase strains that correspond to curves like those in Figure 3.8.5a and 3.8.5b, respectively. These sum to the curve in Figure 3.8.5c and are

$$\varepsilon' = \varepsilon_0 \cos(\delta) \quad 3.8.10$$

$$\varepsilon'' = \varepsilon_0 \sin(\delta) \quad 3.8.11$$

and the vector sum of these two components gives us the overall or complex strain on the sample

$$\varepsilon^* = \varepsilon' + i\varepsilon'' \quad 3.8.12$$

This relationship can be seen as the triangle shown in Figure 3.8.5d and makes sense mathematically. But what does it mean physically in terms of analyzing the polymer behavior?

Basically, this approach allows us to “break” a single modulus (or viscosity or compliance) into two terms, one related to the storage of energy and another related to the loss of energy. This can be seen schematically in the bouncing ball in Figure 3.8.6. One term lets us see how elastic the polymer is (its spring-like nature), while require is one sinusoidal oscillation of the polymer, we can get this information quickly rather than through modulus mapping or capillary flow studies.

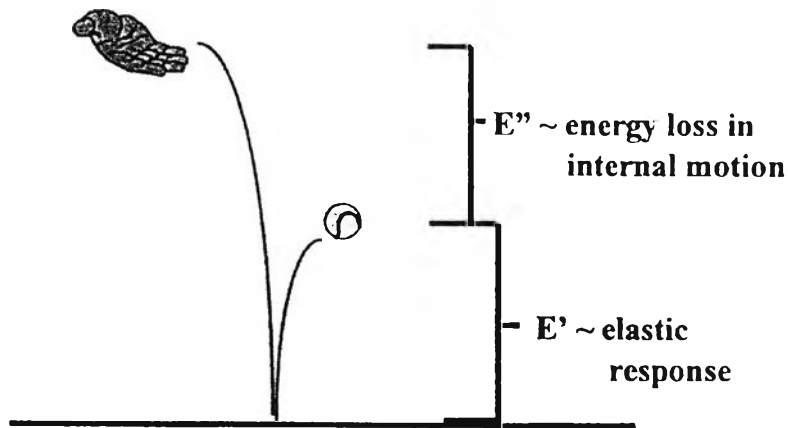


Figure 3.8.6 Storage and loss

3.8.4 Testing Geometries

We are now going to take a quick look at the commonly used fixtures for the DMA. It is important to be familiar with the effect the sample geometry has on stress and strain value, because small dimension changes often have large consequences. For measuring the temperature of transition alone, a great deal of inaccuracy can be tolerated in the sample dimension. This is not true for modulus values. Each of the geometries discussed below has different set of equations for calculating stress and strain from force and deformation. One way of handling this is the use of a geometry factor, b , used to calculate E' and E'' in Eq. (3.8.13) and (3.8.14).

$$E' = (\sigma^\circ / \varepsilon^\circ) \cos \delta = (f_0 / bk) \cos \delta \quad 3.8.1.3$$

$$E'' = (\sigma^\circ / \varepsilon^\circ) \sin \delta = (f_0 / bk) \sin \delta \quad 3.8.14$$

The equations for these geometric factors are given in Table 3.8.1. One practical use of these equations is in estimating the amount of error in the modulus expected due to the inaccuracies of measuring the sample. For example, if the accuracy of the dimensional measurement is 5%, the error in the applied stress can be calculated. Since many of these factors involve squared and cubed terms, small errors in dimensions can generate surprisingly large errors in the modulus.

Table 3.8.1 Geometric factors for fixtures

3 pt. bending bar	$x_s^3 / 4z_s y_s^3$	Parallel Plate in Shear	$y_s / 2\pi r_s^2$
3 pt. bending rod	$4x_s^3 / 6\pi r_s^4$	Cone and Plate	$\theta / 2\pi r_s^3$
Single Cantilever	$4x_s^3 / z_s y_s^3$	Couette	$\frac{1 - (R_1 / R_2)^2}{2\pi L R_1^2}$
Dual Cantilever	$x_s^3 / 16z_s y_s^3$	Torsion Bar	$\frac{3 + 8(z_s / x_s)^2}{x_s z_s^3 / y_s (1 - 0.378)(z_s / x_s)^2}$
Extention	$y_s / x_s z_s$		
Plates Compression	in $y_s / 2\pi r_s^2$		
Shear Sandwich	$y_s / 2\pi r_s^2$		

Note: These factors are used to convert the load and the amount of deformation into stress and strain by using the dimensions of the sample. The letters refer to dimensions as drawn in Figures 4.7-4.12. The dimensions for rectangular samples are width (x), height (y), and depth (z), as drawn in the respective fixture. For sample with a circular cross-section (i.e., a disk, plate, bar, or fiber), r , is the sample radius and y is again the height θ is the cone angle in a cone-and-plate fixture. For the Couette fixture, R_1 and R_2 refer to the inner and outer cylinder diameters, respectively, while L refers to the length of the inner cylinder.

Two other issues need to be mentioned: those of inertia effects and of shear heating. Inertia is the tendency of an object to stay in its current state, whether moving or at rest. When a DMA probe is oscillated, this must be overcome and as the frequency increases, the effect of the instrument inertia becomes more troublesome. Shear heating occurs when the mechanical energy supplied to the sample is converted to heat by the friction and changes the sample temperature. Both of these can occur in either analyzer, but they are more common in the fluid samples.

3.8.4.1 Axial

Axial analyzers allow a great deal of flexibility in the choice of fixture, which allows for the testing of a wide range of materials. Ease of exporting data is also important in these analyzers, as they are often adapted to run very specialized tests. For example, some contact lens manufacturers test samples on spherical plates and tubing manufacturers will use fixtures that test the tubing in its original shape. With

easy access to the raw data, one can go to Rock's and look up the stress and strain formulas for the appropriate geometry.

3.8.4.1.1 Three-point and Four-point Bending

There are four types of bending or flexure fixtures commonly used. The simplest and the most straightforward of these is the three-point bending fixture shown in Figure 3.8.7a. No flexure mode is a pure deformation, as they can all be looked at as a combination of an extension and compressive strain. Three-bending depends on the specimen being a freely moving beam, and the sample should be about 10 % longer on each end than the span. The four sides of the span should be true, i.e., parallel to the opposite side and perpendicular to the neighboring sides. These should be no nicks or narrow parts. Rods should be of uniform diameter. Throughout the experiment the beam should be freely pivoting: this is checked after the run by examining the sample to see if there are any indentations on the specimen. If there are, this suggests that a restrained beam has been tested, which gives a higher apparent modulus. The sample is loaded so the three edges of the bending fixture are perpendicular to the long axis of the sample.

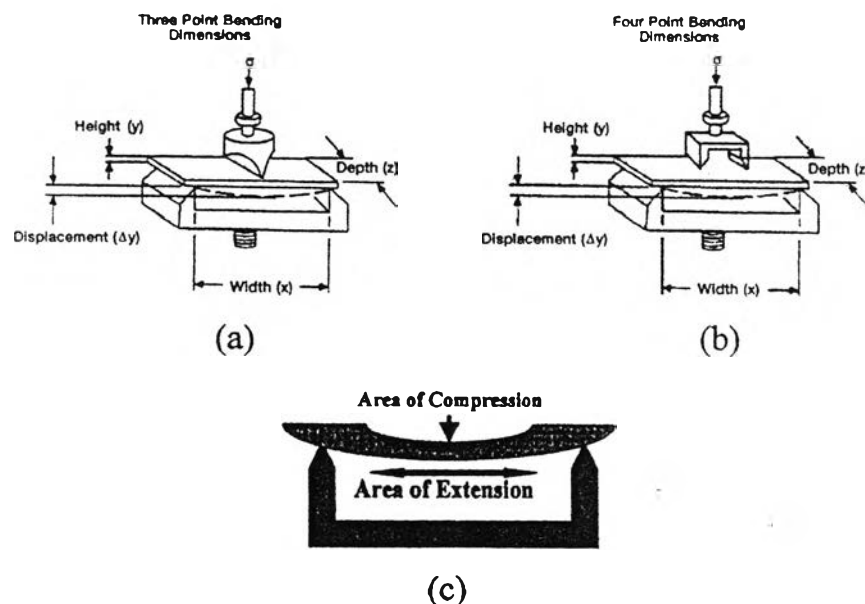


Figure 3.8.7 Flexure test I (a) three point bending (b) four-point bending and (c) compressive and tensile strains in three-point bending specimen

Four-point bending replaces the single edge on top with a pair of edges, as shown in Figure 3.8.7b. The applied stress is spread over a greater area than in three-point bending, as the load is applied on two points rather than one. The mathematics remains the same, as the flexing of the beam is unchanged. One can use either knife-edged or round-edged fixtures and, in some case, a ball probe is used to replace the center knife-edge of the three-point bending fixture to simplify alignment. As long as the specimen shows the required even deflection, these are all acceptable. Sample alignment and deformation are shown in Figure 3.8.7c.

3.8.4.1.2 Dual and Single Cantilever

Cantilever fixture clamp the ends of the specimen in place, introducing a shearing component to the distortion (Figure 3.8.8a) and increasing the stress required for a set displacement. Two types of cantilever fixture are used: dual cantilever, shown in Figure 3.8.8b, and single cantilever, shown in Figure 3.8.8c. Both cantilever geometries require the specimen to be true as described above and to be loaded with the clamps perpendicular to the long axis of the sample. In addition, care must be taken to clamp the specimen evenly, with similar forces, and not to introduce a twisting or distortion in clamping. Moduli from dual cantilever fixtures tend to run 10-20% higher than the same material measured in three-point bending. This is due to shearing strain induced by clamping the specimen in place at the ends and center, which makes the sample more difficult to deform.

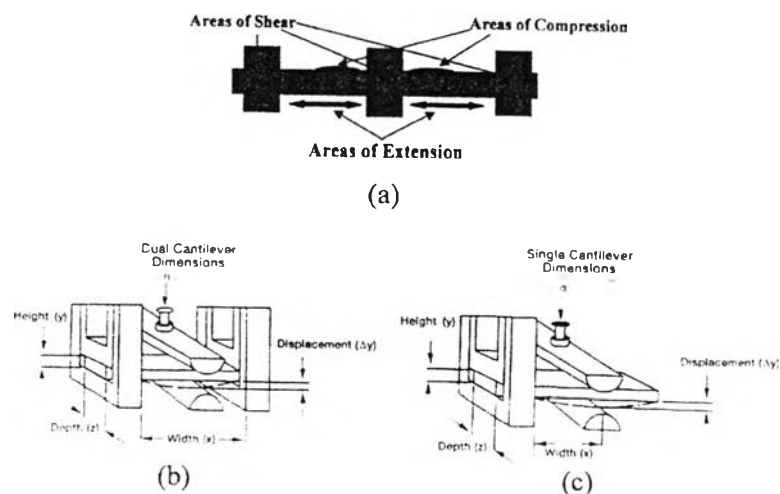


Figure 3.8.8 Flexure test fixtures II (a) Strain in a dual cantilever (b) Dual cantilever and (c) Single cantilever

3.8.4.1.3 Parallel plate and variants

Parallel plate in axial rheometers means testing in compression, and several variations of simple parallel plates exist for special cases (Figure 3.8.9a, 3.8.9b, and 3.8.9c). Sintered or sandblasted plates are used for slippery samples, plates and trays for samples that drip or need to be in contact with a solvent, and plates and cups for low viscosity materials. Photocuring materials can be studied with quartz fixtures. For samples in compression, circular plates are normally used, because these are easily manufactured and the samples can be fabricated by die-cutting films or sheets to size. Rectangular plates and samples are also used. Any type of plate needs to be checked after installation to make sure the plates are parallel. The easiest way to check the alignment is by bringing the plates together and seeing if they are touching each other with no spaces or gaps. Samples should be the same size as the plates with the edges even or flush, having no dips or bulges. On compressing, they should deform by bowing outward slightly in an even, uniform bulge.

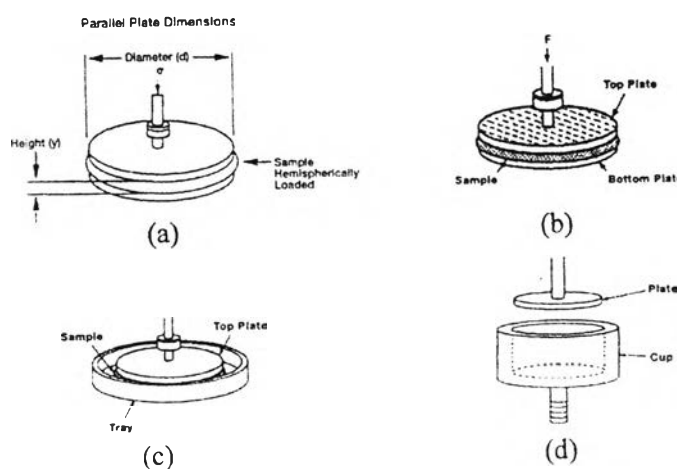


Figure 3.8.9 Parallel plate fixture for axial analyzers (a) Standard parallel plates (b) Sintered plates (c) Tray and plates and (d) Cup and plate

3.8.4.1.4 Bulk

If we run a sample in a dilatometer-like fixture (Figure 3.8.9d) where it is restrained on all side, we measure the bulk modulus of the material. This can be done in a specialized Pressure Volume Temperature (PVT) instrument with very high loads (up to 200 MPa of applied pressure) to study the free volume of the material. In this geometry, alignment is critical, as the fit between the top plate and the walls of the

cup must be very tight to prevent the material from escaping. The cup and plate/plunger system must still be able to move freely without binding.

3.8.4.1.5 Extension/Tensile

Extension or tensile analysis (Figure 3.8.10a) is done on samples of all types and is one of the more commonly done experiments. This geometry is more sensitive to loading and positioning of the sample than most other geometries. Any damage or distress to the edges of the sample as well will cause inaccuracies in the measurements. A nick in the edge will also often cause early failure, as it acts as a stress concentrator. After loading a film or fiber in extension, it is important to adjust it so that there are not any twists, the sides are perpendicular to the bottom, and there are no crinkles.

3.8.4.1.6 Shear Plates and Sandwiches

Figure 3.8.10b shows one of the two approaches to measuring shear in an axial analyzer. Shear measurements are done by a sliding plate moving between two samples. This is the common approach today. Another approach is to use a single sample, but this requires a very rigid analyzer. Again, sample size and shape must be controlled tightly for modulus data to be fully meaningful. It is very important in the shear sandwich fixtures to make sure both samples are as close to identical as possible. This technique can be difficult to run over wide temperature ranges, as the thermal expansion of the fixture can cause the clamping force to vary greatly.

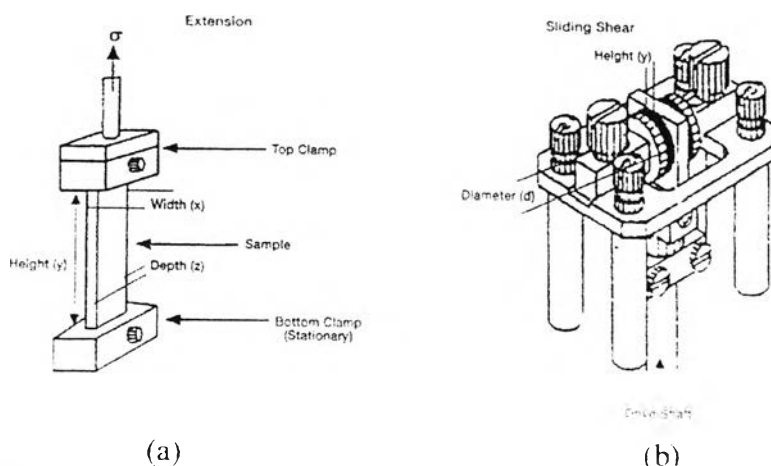


Figure 3.8.10 Extension and sliding shear fixtures (a) Extension fixture (b) Sliding plate shear fixture

3.8.4.2 Torsional

Samples run in torsional analyzers tend to be of lower viscosity and modulus than those run in axial instruments. Torsional instruments can be made to handle a wide variety of material ranging from very low viscosity liquids to bars of composite. Inertia affects tend to be more of a problem with these instruments, and very sophisticated approaches have been developed to address them. Most torsional rheometers can also perform continuous shear experiment and also measure normal forces.

3.8.4.2.1 Parallel Plates

The simplest geometry in torsional shear is two parallel plates run at a set gap height. This is shown in Figure 3.8.11a. Note that the important dimensions are the same as in Figure 3.8.10a. The height or gap here is determined by the viscosity of the sample. We want enough space between the plates to obtain decent flow behavior, but not so much that the material flies out of the instrument. The edge of the sample should be spherical without fraying or rippling. These plates have an uneven strain field across them: the material at the center of the plate is strained very little, as it barely moves. At the edge, the same degree of turning corresponds to a much larger movement. The thrust against the plate can be used to calculate the normal stress difference in steady shear runs.

3.8.4.2.2 Cone-and-Plate

The cone-and-plate geometry uses a cone of known angle instead of a top plate. When this cone angle is very small, the system generates an even, homogeneous strain across the sample. Shown in Figure 3.8.11b, the gap is set to a specific value, normally supplied by the manufacturer. This value corresponds to the truncation of the cone. The cone-and-plate system is probably the most common geometry used today for studying non-Newtonian fluids. As above, at very high shear rate, the material reaches a critical edge velocity and fails. This geometry is discussed extensively by Macosko along with other geometries for testing fluids.

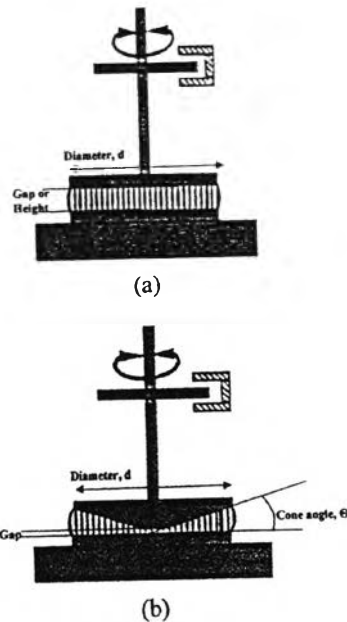


Figure 3.8.11 Plate geometries for torsion (a) Parallel plates (b) Cone and plates

3.8.4.2.3 Couette

Some materials are of such a low viscosity that testing them in a cone-and-plate or parallel plate fixture is inadvisable. When this occurs, one of the Couette geometries can be used. Also called concentric or coaxial cylinders, the geometry is shown in Figure 3.8.12a with the recessed bottom style of bob (inner cylinder). This shape is used to eliminate or reduce end effects. Other choices might be a conicylinder, where the cylinder has a cone-shaped (point) end or a double Couette, where a thin sheet of material has solution around it. The recessed end traps air, which transfers no force to the fluid, and this seems to be the one most commonly used today. This fixture requires tight tolerances, and the side gap is fixed by the design. The bottom gap is also tightly controlled and the tops of the cylinders must be flush. The fluid level must come close, say within 5 mm of the top of the fixture, but not overflow it. Both inertia effects and shear heating are concerns that must be addressed.

3.8.4.2.4 Torsional Beam and Braid

Stiff, solid samples in a torsional analyzer are tested as bars or rods that are twisted about their long axis. This geometry is shown in Figure 3.8.12b. The bar needs to be prepared as precisely as those discussed above. Another variation is the use of a braid of material impregnated with resin for curing studies. This can be a tricky approach as even nondrying oils appear to increase in viscosity or cure(cross-

linked) as they heat up (their viscosity drops and the fibers start rubbing together so that the measured viscosity appears to increase as if the material had cured).

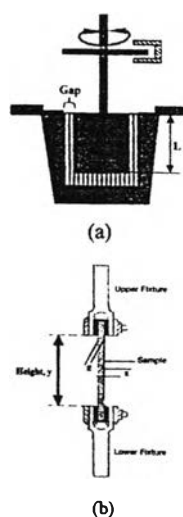
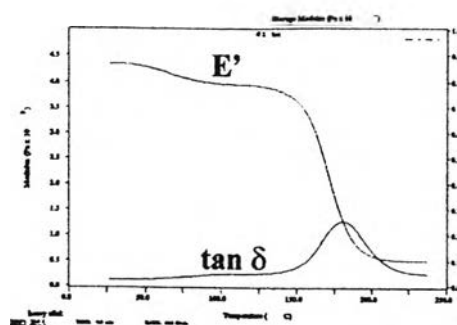


Figure 3.8.12 Couette and torsion bar (a) Couette fixture (b) Torsion bar

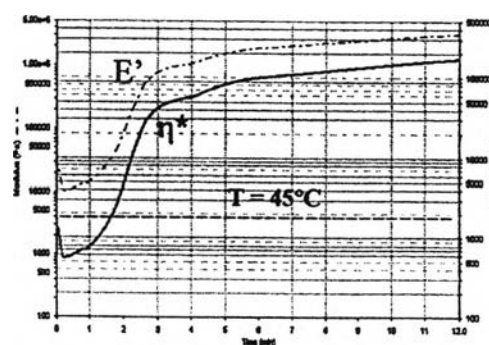
3.8.5 Time-Temperature Scans

One of most common uses of the DMA for users from a thermal analysis background is the measurement of the various transitions in a polymer. A lot of users exploit the greater sensitivity of the DMA to measure T_g 's undetectable by the differential scanning calorimeter (DSC) or the differential thermal analyzer (DTA). For more sophisticated users, DMA temperature scanning techniques let you investigate the relaxation processes of a polymer. In this topic, we will look at how time and temperature can be used to study the properties of polymers.

If we start with a polymer at very low temperature and oscillate it at a set frequency while increasing the temperature, we are performing a temperature scan (Figure 3.8.13a). This is what most thermal analysis think of as a DMA run. Similarly, we could also hold the material at a set temperature and see how its properties change over time (Figure 3.8.13b).



(a) Temperature Scan



(b) Time Scan

Figure 3.8.13 Time-temperature studies in the DMA (a) Vary temperature (b) Hold temperature constant

3.8.5.1 Transition in polymer

The thermal transitions on polymers can be described in terms of either free volume change or relaxation times. While the latter tends to be preferred by engineers and rheologists in contrast to chemist and polymer physicists who lean toward the former, both descriptions are equivalent. 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. Defined as the space a molecule has for internal movement, it is schematically shown in Figure 3.8.14a. 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 3.8.14b). This increased mobility in either side chains or small groups of adjacent backbone atoms result in a greater compliance (low modulus) of the molecule.

3.8.5.1.1 Sub- T_g Transitions

As we move from very low, where the molecule is tightly compressed, we pass first through the solid state transitions. This process is shown in Figure 3.8.15(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 3.8.15(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.

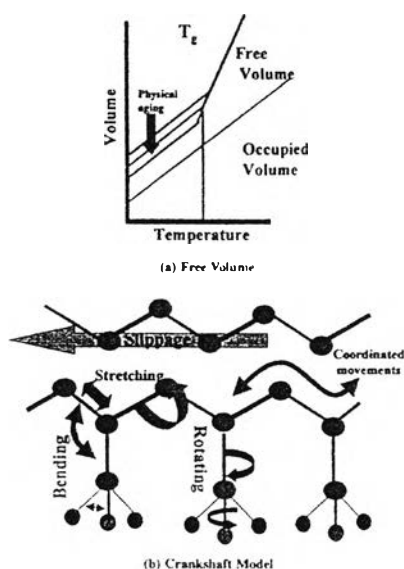
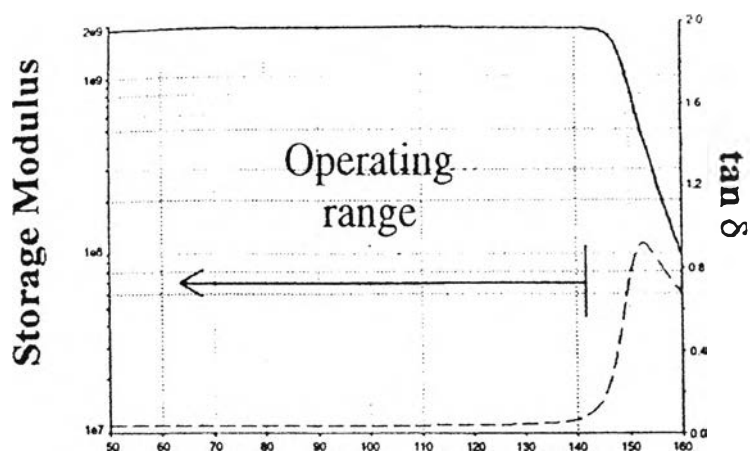
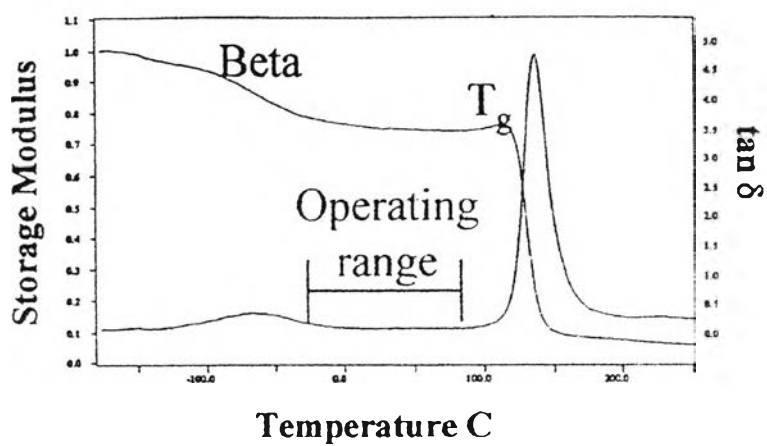


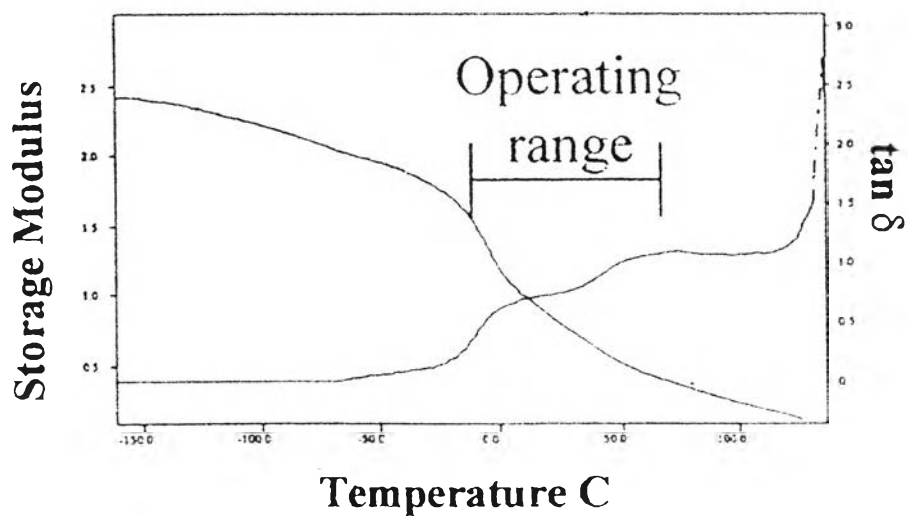
Figure 3.8.14 Free volume in polymer (a) The relationship of free volume to transition (b) A schematic example of free volume and crankshaft model



(a)



(b)



(c)

Figure 3.8.16 Operating range by DMA (a) Polycarbonate (b) Epoxy and (c) Polypropylene

3.8.5.1.3 The rubbery plateau, T_{α}^* and T_{II}

Continued heating bring us to the T_{α}^* and T_{II} (Figure 3.8.15(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 instead see the T_{II} , 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.

3.8.5.1.4 The terminal region

Finally, we reach the melt (Figure 3.8.15(2)) where large-scale chain slippage occurs and the free volume has increased so that the chains slide 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.

3.8.5.2 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.

3.8.6 Time-Temperature Superposition [24]

Remembering that the modulus is a function of time as well as temperature leads one to wonder about the feasibility measuring the modulus as a function of time at constant temperature instead of, as we have done throughout the first part of this topic measuring the modulus as a function of temperature at constant time. In

principle the complete modulus versus time behavior of polymer at any temperature can be measured. A number of convenient approaches are available. The results of such an experiment are shown on the left hand side of Figure 3.8.17 where tensile stress relaxation has been chosen as the experiment. Clearly only a small range of viscoelastic response manifests itself during an experimentally accessible time range of perhaps 10 seconds to 1 hour. Consider, for example, the experiment at temperature T_2 . We observe that the modulus decays by a factor of about 10 in this period of time, a decrease in modulus far short of the five orders of magnitude which we observed in the modulus temperature experiments. If one were to carry out the experiment at a different temperature, different behavior would result; again this is shown on the left hand side of Figure 3.8.17. Clearly then, it is not feasible to directly measure the complete behavior of the modulus as a function of time at constant temperature using methods such as those described in Topic 3.7.

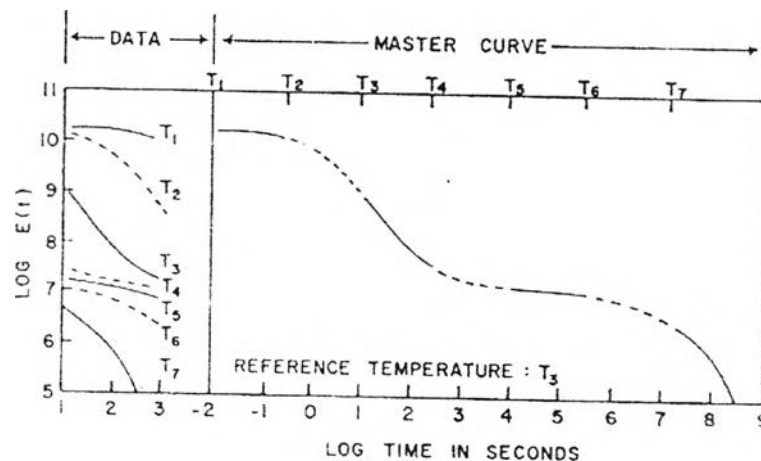


Figure 3.8.17 Preparation of a Stress Relaxation Master Curve from Experimentally Measured Modulus-Time Curves at Various Temperatures

Experimentalists have found a shifting procedure which enables one to construct a "master curve" (complete modulus-time behavior at a constant temperature) in spite of this limitation. This technique is based on the principle of time-temperature correspondence.

Consider, now, the curve measured at T_1 and terminating at about 1000 seconds. The time-temperature correspondence principle states that there are two methods to use in order to determine the polymer's behavior at longer times. First, one may directly measure the response at longer times. This technique rapidly becomes prohibitively time-consuming since the change is so slow (Figure 3.8.17 is plotted on a log scale). Secondly, one may increase the temperature to T_2 , for example, and then carry out the relaxation experiment on an experimentally accessible time scale again. Now one observes that shifting curve T_2 horizontally to the right will result in an exact superposition of the curves measured T_1 at and T_2 in the areas where the modulus values overlap and an extension of the curve measured at T_2 to modulus values lower than those measured at temperature T_1 . The time-temperature correspondence principle states that this extension is identical to that which would be measured at long times at the temperature T_1 . Thus one effectively has a measure of the complete modulus-time behavior by applying the time-temperature correspondence principle to experimental measurements of polymer relaxations carried out on experimentally accessible time scales.

Mathematically these ideas may be expressed as

$$E(T,t) = E(T_2, t/a_T) \quad 3.8.15$$

where the effect of changing temperature is the same as applying a multiplicative factor to the time scale, i.e., an additive factor to the log time scale.

Although this discussion of the time-temperature correspondence principle is essentially correct, one additional correction is necessary. We have, by shifting horizontally, compensated for a change in the time scale brought about by changing temperature. There is also, however, an inherent change in the modulus brought about by a change in temperature. In previously it will be shown that the modulus of a rubbery network is directly proportional to T , the absolute temperature. Thus, in applying a reducing procedure to make a master curve for individual relaxation experiments, not only must one take into account the time scale shift, one must also consider that there will be a slight vertical shift due to the temperature variation. Similarly, since the volume of a polymer is a function of temperature and the modulus, being defined per unit cross sectional area, will obviously vary with the

amount of matter contained in unit volume, a corresponding correction must be made so that changing mass per unit volume as a function of temperature is accounted for. The density is obviously the parameter which must be used. These considerations lead one to write

$$\frac{E(T_1, t)}{\rho(T_1)T_1} = \frac{E(T_2, t/a_T)}{\rho(T_2)T_2} \quad 3.8.16$$

Division by the temperature corrects for the changes in modulus due to the inherent dependence of modulus on temperature while division by the density corrects for the changing number of chains per unit volume with temperature variation.

When constructing a master curve, one arbitrarily picks a reference temperature, T_0 . The modulus at any time t , which one would observe at the temperature T_0 in terms of the experimentally observed modulus values at different temperatures T , is therefore given as

$$E(T_0, t) = \frac{\rho(T_0)T_0}{\rho(T)T} E(T, t/a_T) \quad 3.8.17$$

where a_T is to be discussed more fully. If one is considering compliance functions, equation 3.8.16 takes the form, using $J(t)$ as an example,

$$\rho(T_1)T_1J(T_1, t) = \rho(T_2)T_2J(T_2, t/a_T) \quad 3.8.18$$

and

$$J(T_0, t) = \frac{\rho(T)T}{\rho(T_0)T_0} J(T_2, t/a_T) \quad 3.8.19$$

3.8.7 Master Curve

We may now consider the preparation of a master curve from the data in Figure 3.8.17. First, let us arbitrarily pick T_3 as the reference temperature. With a knowledge of the density at all the temperatures T_i , one applies the vertical correction factor stated in equation 3.8.17 to all the curves. For T_3 the factor $\rho(T_0)T_0/\rho(T)T$ is unity resulting in no shift. This must be so since T_3 has been chosen as the reference. At the other temperatures, however, the correction factor will not in general be unity.

Let us now consider that these corrections have been made to the experimental curves on the left hand side of Figure 3.8.17. The curve at T_3 is reproduced on the right hand side of the figure. Next, the curve at T_2 is shifted to the left giving rise to the dotted extension of the $E(T_3,t)$ curve. This process is repeated until the complete master curve is formed. Again this procedure is mathematically described by equation 3.8.17. The a_T 's are functions of temperature and are known as the shift factors. The subscript T indicates that the shift factors are taken relative to some standard temperature. In our example, all of the curves at temperature higher than T_3 are shifted to the right, those at T_1 and T_2 are shifted to the left. It should be clear that any temperature might have been chosen as the reference temperature. If T_4 had been chosen, for example, some of the shift factors would have been larger than 1.0 -those at lower temperatures- while some of the shift factors would have been less than 1.0-those at temperatures higher than T_4 .

3.8.8 The WLF Equation

It is now common practice to reduce most relaxation or creep data to the temperature T_g ; thus, the reference temperature is picked as the glass transition temperature measured by some slow technique such as dilatometry. The function $\log a_T$ for this choice of reference temperature is shown in Figure 3.8.18. Here again, at the reference temperature a_T is 1.0 and $\log a_T$ is 0. All amorphous polymers exhibit similar behavior on such a plot. The equation of this curve is

$$\log a_T = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \quad 3.8.20$$

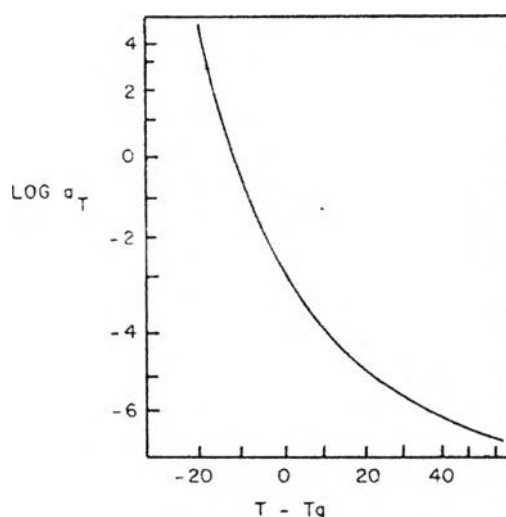


Figure 3.8.18 The WLF Equation for Polystyrene

The equation is called the WLF equation (Williams, Landel, and Ferry) after its discoverers. The constants C_1 and C_2 , originally thought to be universal constants, have been shown to vary rather slightly from polymer to polymer. A list of C_1 and C_2 for several of the most common polymers is presented in Table 3.8.2.

Table 3.8.2 WLF parameters

Polymer	C_1	C_2	T_g ($^{\circ}\text{K}$)
Polyisobutylene	16.6	104	202
Natural rubber (Hevea)	16.7	53.6	200
Polyurethane elastomer	15.6	32.6	238
Poly(ethyl methacrylate)	17.6	65.5	335
"Universal constants"	17.4	51.6	

The form of equation 3.8.20 is straightforwardly predicted from rather simple theoretical considerations. First, however, we must realize that the shift factor a_T is not only meaningful in terms of moduli. The equation

$$\eta(T) = \int_0^{\infty} E(T, t) dt \quad 3.8.21$$

will be developed. $\eta(T)$ is the tensile viscosity of a polymer at the temperature T .

Consider two master curves at the different temperatures, T_g , which we will call the reference temperature, and T , any other temperature. We can write

$$E(T_g, t_{ref}) = E(T, t) \quad 3.8.22$$

where we have constrained that every modulus value $E(T_g, t_{ref})$ has a corresponding modulus value of equal magnitude $E(T, t)$ on the master curve at temperature T . In writing this equation, we have implied a relationship between t_{ref} and t which, in the context of the above discussion, is realized to be

$$t_{ref} = \frac{t}{a_T} \quad 3.8.23$$

where a_T is a function of T_g and T only. This is just another statement of time-temperature correspondence. (We are neglecting the vertical shifts for simplicity; their inclusion would substantially add to the complexity of this discussion but would not substantially affect the outcome.)

From equation 3.8.23 it is clear that

$$dt = a_T dt_{ref} \quad 3.8.24$$

since a_T is not a function of time. Equation 3.8.21 becomes

$$\eta(T) = \int_0^{\infty} E(T, t) dt = \int_0^{\infty} E(T_g, t_{ref}) dt \quad 3.8.25$$

where the last expression results from substitution of equation (3.8.22) into equation 3.8.21). In spite of the similarity of notation, t_{ref} and t are different variables as is obvious from equation 3.8.23. Eliminate dt via equation 3.8.24 yields

$$\eta(T) = \int_0^{\infty} E(T_g, t_{ref}) a_T dt_{ref} \quad 3.8.26$$

where the limits of the integral are unchanged. Under this integration however, a_T is a constant which can be factored out leaving an integral of the form of equation 3.8.21; thus

$$\eta(T) = a_T \eta(T_g)$$

$$a_T = \frac{\eta(T)}{\eta(T_g)} = \frac{\eta(T)}{\eta(T_{ref})} \quad 3.8.27$$

where the latter expression results from the fact that we arbitrarily chose T_g as the reference temperature.

We may now return to the theoretical rationalization of the form of the WLF equation. The starting point is the semiempirical Doolittle equation for the viscosity of a liquid

$$\ln \eta = \ln A + B \left(\frac{V - V_f}{V_f} \right) \quad 3.8.28$$

which gives an expression for the viscosity of a system in terms of two constants A and B. We will assume this viscosity is the tensile viscosity. V is the total volume of the system while V_f is the free volume available to the system (a qualitative rather than quantitative view of free volume is sufficient for this discussion). The interpretation of equation 3.8.28 is that viscosity is intimately connected with mobility which, in turn, is closely related to free volume. As the free volume increases, the viscosity rapidly decreases. This equation has been found to express the viscosity dependence of simple liquids to a high degree of accuracy. Rearrangement of equation 3.8.28 gives

$$\ln \eta = \ln A + B \left(\frac{1}{f} - 1 \right) \quad 3.8.29$$

where f is the fractional free volume V_f/V . It is now assumed that above the glass transition temperature, the fractional free volume increases linearly, that is

$$f = f_g + \alpha_f (T - T_g) \quad 3.8.30$$

where f is the fractional free volume at T , any temperature above T_g , f_g is the fractional free volume at T_g , and a , is the thermal coefficient of expansion of the fractional free volume above T_g . In terms of equation 3.8.25 the Doolittle equation becomes

$$\begin{aligned}\ln \eta(T) &= \ln A + B \left(\frac{1}{f_g + \alpha_f (T - T_g)} - 1 \right) a T > T_g \\ \ln \eta(T_g) &= \ln A + B \left(\frac{1}{f_g} - 1 \right) a T_g\end{aligned}\quad 3.8.31$$

Subtraction yields

$$\frac{\ln \eta(T)}{\ln \eta(T_g)} = B \left(\frac{1}{f + \alpha_f (T - T_g)} - \frac{1}{f_g} \right) \quad 3.8.32$$

which simplifies to

$$\frac{\ln \eta(T)}{\ln \eta(T_g)} = \log a_T = - \frac{B}{2.303 f_g} \left(\frac{T - T_g}{(f / \alpha_f) + T - T_g} \right) \quad 3.8.33$$

a form identical to the WLF equation where C_1 is identified with $(B/2.303f_g)$ and C_2 with α_f/f_g . Thus the form of the WLF equation results from the accurate empirical Doolittle equation and the assumption of a linear expansion of free volume above T_g .

The complete viscoelastic response of any polymer under any experimental conditions may be obtained from knowledge of any two of the following three functions: the master curve at any temperature, the modulus-temperature curve at any time and the shift factors relative to some reference temperature. For example, suppose we are given the constants C_1 and C_2 for a polymer whose master curve is known. For simplicity, we can assume that the master curve is at the same reference temperature as that in the WLF equation, perhaps T_g . Suppose it is desired to calculate the 10-second modulus versus temperature curve for this polymer. The 10-second modulus at T_g is read directly from the master curve. Now however, the master curve can be shifted to exhibit the behavior of the polymer at some other temperature. The amount of shift on a log scale, $\log a_T$, is given by equation 3.8.20 where C_1 and C_2 used are those given. Applying this horizontal shift, with the slight additional vertical correction, if significant, allows one to "predict" the 10-second modulus, at this new

temperature from the shifted curve. This procedure is repeated until the entire modulus-time curve is generated Figure 3.8.21.

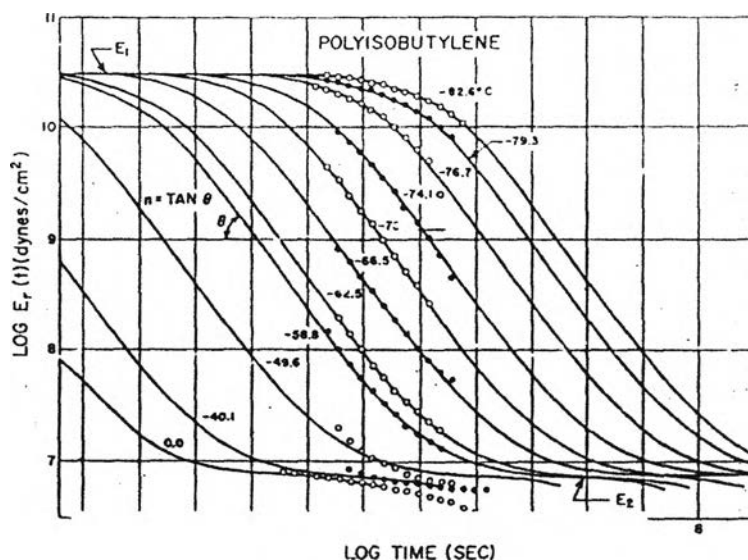


Figure 3.8.19 Plot of a Stress Relaxation Master Curve at Various Temperatures

Having thus generated the manifold of curves shown in Figure 3.8.19, it is possible to view the dependence of the modulus-temperature plots on the arbitrary choice of time. This is done merely by picking points off intersections of the master curves with vertical lines drawn from the point of interest on the time scale. The result of such treatment of the data is shown in Figure 3.8.20. It is apparent that the longer the constant time of measurement, the sharper the resulting curves. In fact, if it is assumed that the ideas embodied in the WLF equation are applicable at temperatures considerably below T_g , it can be shown that an experiment of the type depicted in Figure 3.8.20 carried out infinitely slowly would result in a true second order thermodynamic transition, i.e., a discontinuity in the modulus, at a temperature about 50°C below T_g .

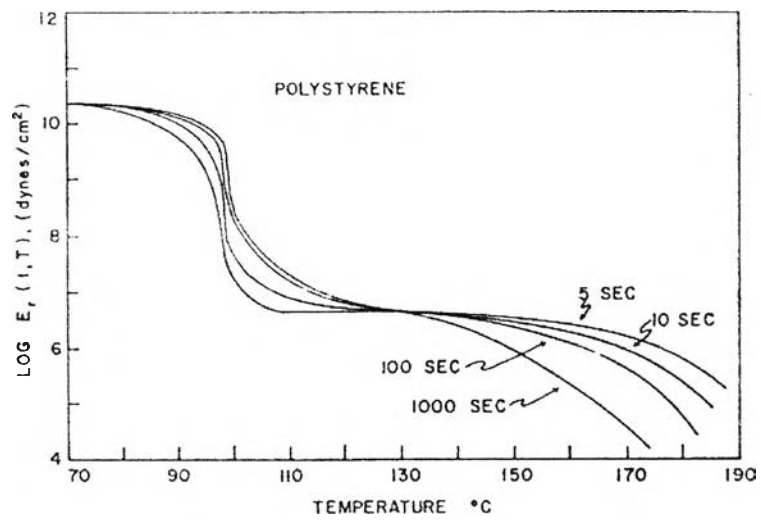


Figure 3.8.20 Plot of Modulus Versus Temperature Curves for Various Values of the Constant Time.