Chapter 4

Glass Transition Temperature in Polymers

1. Introduction
2. Transition or State of Matters
3. Theory (WLF equation)
4. Time-Temperature Superposition Principle
5. Transition T ($T_g$) and End-use T ($T_{use}$)
6. Effect of Chemical Structures on $T_g$
   (Homopolymers, Copolymers & Blends)
7. Effect of Physical Characteristics of Molecules
8. Effect of Plasticizer
1. Introduction

- PVC (thermoplastic):
  - tygon tube (masterplex pump)
  - leather (auto cover sheet)
  - Pipe
  \[ \Rightarrow \text{Plasticizer} \]

- Rubber (thermoset)
  - poly(isoprene)
  - PDMS, poly(dimethyl siloxane)
  - ebonite (hard rubber) ; 딱딱함
Materflex Pump

Chapter 4
1. Introduction

♣ T effect

- PMMA (Lucite®, Plexiglass®): hard, rigid and glassy at RT
- PS
- PDMS, poly(isoprene): soft, flexible and rubbery at RT
- poly(ethyl acrylate)

Variety of changes in state

Variety of mechanical and physical properties
2. Transition or State of Matters

1) Thermodynamic Point of View

small molecules

- 1st order transition:
  - \( T_g \) to \( T_m \) to \( T_v \)

- 2nd order transition:
  - \( V \) to \( S \) to \( L \) to \( V \)
2. Transition or State of Matters

\[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \]

\[ C_P = \left( \frac{\partial H}{\partial T} \right)_P \]
2. Transition or State of Matters

low MW crystalline solids (glycerin)

- glassy
- super-cooled
- crystalline
- liquid

depends on structure cooling rate crystallization rate

V

\[ T_g \quad T_m \]
2. Transition or State of Matters

Polymers

- Glassy (brittle)
- Crystalline
- Rubbery (soft)
- Melt (viscoelastic)

- $T_m$ over certain $T$ range (2~10 °C)
- Subject to hysteresis effect (rate dependency)
- Viscoelastic
- No gases
2. Transition or State of Matters

Summary on $T_g$

stiff and glassy

↓

soften at $T_g$ and become rubbery (leathery)

($T_g$: )
Glossary

- **Transition**: Change of state by changing T & P
- **Relaxation** (이완, 완화): time required to respond to a change in T or P, also implies some measure of molecular motion e.g.
- **Dispersion**: emission or absorption of energy at a transition (i.e. a loss peak)
2) Molecular Motion

2. Transition or State of Matters

a. vibration of atoms about equilibrium position

b. motion of a few (5~ 6 atoms) along the chain or of the side groups (segmental motion or segmental diffusional motion)

c. co-operative wriggling and jumping of approx. 40 ~ 50 carbons

d. transitional motion of entire molecules
Chapter 4

2) Molecular Motion

but not all molecules possess the same energies at given $T (kT)$ and they follow Boltzmann distribution.

- rotational/translational motion of segments
- short range diffusional motion
- increased slip
- some elasticity remains

Frozen (vibration only)

$T_g$ - very rapid but
restricted by entanglement

RP

RF
2. Transition or State of Matters

2) Molecular Motion

Boltzman distribution
Glass Transition Temperature, $T_g$

- onset of long-range, coordinated molecular motion
  - at $T < T_g$, 1~4 chain atoms in motion
  - at $T \sim T_g$, 10~50 atoms in motion

- modulus drops a factor of 1,000 in a 20~30 °C range
3. Theory of Glass Transition Temperature

1) Free Volume Theory

\[ V(T) = V_o(T) + V_f(T) \]

\( V_o \): occupied volume, \( V_f \): free volume

\( V_o \): occupied by molecule
\( T \) dependency due to changes in amplitude of molecular vibrations with \( T \)

\( V_f \): empty space btw molecules
regarded as an elbow room that molecules require to undergo rotational and translational motion

at \( T \leq T_g \): frozen (\( V_f \) critical)

as \( T \) increases, \( V_f \) and motion increase
3. Theory of Glass Transition Temperature

1) Free Volume Theory

\[ V_0(T = 0) + V_f(T = 0) \]

\[ V_0(T = 0) \]

\[ V^*_f \]

\[ T_g \]

\[ V_f(T) \]

\[ V_0(T) \]

free volume, \( V_f(T) \)
fractional free volume, \( f \)

\[
f = \frac{V_f}{V}
\]

at \( T \leq T_g \):

\[
f = \frac{V^*_f}{V} = \text{constant} = f_g
\]

at \( T > T_g \):
3. Theory of Glass Transition Temperature

1) Free Volume Theory

- free volume, $V_f$:

As $T$ increases, molecular motion and $V_f$ increase, but
3. Theory of Glass Transition Temperature

By Fox and Flory (1950)

\[ T_g \equiv \text{Iso-free volume state} \]
\[ f_g = 0.025 \text{ or } 2.5\% \text{ for most polymers} \]

valid for \( T_g < T < T_g + 100 \) °C
3. Theory of Glass Transition Temperature

2) William-Landel-Ferry Equation (WLF)

By Doolittle (empirical):

internal mobility (expressed by viscosity) is related to fractional free volume \((V_f, f)\)

\[ \text{viscosity, } \eta \]

\[ \equiv \] occupied volume과 free volume과의 비에 의해 결정

cf. Arrhenius equation
3. Theory of Glass Transition Temperature

at $T = T_{ref}$,
if $T_{\text{ref}} = T_g$, $f_{\text{ref}} = f_g$,

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

$$\ln a_T = \frac{f_g}{\left(\frac{f_g}{\alpha_f}\right) + (T - T_g)}$$

$$\log a_T = -\frac{B}{2.303f_g} \frac{(T - T_g)}{\left(\frac{f_g}{\alpha_f}\right) + (T - T_g)} = \frac{-C_1 \Delta T}{C_2 + \Delta T}$$

**WLF Equation**

where $a_T$:

$C_1$ and $C_2$:

$\Delta T = T - T_g$
## 3. Theory of Glass Transition Temperature

### 2) WLF Equation

Table 4.4 Some Polymers Ranked in Order of Decreasing $T_g$ Values, Along with Numerical Values for Quantities Appearing in the DoLittle Equation

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (K)</th>
<th>$B/f_g$</th>
<th>$f_g/\alpha$ (K)</th>
<th>$f_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyesters</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>388</td>
<td>76.9</td>
<td>76.5</td>
<td>0.013</td>
</tr>
<tr>
<td>Styrene</td>
<td>373</td>
<td>31.3</td>
<td>50.8</td>
<td>0.032</td>
</tr>
<tr>
<td>Ethyl methacrylate</td>
<td>335</td>
<td>40.0</td>
<td>67.6</td>
<td>0.025</td>
</tr>
<tr>
<td>$n$-Butyl methacrylate</td>
<td>300</td>
<td>38.5</td>
<td>100</td>
<td>0.026</td>
</tr>
<tr>
<td>Methyl acrylate</td>
<td>276</td>
<td>41.7</td>
<td>45.3</td>
<td>0.024</td>
</tr>
<tr>
<td>$n$-Hexyl methacrylate</td>
<td>268</td>
<td>40.0</td>
<td>132</td>
<td>0.025</td>
</tr>
<tr>
<td>$n$-Octyl methacrylate</td>
<td>253</td>
<td>37.0</td>
<td>108</td>
<td>0.027</td>
</tr>
<tr>
<td>Urethane rubber</td>
<td>238</td>
<td>35.7</td>
<td>32.9</td>
<td>0.028</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Hexene</td>
<td>218</td>
<td>50.0</td>
<td>20.6</td>
<td>0.020</td>
</tr>
<tr>
<td>Butyl rubber</td>
<td>205</td>
<td>38.5</td>
<td>108</td>
<td>0.026</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>205</td>
<td>38.5</td>
<td>104</td>
<td>0.026</td>
</tr>
<tr>
<td>1,4-Butadiene</td>
<td>172</td>
<td>25.6</td>
<td>60.9</td>
<td>0.039</td>
</tr>
<tr>
<td>Dimethyl siloxane</td>
<td>150</td>
<td>14.1</td>
<td>68.9</td>
<td>0.071</td>
</tr>
</tbody>
</table>

*Source: Data from J. D. Ferry, *Viscoelastic Properties of Polymers*, John Wiley and Sons, New York, 1980.*
### 3. Theory of Glass Transition Temperature

#### 2) WLF Equation

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( C_1 )</th>
<th>( C_2 )</th>
<th>( T_g, \text{K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyisobutylene</td>
<td>16.6</td>
<td>104</td>
<td>202</td>
</tr>
<tr>
<td>Natural rubber (Hevea)</td>
<td>16.7</td>
<td>53.6</td>
<td>200</td>
</tr>
<tr>
<td>Polyurethane elastomer</td>
<td>15.6</td>
<td>32.6</td>
<td>238</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>14.5</td>
<td>50.4</td>
<td>373</td>
</tr>
<tr>
<td>Poly(ethyl methacrylate)</td>
<td>17.6</td>
<td>65.5</td>
<td>335</td>
</tr>
<tr>
<td><strong>“Universal constants”</strong></td>
<td><strong>17.4</strong></td>
<td><strong>51.6</strong></td>
<td></td>
</tr>
</tbody>
</table>

3. Theory of Glass Transition Temperature

experimentally for many linear amorphous polymers

\[
\log a_T = -\frac{17.44 (T - T_g)}{51.6 + (T - T_g)}
\]

\[
B = \frac{2.303 f_g}{\frac{f_g}{\alpha_f}} = 17.44
\]

\[
f_g = 0.025
\]

\[
\alpha_f = 4.8 \times 10^{-4} \text{ deg}^{-1}
\]

\[
(B = 1.0 \text{ is assumed})
\]

\[
a_T = \frac{\eta}{\eta_{ref}} \Rightarrow \frac{\eta}{\eta_{Tg}} \Rightarrow \frac{t}{t_{Tg}} \Rightarrow \left(\frac{\tau}{\tau_{Tg}}\right)
\]

t: experimental time

\tau: relaxation time
3. Theory of Glass Transition Temperature

meaning

\[ \log a_T = \log \frac{\eta}{\eta_{Tg}} \approx \log \frac{t}{t_{Tg}} = -\frac{17.44 (T - T_g)}{51.6 + (T - T_g)} \]

log \( a_T \) vs. \( (T - T_g) \)
1) Stress Relaxation Experiment

\[ \varepsilon = \text{constant} \]

(strain)

\[ F = \frac{F(t)}{A} \]

\[ = \text{stress} = \sigma \]

(Relaxation) Modulus

\[ E(t,T) = \frac{\sigma(t,T)}{\varepsilon(0)} \]

modulus (rigidity): 힘을 줘도 변형이 일어나기 어려운 정도
4. Time-Temperature Superposition Principle

- Modulus drops a factor of 100 °C in a 20~30 °C range
- $T_g$: The onset of long-range, coordinated, molecular motion
- $T < T_g$: 1-4 chain atoms in motion
- $T \sim T_g$: 10~50 (segmental motion)
4. Time-Temperature Superposition Principle

1) Stress Relaxation Expt

\[ T_g \quad \text{RP} \quad \text{RF} \quad \text{Flow Viscous} \]

① Frozen (vibration only)
② Rotation, Transition (chain end, chain loop)
③ Very rapid but restricted motion by entanglement
④ Slip some elasticity remains
2) Time-Temperature principle
(correspondence=superposition=equivalency)

온도에 따라 Time scale이 변할 수 있음

PS = 125 °C
$T_g = -68 \, ^\circ C$

Poly(isobutylene)
$T_g = -68 \, ^\circ C$

颖도에 따라 Time scale이 변할 수 있음
4. Time-Temperature Superposition Principle

- Exptally at difference $T$ over modest $T$ range
- $T$: Measure of molecular motion
- WLF: Logarithmic relationship between $t$ & $T$

$\Rightarrow$ $t$ & $T$ are equivalent to the extent that data at $T_1$ can be superimposed on data at $T_2$ by shifting data set 1 (or curve)
4. Time-Temperature Superposition Principle

\[ E(t_1, T_1) = E(t_2, T_2) \] at a point of overlap

drop subscript on t in mater curve

\[ E\left(\frac{t_1}{a_{T_1}}, T_1\right) = E\left(\frac{t_1}{a_{T_2}}, T_2\right) \]

reduced variable

if \( T = T_{ref}, a_r = 1, \) \( \therefore \log a_r = 0 \)

\( T > T_{ref}, a_r < 1 \)

\( T < T_{ref}, a_r > 1 \)
3) Principle of Corresponding $T$ for linear and amorphous polymers

- Glass polymers $10^{10} \sim 10^{11}$ dyne/cm$^2$
- Rubbery zone $10^{6.5} \sim 10^{7.5}$

$\Rightarrow$ Two linear and amorphous polymers of the same MWD are approximately equivalent at corresponding

$$T_r = \frac{T}{T_g}$$
5. Transition T and End-use T

1) Elastomer

- $T_{use} > T_g$: High segmental motion

  ex) SBR $T_g = -57 \, ^\circ C$
  
  Poly(isoprene) $T_g = -70 \, ^\circ C$
5. Transition T and End-use T

2) Amorphous structure polymers

- $T < T_g$: Segmental motion이 있으면 안되
- Glasslike rigidity (no motion)
- PS, PMMA $T_g = \sim 100 \, ^\circ C$ 정도
  - Tough leather like polymer: $\sim T_g$
    (auto-seat, ladies handbag, travel luggage)
- Highly crystalline and oriented polymer: $T_{use} = T_m - 100$
- Semi crystalline. 반결정성: $T_g < T < T_m$
- LDPE $T_g = \sim 120 \, ^\circ C$, $T_m = \sim -115 \, ^\circ C$
6. Effect of Composition on $T_g$

1) Steric factors

- Chain flexibility
  : Determined by the ease with which rotation can occur about primary chemical bonds ($E_a = 1\sim5$ kcal/mole) (steric hindrance increases $T_g$)

- Intermolecular packing distance (pendant group effect)
  : $V_f$, 분자 chain 간이 멀어지면 free volume이 많아져
6. Effect of Composition on $T_g$

a) Backbone stiffness on flexibility

- Stiffening agent

\[
\text{Epoxy 복합재료, PC} \quad \Rightarrow \quad T_g = 150 \, ^\circ\text{C}, \ T_m = 267 \, ^\circ\text{C}
\]
6. Effect of Composition on $T_g$

- Flexibility agent
6. Effect of Composition on $T_g$

b) Intermolecular packing distance

- If pendent groups are bulk/stiff and close to backbone, steric hindrance will be increased.

- If substituents (치환기) are flexible, the effect of increasing intermolecular distance and free volume effect dominate $\Rightarrow T_g$
6. Effect of Composition on $T_g$

ex 1)

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>-100 °C</td>
<td>-H</td>
</tr>
<tr>
<td>PP</td>
<td>-10 °C</td>
<td>-CH3</td>
</tr>
<tr>
<td>PS</td>
<td>100 °C</td>
<td>Benzene ring</td>
</tr>
</tbody>
</table>
6. Effect of Composition on $T_g$

ex 2) Poly(acrylate) $T_g$: ~5 °C

Poly(methacrylate) $T_g$: ~100 °C

Methyl > Ethyl > Propyl: 길수록 flexible

Q) Chain이 매우 길어지면 $T_g$가 낮아져야 정상, 그러나 N이 12개 이상이면 $T_g$가 오히려 증가한다. Why?

A) 12개 이상이 되면 결정이 형성되어 뭉치고 움직임이 둔화됨.
6. Effect of Composition on $T_g$

c) Symmetry (backbone)

PP ($T_g = -10 \, ^\circ C$, $T_m = 165 \, ^\circ C$)

PDMS ($T_g = -70 \, ^\circ C$, $T_m = 44 \, ^\circ C$)

cf) PVDC ($T_g = 87 \, ^\circ C$) vs PVC ($T_g = -19 \, ^\circ C$)
6. Effect of Composition on $T_g$

d) Effect of isomerism

- Cis
- Trans: 열역학적으로 안정한 상태, 펼쳐져 있는 상태, $T_g \uparrow$

<table>
<thead>
<tr>
<th></th>
<th>$T_g$</th>
<th>$T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyisoprene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cis</td>
<td>-72 °C</td>
<td>25 °C</td>
</tr>
<tr>
<td>Trans</td>
<td>-60 °C</td>
<td>60 °C</td>
</tr>
<tr>
<td>PB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cis</td>
<td>-95 °C</td>
<td>2 °C</td>
</tr>
<tr>
<td>Trans</td>
<td>-83 °C</td>
<td>143 °C</td>
</tr>
</tbody>
</table>
6. Effect of Composition on $T_g$

e) Effect of Tacticity

- Profound effect on $T_m$
- (a-, S-, I-) Tacticity in general, no effect on $T_g$ 

Exception) PMMA

Atactic: 104~108 °C → 결정이 안됨
Isotactic: 42~45 °C → 결정이 잘됨
Syndio: 105~120 °C
6. Effect of Composition on $T_g$

2) Intermolecular bonding forces of attraction

ex) PP (CH$_3$): -10 °C
PVC (Cl): 85 °C
PAN (C=N): 105 °C

⇒ 밑으로 갈수록 polarity가 있음
   (→ Almost same size of side groups)
6. Effect of Composition on $T_g$

ex) Poly(Methyl acrylate): 3 °C
Poly(Acrylic acid): 106 °C
Poly(Zinc acrylate): Ionic bonding > 400 °C

☞ $T_g$가 점점 증가하는 방향
  : Van der Waals → H-bonds → Ionic bonds
  → Chemical crosslinking
7. Effect of Physical Characteristics of Molecules

1) MW effect

\[ T_g = T_g^\infty - \frac{K}{M_w} \]
\[ T_g^\infty = T_g + \frac{K}{M_w} \]

- 분자량이 적으면 chain end 수 증가 → free volume ↑ → \( T_g \) ↓

- \( T_g \)에는 분자자체의 volume보다 free volume의 크기가 더 중요
2) Branch effect

- For small no. of branching,

\[ T_g = T_g^\infty - \frac{y \cdot \rho \cdot N_A \cdot \theta}{\alpha_f M_w} \]

- For high density of branching \( \Rightarrow T_g \) increases
  (due to restriction of chain mobility)
7. Effect of Physical Characteristics of Molecules

- $f = 2$ (end group)
- $f = 3$
- $f > 10$
- Cyclic polymer
- Linear

Graphs showing the relationship between $T_g$, $f$, and $M_n^{-1}$.
7. Effect of Physical Characteristics of Molecules

3) Crosslinking effect

\[ T_g - T_{g0} = \frac{3.9 \times 10^4}{M_c} \]

- Not crosslinked
- Molecular weight between crosslinks

\(-\) Specific volume을 가지고 측정

\(-\) As mole of DVB is added, 
\(T_g\) increases but becomes obscure.
8. Effect of Plasticizer

1) Plasticizer

- A substance which is added to material to improve its processibility (melt viscosity), flexibility ($T_g$) and strechability. (deformability or elastic modulus)

- W/O altering chemical nature of the polymer
8. Effect of Plasticizer

2) Plasticization

- Refers to a process of making a material more susceptible to flow

ex 1) H$_2$O for paper (cellulose $T_g = 225 \, ^\circ$C)

$\Rightarrow$ Steam ironing for cotton fabric (물이 가소화 역할)

H$_2$O for nylon poly acrylate methacrylate

ex 2) CO$_2$ for glassy polymers PC

$\Rightarrow \Delta T_g = 9 \, K$ at 6.8 atm (gas를 이용해서 가소화)
8. Effect of Plasticizer

ex 3) Weakly polar ester for PVC (phthalate: 86%)
DIOP/DOP: 40% 정도 차지

**DIOP (di iso octyl phthalate)**

\[
\text{C}_2\text{H}_5 \quad \text{O} \quad \text{C} - \text{OCH}_2\text{CCHC}_4\text{H}_9
\]

**DOP (n-dioctyl phthalate)**

\[
\text{C} - \text{O} - \text{(CH}_2\text{)}_5 - \text{C} - \text{CH}_3 \quad \text{O} \quad \text{C}\text{H}_3
\]
8. Effect of Plasticizer

a) External plasticizer

- By dissolves gases on liquids in polymers
- Add to weaken intermolecular forces by salvation
- No stoichiometric upper limit to plasticizer uptake
- Organic, non-polymeric
  (exude to the surface ⇒ polymeric) plasticizer:
  분자량 수천, high bp, weakly polar compounds
  Plasticizer T_g가 낮다 (T_g: -50~150 °C 정도)
8. Effect of Plasticizer

\[ G \quad \text{(Shear modulus)} \]

\[ T_g^* \text{ : Plasticizer의 } T_g \]
\[ T_g^p \text{ : Polymer의 } T_g \]

\[ T_g \text{가 broad하게 변함} \]

\[ T_m \]
\[ \text{Due to limited compatibility} \]
8. Effect of Plasticizer

\[ T_g = T_{gA} \Phi_A + T_{gB} \Phi_B \]

\[ \frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}} \]

\[ T_g = \frac{\Phi_A \alpha_P - T_g(1 - \Phi_p)}{\Phi_A \alpha_P + (1 - \Phi_p)} \]

☞ Rule of thumb \( \Phi_n = 1 \) vol\%

\[ \Rightarrow \Delta T_g = 2 \degree K \]
8. Effect of Plasticizer

b) Internal plasticizer

- Selective copolymer of monomers leading to high $T_g$ and monomers leading to low $T_g$

- Random copolymers

- Very limited