

## Glass Transition Temperature ( $T_g$ ) and Determination of $T_g$

Glass transition represents the sharp change that occurs from the glassy to the rubbery or flexible thermoplastic states in nearly all linear type polymers. It is known as a “second-order transition.” The glass transition temperature varies with types of skeletal atoms present, with the types of side groups, and even with the spatial disposition of the side groups.

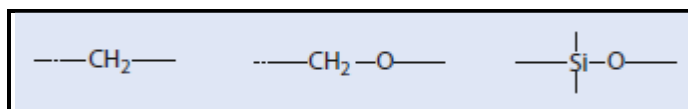
### Factors that Influence the Glass Transition Temperature

The temperature at which the glass transition occurs is essentially determined by the mobility of the polymer chains. In turn the chain mobility is most strongly influenced by the following factors:

1. Chain flexibility
2. Steric effects
3. Tacticity
4. Branching, Crosslinking and Molar mass
5. Plasticizers

#### 1. Chain flexibility

Fundamentally, flexible chains are more mobile and lead to a lower glass transition temperature. Examples of flexible chain elements are alkyl, ether, or silicone moieties (**Fig. 1**). In contrast, chain rigidity is increased by the incorporation of rigid segments such as aromatic rings into the polymer backbone. **Table 1** shows the influence of chain flexibility on the glass transition temperature of some selected examples.



*Fig. 1: Examples of flexible chain elements*

Sterically demanding, stiff segments in the main polymer chain lead to a less mobile polymer chain and the glass transition temperature increases. Thus, polyphenyl ether has a glass transition temperature of +83 °C.

#### 2. Steric Effects / Substituents

Flexible side chains increase the available free volume and thus the mobility of the polymer chain. As a result of this the glass transition temperature is lowered (**Table 2**).

Polar substituents can form hydrogen bonds or dipole-dipole interactions which fix the position of the polymer chains and decrease their mobility; the glass transition temperature is increased (**Table 3**).

**Table 1: Glass transition temperature ( $T_G$ ) of selected polymers having chains of varying flexibility (decreasing from top to bottom)**

	$T_G$ (°C)
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \text{CH}_3 \end{array} \right]_n$	-123
$\left[ \text{---CH}_2\text{---CH}_2\text{---} \right]_n$	-93
$\left[ \begin{array}{c} \text{HC=CH} \\   \quad   \\ \text{H}_2\text{C} \quad \text{CH}_2 \end{array} \right]_n$	-85
$\left[ \text{---CH}_2\text{---CH}_2\text{---O---} \right]_n$	-67
$\left[ \text{---} \langle \text{C}_6\text{H}_4 \rangle \text{---O---} \right]_n$	+83

Additional methyl groups in a  $\alpha$ -position relative to the substituent result in a substantial stiffening of the polymer chain and so to an increase in the glass transition temperature of 70–100 °C. A classic example of this is polymethacrylates, which have higher glass transition temperatures than the corresponding polyacrylates.

**Table 2: Influence of linear alkyl substituents on the glass transition temperature ( $T_G$ ) of polymers with the structure  $(\text{CH}_2\text{---CHX})_n$**

-X	$T_G$ (°C)
-H	-93
-CH <sub>3</sub>	-20
-C <sub>2</sub> H <sub>5</sub>	-24
-C <sub>3</sub> H <sub>7</sub>	-40
-C <sub>4</sub> H <sub>9</sub>	-50

### 3. Tacticity

The influence of the configuration or tacticity of polymers from vinyl monomers is only pronounced if there is more than one substituent, such as an additional methyl group, adjacent to the double bond – as is the case for the polymethacrylates mentioned above. Such monomers are, however, usually radically polymerized, whereby the tacticity of the polymer formed cannot be, or is only marginally, controlled. The glass transition temperature of typical polyolefins such as polypropylene is, in contrast, not (or only marginally) dependent on the tacticity because of the missing second substituent.

**Table 3: Influence of polar substituents on the glass transition temperature ( $T_G$ ) of  $(\text{CH}_2\text{-CHX})_n$**

-X	$T_G$ (°C)
-CH <sub>3</sub>	-20
-Cl	+81
-CN	+105

### 4. Branching and crosslinking

If the material is cross-linked, the cross-links function as permanent entanglements and chain movement is restricted. At low cross-link densities the glass transition temperature increases almost linearly with the number of cross-links. Materials with a high cross-link density tend to exhibit a broad, ill-defined glass transition.

The polymer chain ends are, in contrast to the other segments along the chain, relatively mobile. Because of this they are able to 'create' comparatively more free volume around themselves. By the same argument as that used above, polymers with lower molar mass have lower glass transition temperatures. This effect can be described by Bueche's empirical equation:

$$T_G = T_G^\infty - \frac{\text{const.}}{M_n}$$

$T_G^\infty$  be the Glass transition temperature for  $M_n \rightarrow \infty$

The equation can be applied to molar masses  $M_n$  of above ~5000 g/mol. Thus, the glass transition temperature asymptotically increases to a limiting temperature valid for very high (infinite) molar mass.

## Theories Describing Free Volume

The term 'free volume' has already been used several times when describing the glass transition temperature. It is assumed that the volume  $V$  of a polymer sample is made up of a volume  $V_0$  that is occupied by the polymer molecules and an additional free volume  $V_f$  that is available for the rotational and translational movement of the molecules:

$$V = V_0 + V_f$$

$V$  = Total volume

$V_0$  = Volume of the chains

$V_f$  = Free volume

All  $V$ ,  $V_0$ , and  $V_f$  are dependent on the temperature. For a polymer in its fluid or a rubber-elastic state, the free volume increases with temperature. Visually, the mobility of the molecules increases. However, if the temperature decreases, the free volume shrinks and below a critical temperature—the glass transition temperature—it doesn't change any more; the molecules are immobile.

The main difficulty of theoretically describing the glass state using free volume is that free volume is not an equilibrium state. Basic approaches to a theoretical description of the glass state that should be mentioned are:

- Williams, Landel, and Ferry's kinetic approach (WLF equation)
- Gibbs and DiMarzio's thermodynamic approach
- Gibbs and Adam's combination approach

Estimating what proportion of the material is free volume is both theoretically and experimentally difficult, and estimates vary according to parameters such as polymer and temperature between 2.5 % and 12 % of the total volume.

## 5. Plasticizers

Plasticizers are low molar mass, non-volatile compounds added to a polymer to change its properties. Generally these compounds have a 'lubricating effect' on the polymer chains. The molecules can move more easily when surrounded by low molar mass material. The addition of a plasticizer thus results in an increase in the mobility of the chains and consequently to a lowering of the glass transition temperature. Plasticizers are therefore used so that soft, flexible materials can be obtained from stiff, brittle base polymers. A technically important material, which often has large quantities of plasticizers added to it, is polyvinyl chloride (PVC). PVC without plasticizer has a glass transition temperature of 81 °C. If 30–40 % plasticizer is added, so-called soft-PVC is obtained, which has a glass transition temperature of < 0 °C. Important uses of this material are for the manufacture of raincoats, curtains, and cable sheathing. The effect

of the addition of a plasticizer on the glass transition temperature can be estimated using

$$\frac{1}{T_G} = \frac{w_{Pol}}{T_{G, Pol}} + \frac{w_W}{T_{G, W}}$$

$w_{Pol}$  : Mass fraction of the polymer

$w_W$  : Mass fraction of the plasticizer

$T_{G, Pol}$  : Glass transition temperature of the polymer

$T_{G, W}$  : Freezing point or glass transition temperature of the plasticizer

$T_G$  : Glass transition temperature of the plasticized polymer

Water can have a strong plasticizing effect on hydrophilic polymers. In these cases, the properties of the material are very dependent on the surrounding conditions, especially the humidity of the surroundings. This effect, which, for example, can be observed with the biopolymer starch, means that using such materials is a challenge.

### **Williams-Landel-Ferry Equation (or WLF Equation)**

The method of reduced variables, or time temperature superposition, has traditionally been applied to pure polymers, where it is used to make predictive measurements of the material. It has also found wider application in the foods area with the treatment of sugar rich hydrocolloid gels and gelatin.

The fundamental WLF equation can be derived from the Doolittle equation which describes the variation of viscosity with free volume.

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

Where  $\eta$  is the tensile viscosity,  $V$  and  $V_f$  are the total volume and free volume of the system respectively, and  $A$  and  $B$  are constants.

$$\Rightarrow \ln \eta = \ln A + B(1/f - 1)$$

If it is assumed that the fractional free volume increases linearly with temperature then

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

Where  $\alpha_f$  is the thermal coefficient of expansion,  $f$  is the fractional free volume at  $T$ , a temperature above  $T_g$ , and  $f_g$  is the fractional free volume at  $T_g$ .

Therefore

$$\ln \eta(T) = \ln A + B(1/[f_g + \alpha_f (T - T_g)] - 1) \text{ at } T > T_g$$

And  $\ln \eta(T) = \ln A + B(1/f - 1)$  at  $T = T_g$   
 Subtracting  $\log \eta(T)/\eta(T_g) = -B/2.303 f_g [T - T_g]/\{(f_g/\alpha_f) + T - T\}$

Where, the universal constants  $C_1 = B/2.303 f_g$  and  $C_2 = f_g/\alpha_f$

It can be shown that  $\log \eta(T)/\eta(T_g) = \log a_T$

The method of extracting the universal constants of the WLF equation is to use the method of reduced variables (time temperature superposition). A number of DMA frequency scans are recorded at a series of isothermal temperatures, and the resulting data displayed on a BLUK105-Gabbott August 2, 2007 1:28 The Williams Landau Ferry (WLF) equation and Time Temperature Superposition 451 screen. A reference temperature is chosen (typically the isothermal temperature from the middle section of data where properties vary most as a function of frequency, equivalent to  $T_g$ ) and the factors required to shift the responses at the other temperatures calculated so that one continuous smooth mastercurve is produced. Most commercial analysers provide software to create the mastercurve and calculate the shift factors involved. Different approaches have been used to obtain this type of data including a frequency multiplexing approach where a low underlying scan rate is used and the frequency continuously varied. However this means that data collected at each individual frequency will be at a slightly different temperature, and it is best to ensure that truly isothermal conditions are employed.

The factor for the reference temperature ( $a_T$ ) is 1 with those for temperatures less than the reference temperature being less than 1 and those for temperatures greater than the reference temperature being greater than 1. The master curve, in conjunction with either the modulus temperature curve or the shift factors ( $a_T$ ) relative to a reference temperature ( $T_{ref}$ ), enables the response of the polymer under any conditions of time and temperature to be obtained.

There is also a correction to be applied in the vertical direction as well as the shift along the x-axis. This is related to the absolute value of temperature, on which the moduli depend, and the change in density as the temperature changes. The entire procedure can be expressed thus

$$E(T_1, t)/\rho(T_1)T_1 = E(T_2, t/a_T)/\rho(T_2)T_2$$

This correction should only be made for the rubbery state, ie above  $T_g$ . It is invalid for the glassy state. By fitting the WLF equation to the shift factors, (y-axis), at a particular temperature, (x-axis) we can obtain an estimate of the universal constants  $C_1$

and  $C_2$  and hence obtain an estimate of  $T_\infty$ , the underlying true second order transition temperature, where viscosity becomes infinite. The WLF equation can also be expressed in terms of the shear moduli as

$$\log a_T = G(T)/G(T_{ref}) = -C_1(T - T_{ref})/(C_2 + T - T_{ref})$$

and can be rearranged to obtain the universal constants  $C_1$  and  $C_2$  from a linear graphical plot.

$$(T - T_{ref}) / \log a_T = -1/C_1 (T - T_{ref}) + (-C_2/C_1)$$

$$y = mx + c$$

If the term  $[C_2 + T - T_0]$  went to zero the term  $\log a_T$  would tend to  $\infty$  which would correspond to a shift factor of 0 and the response of the polymer at the limiting true transition temperature  $T_\infty$ .

and 
$$T_\infty = T_{ref} - C_2 = T_g - 50$$

if,  $T_g$  is chosen as the reference temperature. BLUK105-Gabbott August 2, 2007 1:28 452 Principles and Applications of Thermal Analysis  $T_\infty$  is thought to be the true underlying 2nd order transition for these materials and only accessible for experiments carried out over very long time scales. In practice the  $50^\circ\text{C}$ , which is normally added to the  $T_\infty$ , returns a value for  $T_g$  more in keeping with everyday experience and measured values. This procedure places the glass transition somewhere in the transition region. It can therefore be seen that  $C_1$  can give information on the free volume at the glass transition whilst  $C_2$  can give information on the thermal expansion as well as the underlying glass transition.