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Chapter 1

Review (Chapters 1-4 Tadmor and Gogos).

Processing is the source of much of the variability in properties of synthetic polymers. Different processing conditions determine the difference between a milk jug and, to a great extent, a high strength PE fibers (Ultra oriented). Processing is one component of a series of steps that lead to a plastic product or component from raw feed stocks. ALthough each commodity polymer has a somewhat different sequence of industrial stages involved in bringing it to market, a simple and fairly examplary case is a polyethylene bottle a Shampoo.

Polyethylene is polymerized from ethylene monomer that is a byproduct of the refining of crude oil and is a component of natural gas. A large oil company such as Exxon separates ethylene from crude oil in a refinery and sells the ethylene to a relatively small company that owns an ethylene pipeline. Ethylene pipelines exist throughout the southern United States along the Gulf Coast. The pipeline company is usually a small company due to the high liability associated with the mantainance of this critical system (*pipelines periodically blow-up!*). The pipeline industry is a high-risk/high-profit industry. Sales of ethylene, e.g. Exxon, is a lower-risk, commodity industry that is basically subject to the price of oil.

Polyethylene companies, including the same companies that sold ethylene to the pipeline company, then purchase (or buy back) ethylene from a variety of sources by taping into the extensive pipeline system. Companies such as Equistar, for example, enter the olefin business largely at this point. Depending on the catalyst system and type of reaction, a variety of polymer products can be produced at this stage ranging from elastomeric metallocene ethylenes and copolymers to rigid high density polyethylene (milk jugs) and abrasion resistant ultra high molecular weight polyethylene (truck bed liners). *The processability of the final product depends*

on the details of the synthetic protocol so many process engineers are involved to work with the synthesis plants in control of the product and trouble shooting of the synthetic operation.

The various grades offered by a large polyolefin producer, such as Equistar, are partly composed of blends of different branch content, molecular weight and density polyethylenes from different synthetic reaction conditions. For example, a film blowing grade of polyethylene for clear baggies might contain a blend of linear low density polyethylene, controlled branch content metallocene polyethylene and low density polyethylene. These blends might include polymers made in-house as well as some components from competitor olefin producers. Polyolefin producers often purchase or "rent" each others synthetic technology (license patents) and such patent royalties can often be a large component of profits for some polyolefin companies (Phillips Petroleum for instance). *Blending of different grades and production of pellets from the usually powder reactor products involve a variety of processing steps and require process engineers.*

The polyethylene industry is a commodity product industry governed on the supply-side by the price of oil on the world market and on the demand-side by the consumer product, housing and automotive industries. The combined action of these markets has lead to a characteristic boom/bust cycle of about 10 years time-period driven by under capacity for olefin production at the peak and over capacity at the valley. Typically, the large corporations involved in this boom and bust cycle are too slow to react to a fairly predictable economic cycle, constructing new plants at the worst possible time and failing to construct new capacity at exactly the wrong time! Despite this boom/bust cycle the polyolefin producers have proven the most reliable employment in the polyolefin system with the exception of the end users in the consumer product/automotive/construction products industries.

An example of a final product is a shampoo bottle that is injection molded from a high density grade of polyethylene sold by a company such as Equistar. The shampoo is sold by a company like Procter and Gamble and there is extensive interaction between a company like Equistar and the "end" user, P&G, although P&G may never purchase Equistar polyethylene at all. The purchaser of the polyethylene pellets is usually a small processing company that owns a number of injection molders and proprietary molds. The molds are provided by P&G, for instance, under a proprietary license to the processing company. P&G may also require the processor to purchase a certain type of polyethylene such as a certain Equistar grade of high density polyethylene. The processing company is typically a high throughput, low profit margin facility and may be producing bottles from competitive brands in the same facility! The low profit margin and high throughput make such a processing operation unable to support a large engineering staff, although the owners of such a processing plant and the executive officers might typically come from either a company like Equistar or Procter & Gamble. *Some jobs exist at such processing facilities, however, perhaps the best jobs in the processing industry are at the*

end-user company where new concepts for products, bottles in this case, are designed and tested with different grades of polymers from a variety of sources.

In the end, the bottle for the shampoo product may represent only a small fraction of the total cost of the product (1 to 5 cents) but may be of utmost importance to the consumer product company in terms of product recognition and in terms of effective storage and dispensing of the product.

Polymer processing, then is of importance to a variety of parts of a fairly intricate industrial complex. Understanding some of the features of polymer processing can be an asset in dealing with production problems encountered not only in the polymer and plastics industry but in almost every area of manufacturing ranging from biomedical devices to micro-electronics. In almost every case of the processing of polymers, the materials are processed in the liquid state and the crucial step of formation involves flow. For this reason, the chief topic of polymer processing is polymer rheology (flow). *Rheology* is a subtopic of the physical subject of *dynamics* and deals with non-equilibrium or *kinetic* phenomena. In general, the subject of polymer processing and rheology has been best suited for the field of Chemical Engineering since this subject area has had the largest interest and has made the most contributions to fluid flow problems. Polymer flow problems are the primary topic of a subfield of rheology that deals with *non-Newtonian fluids or non-Newtonian rheology*. Non-Newtonian rheology deals with fluids that differ dramatically from Newtonian fluids such as water or gas flow.

Following the motif of other Chemical Engineering disciplines, Polymer Processing can be categorized according to type of equipment used (Unit Operations):

- Extrusion
- Injection Molding
- Blow Molding
- Calendering
- Mixing/Dispersion
- Rotational Molding

These can be further categorized into Batch or Continuous Unit Operations. The unit operations approach is a historic approach (1940's) and was largely given up in the Chemical Engineering field with the rapid advent of new and diverse operations. It became extremely cumbersome to include new unit operations for each new type of operation and it became evident that all unit operations rely on certain universal physical steps of the handling of materials.

The modern Chemical Engineering approach is to study the Elementary Steps (or physical stages) of all Unit Operations in a single focal area and to then demonstrate how these Elementary Steps fit into each of the typical unit operations. This allows the student the

flexibility of understanding new operations in the context of known operations. The typical Elementary steps of polymer processing are:

- 1) particulate solids processing
- 2) melting
- 3) pressurization and pumping
- 4) mixing
- 5) devolatilization and stripping

Figure 17.1 in the text(Tadmor and Gogos) shows how an extruder, *the most fundamental unit operation of polymer processing*, can be broken down into these steps.

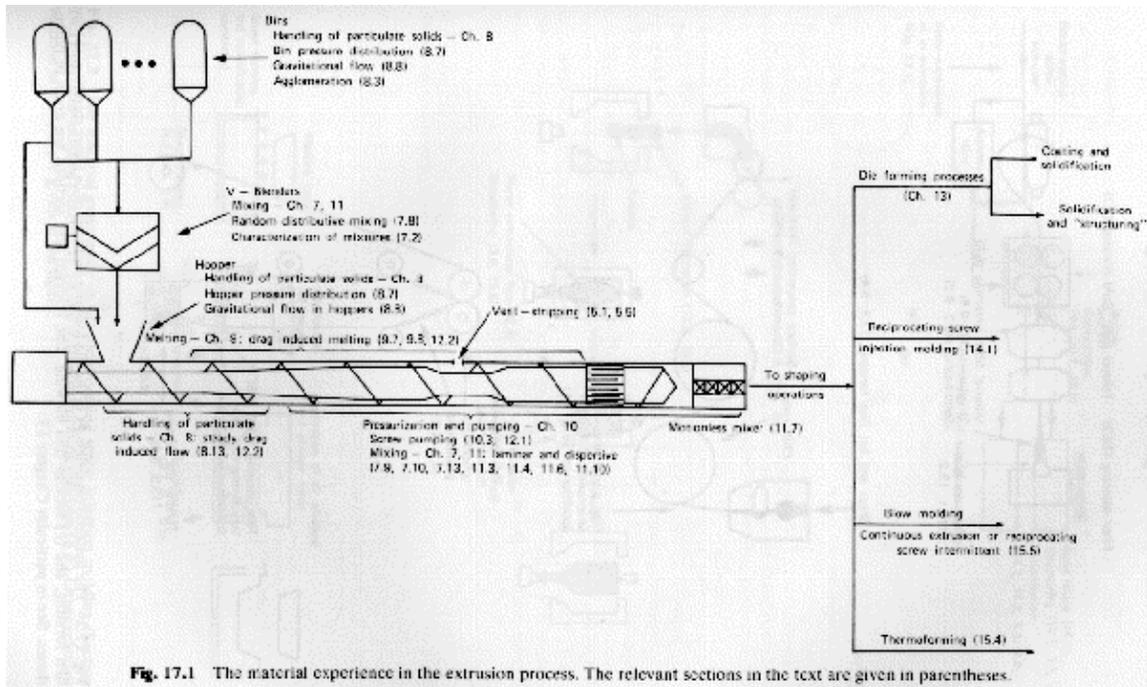


Figure 17.1, Tadmor and Gogos, "Principles of Polymer Processing"

[Click for Full Scale Picture](#)

Since the most most important and most difficult topic in processing involves polymer flow, the focus in this course will be on *the rheology of complex fluids in processing geometry's*. This is the only course in the undergraduate materials curriculum that deals with non-newtonian rheology so some overview of the basics of fluid flow, as described by Chemical Engineers, will be discusses. The tools needed to understand polymer flow include:

1. Transport Equations

2. Vectors and Tensors
3. Models for Flow
4. Constitutive Equations

We will also cover the fundamentals of mixing since this is a crucial stage in most polymer processing operations.

Polymer Processing Industry

Polymers offer certain unique problems in processing. They are visco-elastic fluids which display high viscosity's and broad transition temperatures. Machinery is large and involves a significant energy input. Polymers degrade (chain breakup) resulting in a loss of properties with exposure to high temperatures and shear for an extended period of time. Due to the chain nature of polymers, the molecular structure tends to align when subjected to a shear field. Such a change in structure is usually involved in non-Newtonian flow, and in the case of linear polymers the orientation of chains leads to a reduction in the force required to drive flow as the shear rate increases. This is termed *shear-thinning behavior* in rheology. The orientation of chains also results in a net force lateral to the direction of flow associated with the *spring-back* of the deformed polymer chains. Forces lateral to the direction of flow in a shear flow operation are called *normal forces*. Normal forces are a dominant feature of polymer processing.

Screw Extruder

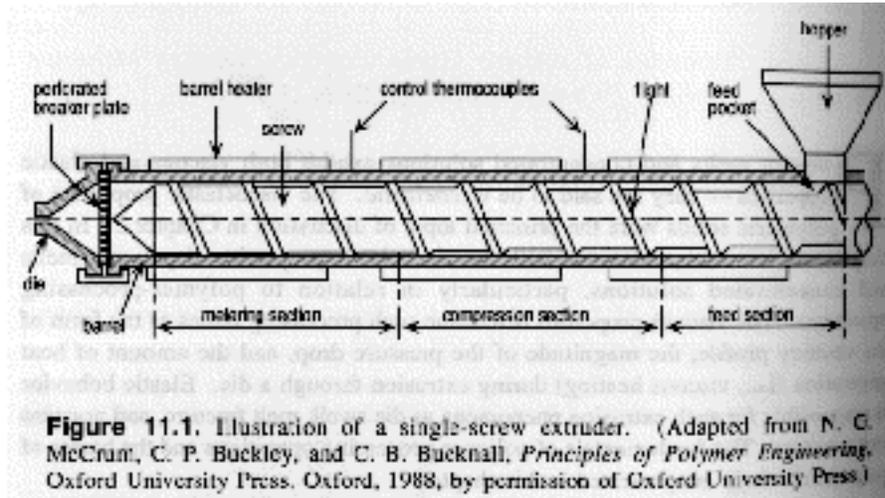
Because of its simplicity and ability to deliver high shear rates the *screw extruder* is a crucial component of almost every polymer processing operation. For example a screw extruder is a component of injection molding, fiber spinning, film casting, film blowing, wire coating and is used as a feed to calanders etc. The screw extruder serves three main functions:

1. Pumping
2. Melting
3. Mixing

Some basic processing terms for various processing operations are:

1. Extruder:
 - Die Swell = polymer stream expands on exiting die due to normal forces related

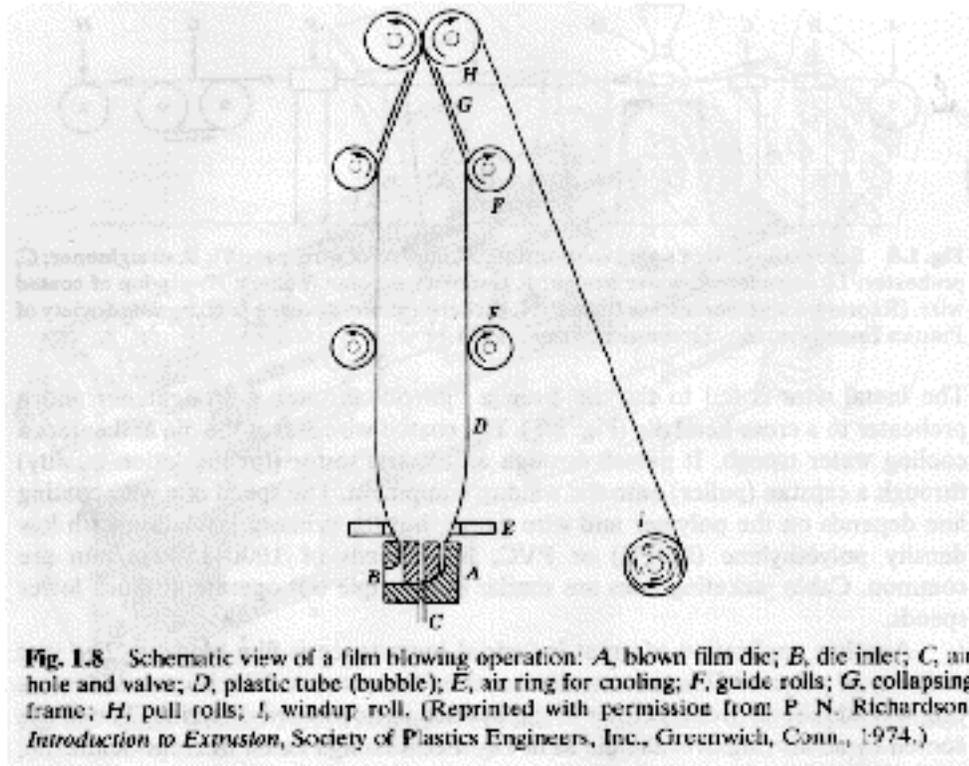
to relaxation of the coils.



From J. R. Fried, "Polymer Science and Technology"

2. Film Blower (fed by a screw extruder):

- i. Blow-up ratio = Bubble Diameter/Die Diameter (typically 1.5 to 4)
- ii. Biaxial Orientation
- iii. Frost Line= in blowing a semi-crystalline film (PE) the point where the polymer crystallizes



Tadmor and Gogos, "Principles of Polymer Processing" Figure 1.8

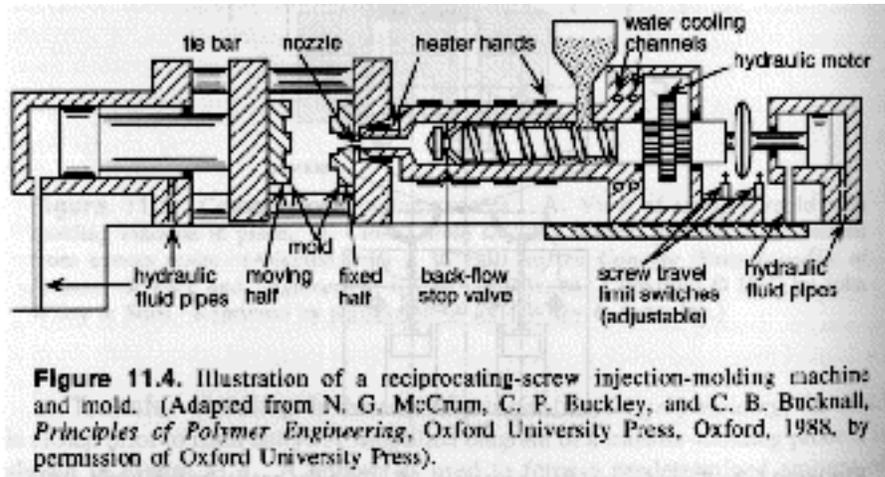
3. Fiber Drawing Machine

- i. Draw Ratio= Take-up Rate/Extrusion Rate (typically 10 to 100)
- ii. Uniaxial Orientation

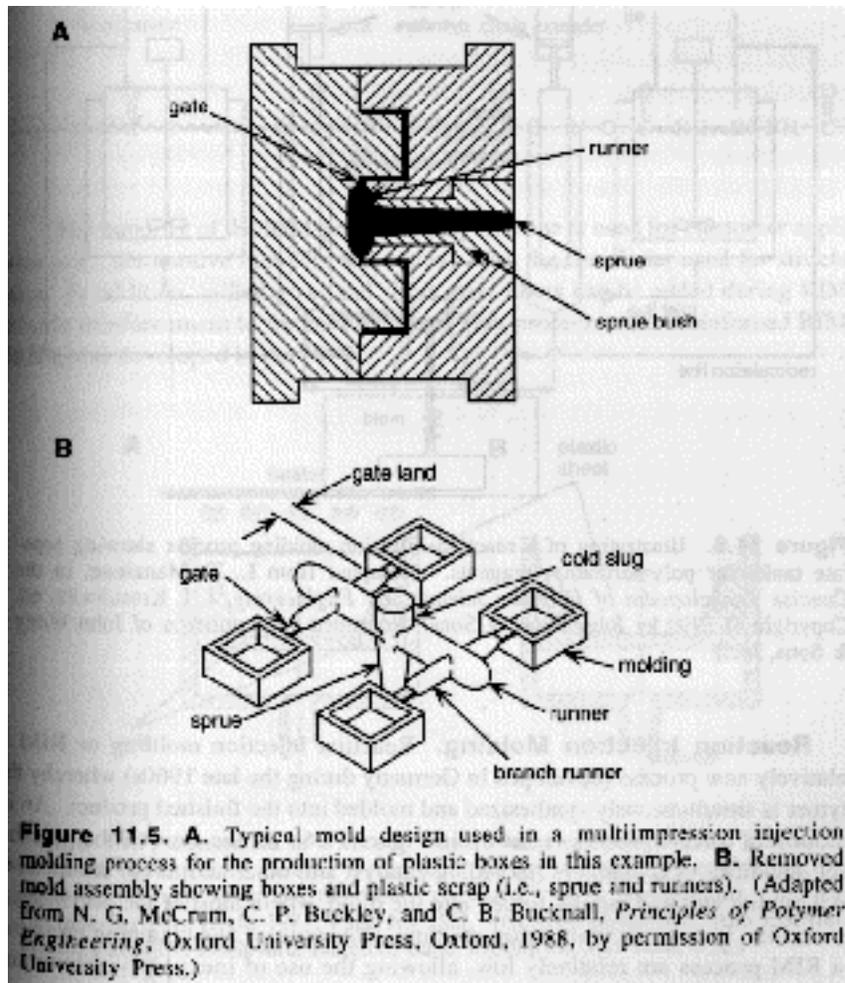
4. Injection Molding Machine

- i. Semi-Continuous Process = Parts come out regularly but process involves a series of "batch-like" operations, i.e. steps.
- ii. Reciprocating Screw = Rotates like a screw extruder, Axial Reciprocating Motion like an Injection Plunger
- iii. Hold Time = Time when polymer is injected into Mold and Wait for Gate to Freeze
- iv. Gate=The die between injector and mold
- v. Recharge=Screw rotates to pull back and refill the Barrel
- vi. Shot= Injection of polymer into mold or the polymer injected into the mold

- vii. Soak Time= Polymer melts in barrel, this is the RATE LIMITING STEP
- viii. Stages of Injection Molding:
Shot=>Hold Time=>Gate Freezes=>Recharge=>Soak=>REPEAT
- ix. Injection molding machines are rated by injection capacity in gram to kilogram and in clamp force up to 5,000 Tons
- x. Weld Line= where two melt fronts meet



From J. R. Fried, "Polymer Science and Technology"



From J. R. Fried, "Polymer Science and Technology"

5. Blow Molding Machine (**Fig 1.17 Tadmor**):

- i. Parison from extruder = a tube of plastic
- ii. Partial Biaxial orientation = polymer tube is drawn in two normal directions at different rates
- iii. Problems: Slow Cooling and Parison Sagging

6. Compression Molding

- i. Charge=> polymer which is molded
- ii. Flashing=> excess polymer

Casting and Dip coating are also discussed in Chapter 1. These are typically for low viscosity systems such as prepolymers, monomers and plasticized polymer.

Polymer Properties Important to Processing Operations.

The basic issues associated with all processing operations were given above,

1. Solids processing (Continuum Mechanics/Powder flow/Mixing/Packing)
2. Mixing (Statistics)
3. Melting (Heat Transfer/Thermodynamics)
4. Pressurization and Pumping (Rheology)
5. Devolatilization/Stripping (Mass Transport/ Diffusion)

Items 3, 4, and 5 and to some extent 1 have associated **Constitutive Equations**. These governing equations are crucial to processing and for this reason some discussion of the features of constitutive equations are given in this chapter. (see also [=Polymer Dynamics.](#))

A Constitutive Equation relates a *perturbation* (tweak) on a system to a *response* (yelp) through a *constitutive parameter*, i.e. for item 1 above, **stress** is related to **strain** by the **modulus**: $\sigma = E \epsilon$ where the modulus is a constitutive parameter. All Constitutive equations have ideal cases (Hookean Elastic) where the constitutive parameter is a constant (spring constant) and deviatoric conditions where the constitutive parameter is some function of either the perturbation (stress) or the response (strain).

1) Hookean Elastic $\sigma = E \epsilon$

4) Newtonian Fluid $\tau = (\eta) (dv_x/dy)$ τ is the shear stress

3) Fourier's Law $q_y = -k(dT/dy)$

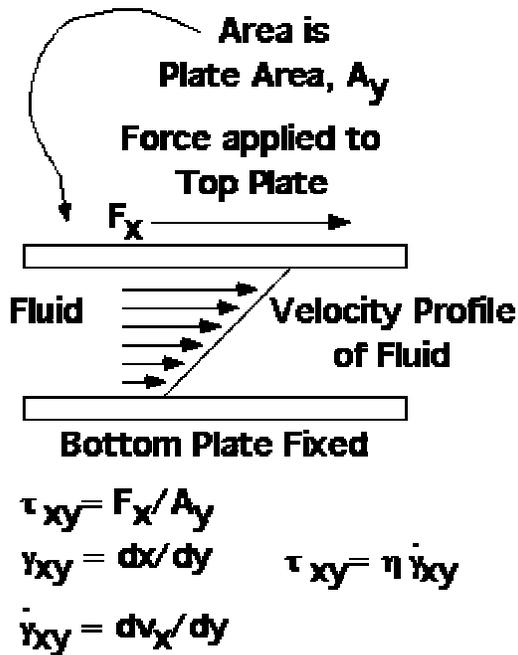
5) Fick's Law $j_{Ay} = -D_{AB}(dc_a/dy)$

Since all of these laws have a parallel form, geometric derivations based on one can be easily translated to the others by a conversion of variables. This is important since virtually all problems in heat transport were solved in the 1800's and the math can be directly translated to strange diffusion and flow problems.

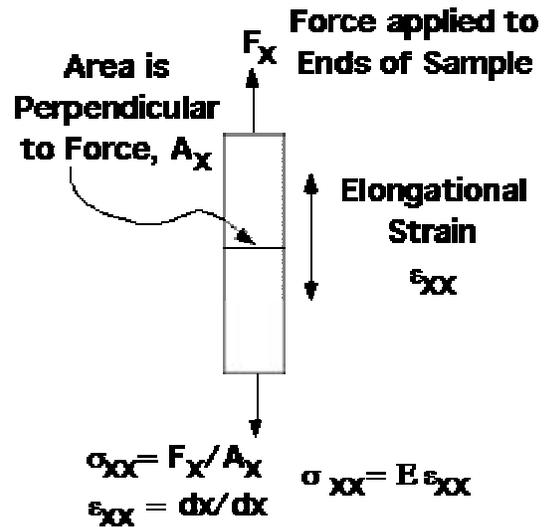
Simple Shear/Tensile Strain Definition of Terms

It is important to understand the definition of terms in the two of the most common constitutive equations, Newtonian Fluid in simple shear flow and a Hookean Elastic under tensile strain.

Simple Shear Flow



Tensile Strain



Chain Entanglement

The viscosity of polymer melts is Newtonian (obeys 4 above) at low rates of strain. At high rates of strain the viscosity typically decays and this decay could be associated with orientation of the chains in flow (molecular orientation). A typical plot of viscosity versus rate of strain is given on **page 696** of the book. The viscosity measured at low strain rates is called the zero shear rate viscosity, η_0 .

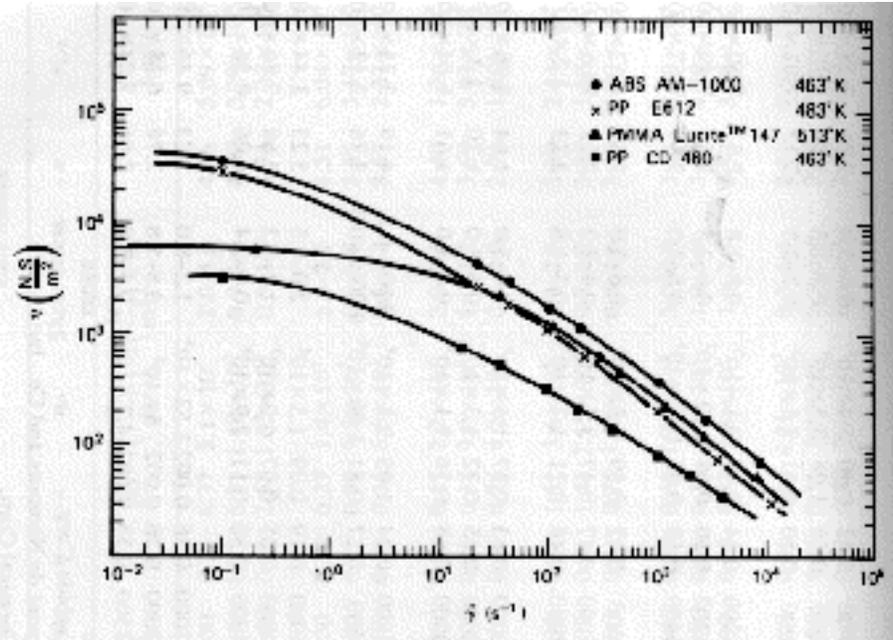


Fig. A.1

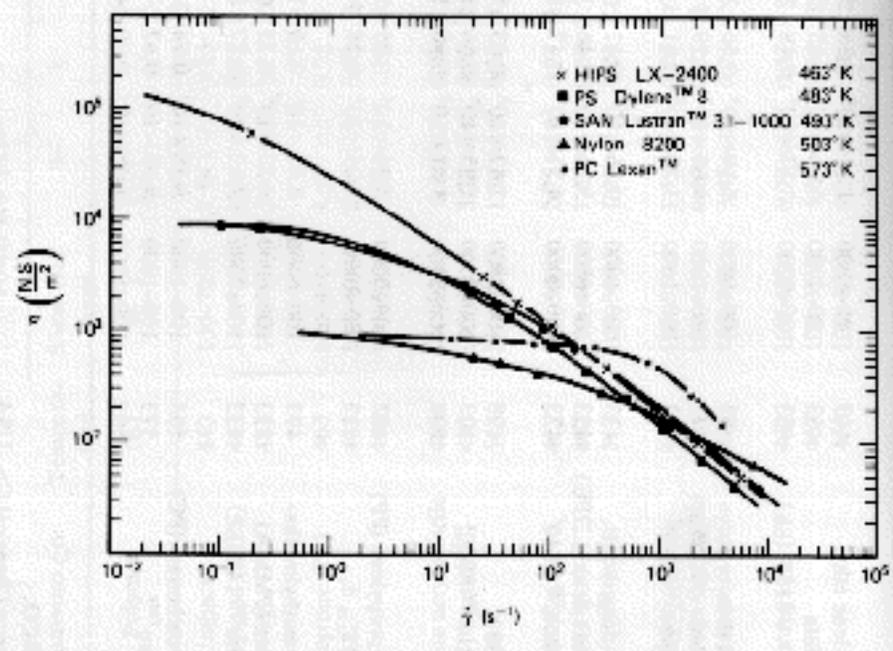


Fig. A.2

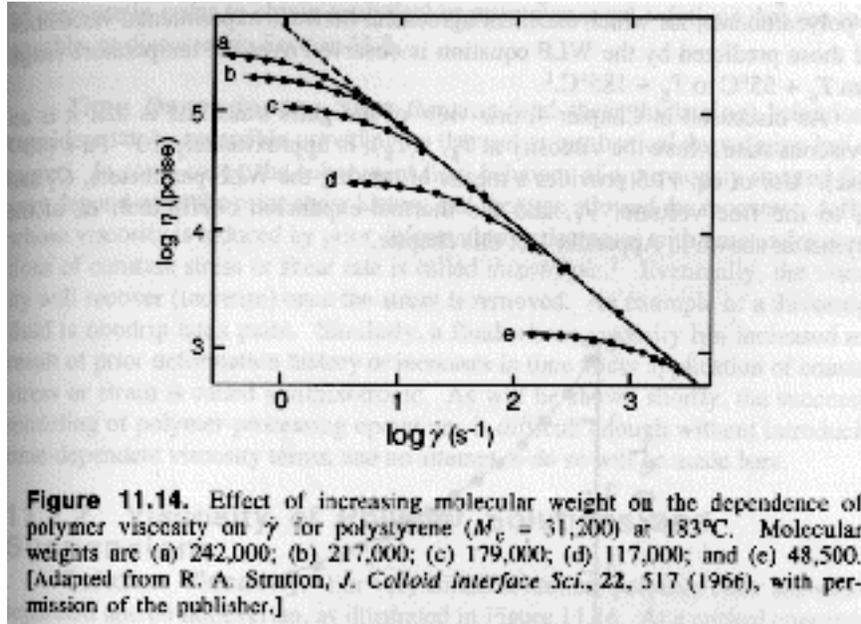
Tadmor and Gogos, "Principles of Polymer Processing" Appendix p. 696

If one plots log of the zero shear rate viscosity versus log of the molecular weight two distinct power-law regimes are observed,

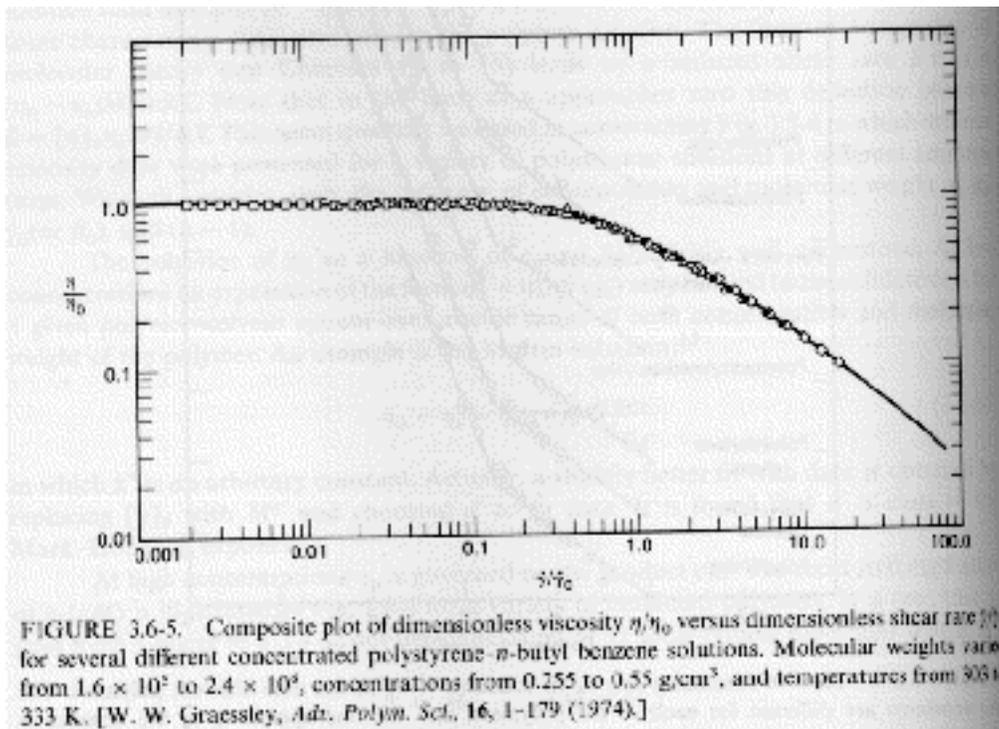
$$\eta_0 = K (MW)^P$$

At low molecular weights $P=1$ and $\eta_0 = K MW$.

At high molecular weights $P=3.4$ and $\eta_0 = K (MW)^{3.4}$.



From J. R. Fried, "Polymer Science and Technology"



From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids Vol. 1"

- 2) The transition between these two regimes is called **the entanglement molecular weight**.

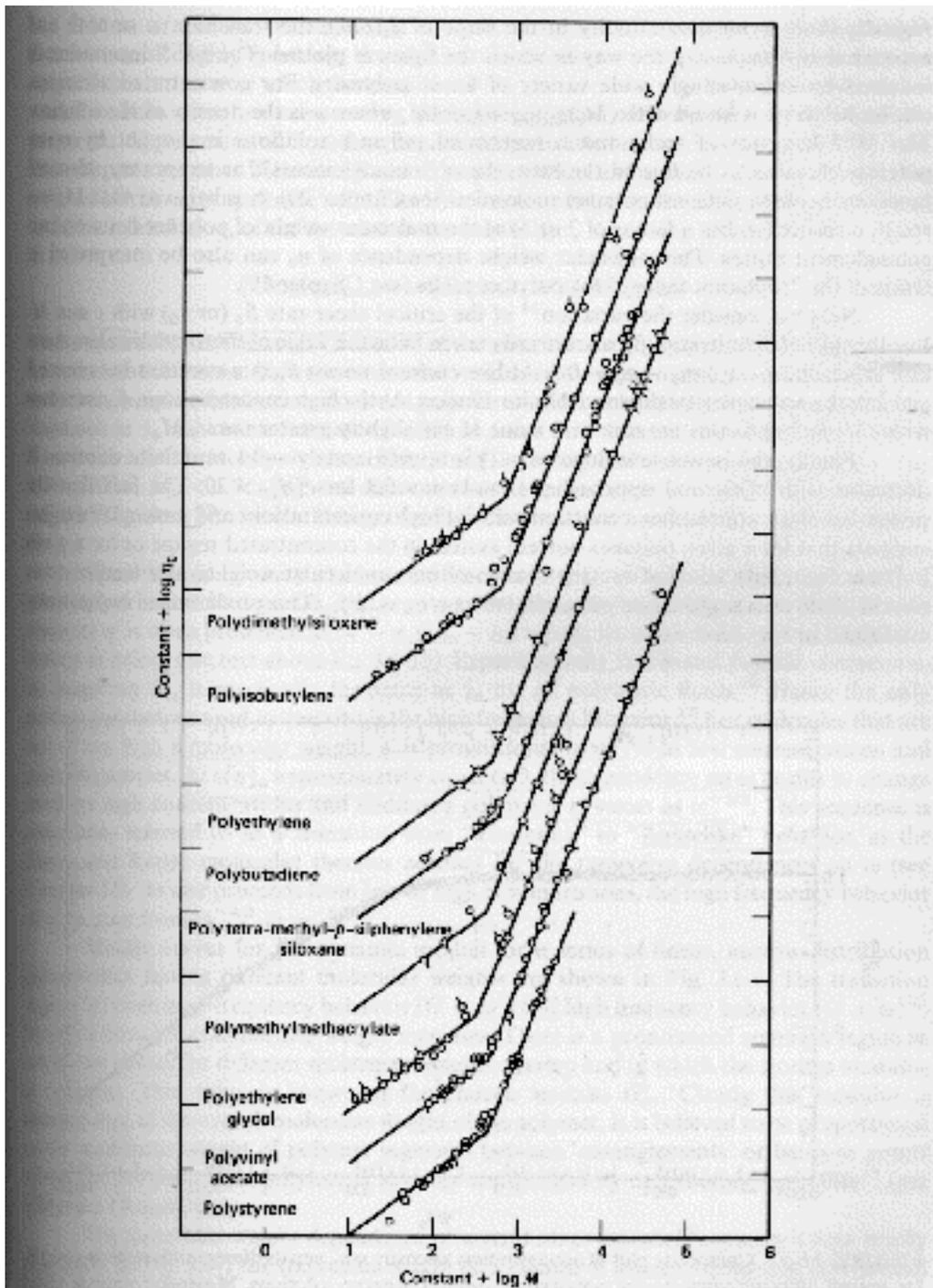
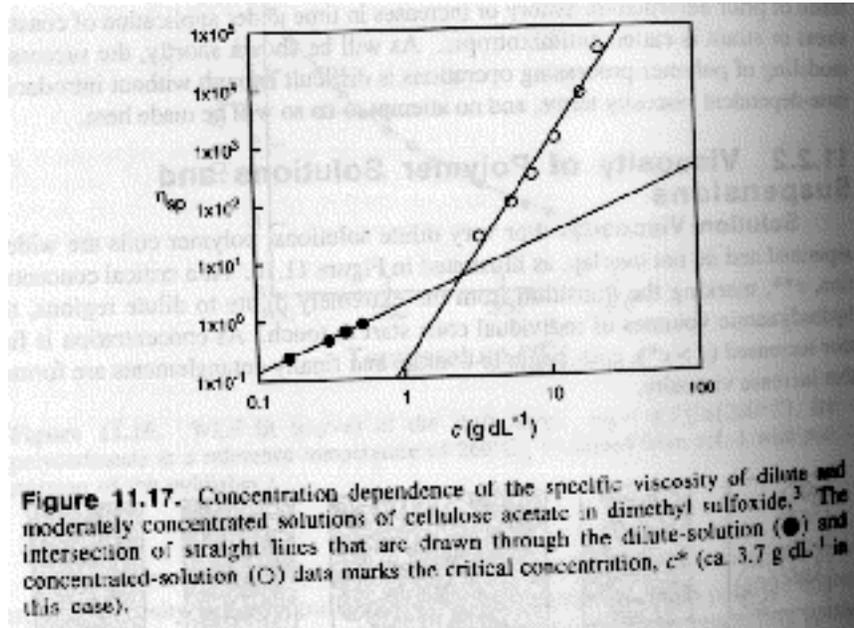


FIGURE 3.6-4. Plots of constant + $\log \eta_c$ vs. constant + $\log M$ for nine different polymers. The two constants are different for each of the polymers, and the one appearing in the abscissa is proportional to concentration, which is constant for a given undiluted polymer. For each polymer the slopes of the left and right straight line regions are 1.0 and 3.4, respectively. [G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*, **5**, 261-357 (1963).]

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids Vol. 1"



From J. R. Fried, "Polymer Science and Technology"

3) The entanglement molecular weight distinguishes a **polymer** from and **oligomer**. Below the M_e oligomers are brittle solids, white powder. Flow behavior is similar to low-molecular weight materials, no normal forces are observed, a wide range of Newtonian viscosity is observed in shear rate etc.

Above M_e polymers are robust solids, i.e. plastics with good engineering properties. Flow behavior becomes non-Newtonian with large strain rate and temperature dependencies, elasticity and large normal forces.

4) Below M_e polymer molecules can be considered independent colloidal particles with a molecular friction factor which is proportional to the number of mers, i.e. MW.

5) Above the entanglement molecular weight this simple model doesn't work because the molecules have sufficient length to intertwine just as long spaghetti intertwines when cooked. Intertwining of chains leads to a power-law dependence of viscosity on molecular weight. Intertwining = Entanglement.

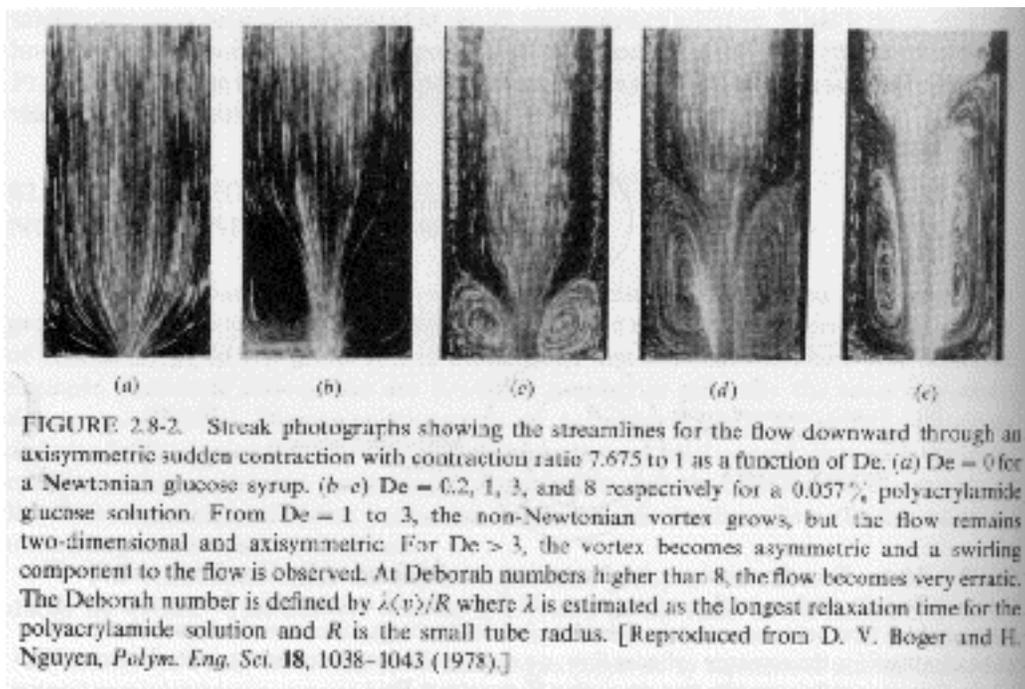
6) Because of the dramatic dependence of viscosity on molecular weight, molecular weight distributions are extremely important to processing. Viscosity amplifies the high molecular weight end of a distribution by a power 3.4.

Time Dependence to Polymer Properties

1) Consider a coil above its entanglement molecular weight, in its maximum entropy state, random coil, which is subjected to a strain field and deforms. When the strain field is released the molecule will relax back to its most random state, however this relaxation will take time. The time for a coil to relax is termed a **Relaxation Time** and is associated with the molecular structure, molecular weight and temperature of the system since the entropy of the coil is related to temperature.

2) In #1 the application of stress and release of stress are also associated with a characteristic time which could be called the **experimental time constant**. For a flow process the experimental time is $1/(d/dt)$. The relationship between the rate of strain (controlled by processing speed) and the molecular relaxation rate of the polymer (controlled by temperature, molecular structure and molecular weight) is a critical feature for processing operations. The **Deborah number**, **De**, has been defined as the ratio between the relaxation time and the experimental time.

3) Large **De** means the material will behave like a solid in the operation (this is bad for extrusion). Small **De** means the material will behave like a liquid (good for processing) Intermediate **De** means the material will behave as a visco-elastic displaying both solid (elastic) and liquid (viscous) features.



From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids Vol. 1"

4) Optimization of a process will involve manipulation of temperature, molecular weight, process rate, processed material.

5) From #3 and #4 it would seem that high temperature would be good for processing. #3 and #4 are opposed by the degradation of the polymer which leads to an "Operating Window" for any given operation in Temperature and Rate. (Figure 14.3 pp. 591 for example also fig 12.3)

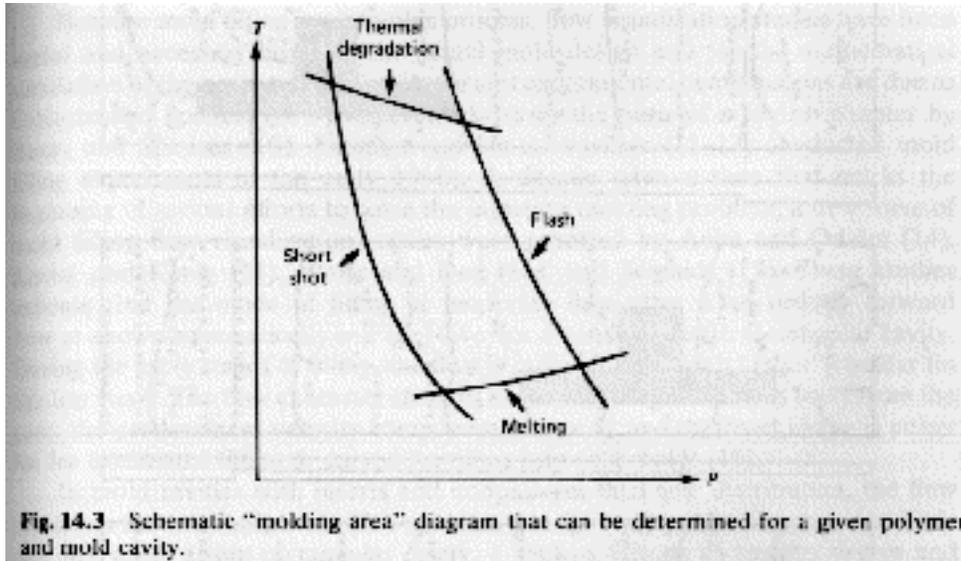


Figure 14.3 Tadmor and Gogos "Principles of Polymer Processing"

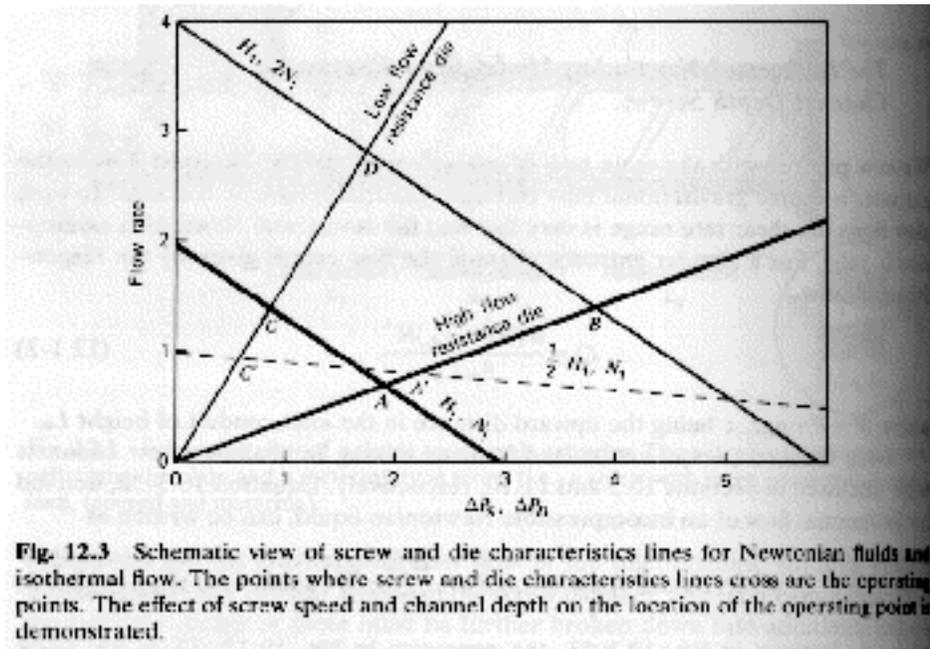


Figure 12.3 Tadmor and Gogos "Principles of Polymer Processing"

6) If viscosity gets too low (high temperature), sag occurs in extrusion; if viscosity gets too high (low temperature), melt fracture or shark skin occur.

Glass Transition (see: Free Volume and T_g , WLF)

In a plot of specific volume (1/density) versus temperature for an amorphous polymer a transition in slope occurs at low temperature corresponding to a transition from a viscoelastic fluid to a solid glass. This transition depends on the rate of the experiment (De effect). The glass transition reflects a locking up of structural elements on a very small scale (10 mer units). Because this is at least partially a kinetic effect (rate dependent effect), it is important to processing operations which can run at high shear rates or small experimental times.

1) At T_g coordinated chain motion of about 10 mer units leads to a "freeing-up" of the structure which increases "free-volume" above about 2.5%.

2) It was found in the 1940's that the mechanical properties of a polymer at a given temperature could be related directly (by a constant shift factor) to the behavior at another temperature. Similarly, the behavior at a given rate could be related directly to another rate by a similar shift factor. Rate and temperature are inversely related for these materials by the **Time-Temperature superposition** principle which is based on the Williams-Landel-Ferry (**WLF**) equation and a free volume approach.

$$\log(a_T) = C_1(T - T_g) / \{C_2 + T - T_g\}$$

$T = T - T^*$, $T^* = T_g - K$ where K is about 20°C or T^* is sometimes taken as T_g . C_1 and C_2 are constants that have values pertaining to free-volume theory.

a_T is the shift factor which for our purposes is given by:

$a_T = \tau_s / \tau = \tau_s / \tau$ where τ_s is the standard state viscosity, viscosity at T^* for instance. τ is the experimental time which is related to $1/\{d\epsilon/dt\}$ for a flow experiment.

Through the WLF equation there is an equivalence between time, through τ , and temperature, T . High Temperature is equivalent to long times and Low temperature are equivalent to short times.

3) Dynamic mechanical thermal analysis (DMTA)

A viscoelastic sample (polymer melt or rubber) can be subjected to an oscillating stress,

$$\sigma = \sigma_0 \sin(\omega_1 t)$$

which results in an oscillating strain,

$$\epsilon = \epsilon_0 \sin(\omega_2 t)$$

The relationship between stress and strain becomes complex since ω_1 doesn't equal ω_2

$$= E^*$$

where "*" indicates a complex number, $E^* = E' - i E''$

In a plot of E'' versus E' in complex space the angle with the x-axis is δ , the loss angle and $\tan \delta$ is the loss tangent which describes the loss in the sample which peaks at T_g .

4) T_g is always below T_m and for all polymers follows $T_g = K T_m$ where T_g and T_m are in $^{\circ}\text{K}$ and K is 1/2 to 2/3.

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