INFLUENCE OF PHYSICAL AGING
ON THE THERMAL AND MECHANICAL BEHAVIORS
OF GLASSY POLYCARBONATE

Thesis of doctorate of applied sciences
Speciality: mechanical engineering

Chinh HO-HUU

Sherbrooke (Québec), Canada  December 2003
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INFLUENCE DU VIEILLISSEMENT PHYSIQUE SUR LES COMPORTEMENTS THERMIQUES ET MÉCANIQUES DU POLYCARBONATE VITREUX

Thèse de doctorat ès sciences appliquées
Spécialité : génie mécanique

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Sherbrooke (Québec), Canada
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RÉSUMÉ

Le polycarbonate (PC) est un plastique amorphe ayant la résistance au choc très élevée, la bonne ductilité et la rigidité moyenne. C'est très difficile à casser et ce matériau est donc considéré comme anti-rupture. En raison du phénomène de vieillissement physique, les caractéristiques mécaniques des produits de PC peuvent être changées. L'objectif de cette thèse est d'étudier les effets du vieillissement sur les comportements de l'écoulement plastique et à la rupture de différents polycarbonates non modifiés: deux catégories à masses molaires hautes et basse, barres moulées par injection, et feuilles extrudées.

Les effets du temps et de la température sur le vieillissement physique du PC ont été d'abord étudiés avec le calorimètre différentiel à balayage (DSC). Le vieillissement du PC est un processus progressif impliquant plusieurs mécanismes. Pendant la trempe, le rajeunissement et le vieillissement ont lieu simultanément. En première étape de la trempe, le rajeunissement est plus important. À l'étape plus tard, le vieillissement devient prédominant et est supérieur au processus de rajeunissement.

La deuxième partie de cette thèse est d'étudier les effets du vieillissement physique sur la cinétique de l'écoulement plastique dans le PC. En termes de mouvement moléculaire, le processus de l'écoulement plastique est un processus thermiquement activé comportant des mouvements inter- et intramoléculaires. La dépendance temps-température de l'écoulement plastique peut être séparée en deux régions (α et β). Le vieillissement thermique cause également une diminution de l'entropie d'activation (ΔS) dans le PC, et cette diminution est plus importante quand la masse molaire est réduite. L'augmentation du temps (t_{ag}) et de la température (T_{ag}) du vieillissement provoque une réduction continue de ΔS. Le taux de vieillissement baisse avec diminution de T_{ag}, et au-dessous de 30°C il n'y a pas de vieillissement dans l'écoulement plastique. Les cinétiques des processus de l'écoulement plastique et du vieillissement dans le PC sont différents.

La troisième partie de cette thèse concerne les effets du vieillissement physique et de la température sur le comportement à la rupture du PC. Les mesures de l'énergie à la rupture ont montré une réduction continue avec t_{ag} et T_{ag} qui augmentent. Ces effets de vieillissement sont confirmés par le changement de la ténacité à la rupture mesuré par des essais de flexion troïs-point, et par la variation de la température fictive mesurée par DSC. Ces résultats contredisent les effets du vieillissement sur la ténacité à la rupture observée par l'approche du travail essentiel de rupture (EWF) qui montre les régions anormales d'augmentation de la ténacité à la rupture en fonction du vieillissement. La transition fragile-ductile dans le comportement à la rupture est analysée par une approche d'énergie d'activation. Le vieillissement augmente la température de la transition fragile-ductile, et l'effet est plus prononcé pour l'échantillon à masse molaire plus basse.

III
SUMMARY

Polycarbonate (PC) is an amorphous plastic with very high impact strength, good ductility and fair stiffness. It is very difficult to break and the material is therefore considered fracture-proof. Due to physical aging phenomenon, the mechanical characteristics of PC products can be altered. The focus of this thesis is to study the effects of aging on the yielding and the fracture behaviors of various unmodified polycarbonates: high and low molecular-weight grades, injection molded bars, and extruded sheets.

The effects of time and temperature on physical aging of PC have been firstly investigated by differential scanning calorimetry (DSC). Aging of PC is a progressive process involving several mechanisms. During annealing, rejuvenation and aging take place simultaneously. At the early stage of annealing, rejuvenation is more important and can be easily detected by DSC analysis. At a later annealing stage, aging becomes predominant and outweighs the rejuvenation process.

The second part of this thesis is to investigate the effects of physical aging on the kinetics of yielding in PC. In terms of molecular movement, the yielding process is a thermally activated process involving inter- and intra-molecular motions. The time-temperature dependence of yielding behavior can be separated into two regions (α and β). Aging does not affect localized molecular motions of the β process during yielding. Heat aging also causes a decrease of the activation entropy (ΔS) in PC, and this decrease is more important when the molecular weight is reduced. Increasing the aging time (t_{ag}) and aging temperature (T_{ag}) results in a continuous reduction of ΔS. The rate of aging decreases with decreasing T_{ag}, and below about 30°C no aging takes place in yielding behavior. The kinetics of yielding and aging processes in PC are different. An increase in the strain rate does not have the same effect on the yield stress (σ_y) as an increase in the aging time by a same factor.

The third part of this thesis deals with the effects of physical aging and time-temperature on fracture behavior of PC. Measurements of the strain energy density showed a continuous reduction when t_{ag} and T_{ag} increase. These aging effects are confirmed by the change in fracture toughness, as measured by three-point bending tests. The variations of fictive temperature, measured by DSC, also show the same trends when t_{ag} changes. These results contradict the effects of aging on fracture toughness observed by the essential work of fracture (EWF) approach which shows anomalous regions of increasing fracture toughness with aging. The brittle-ductile transition in fracture behavior is analyzed by an activation energy approach. Aging increases the brittle-ductile transition temperature, and the effect is more pronounced for the lower molecular-weight sample.
ACKNOWLEDGMENTS

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<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>$a$</td>
<td>Crack length of SENB sample (mm).</td>
</tr>
<tr>
<td>$a_o$</td>
<td>Pre-notched length of SENB sample (mm).</td>
</tr>
<tr>
<td>$C_1$, $C_2$</td>
<td>Experiment constants in Equation (3-8).</td>
</tr>
<tr>
<td>$D$</td>
<td>Width of SENB sample (mm).</td>
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<tr>
<td>$(dW/dV)^*$</td>
<td>Strain energy density (MJ/m$^3$).</td>
</tr>
<tr>
<td>$G_c$</td>
<td>Fracture energy in brittle mode (kJ/m$^2$).</td>
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<tr>
<td>$G_i$</td>
<td>Fracture energy at crack initiation in ductile mode (kJ/m$^2$).</td>
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<tr>
<td>$G_{inst}$</td>
<td>Fracture energy at unstable crack propagation in semi-ductile mode (kJ/m$^2$).</td>
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<td>$L$</td>
<td>Ligament in DENT sample (mm).</td>
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<td>$N_1$, $N_2$</td>
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<td>$P$</td>
<td>Load (N).</td>
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<tr>
<td>$R$</td>
<td>Universal gas constant (J/mol/K).</td>
</tr>
<tr>
<td>$S$</td>
<td>Span of sample in fracture test (mm).</td>
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<tr>
<td>$T$</td>
<td>Temperature (°C or K).</td>
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<td>$T_{ag}$</td>
<td>Aging temperature (°C or K).</td>
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<td>$T_{bd}$</td>
<td>Brittle-ductile transition temperature in fracture (°C or K).</td>
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<td>$T_f$</td>
<td>Fictive temperature in DSC measurements (°C or K).</td>
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<td>Glass transition temperature (°C or K).</td>
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<td>$t$</td>
<td>Time (sec).</td>
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<td>$t$</td>
<td>Thickness of sample (mm).</td>
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<td>$t_{ag}$</td>
<td>Aging time (hour).</td>
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<td>$V^*$</td>
<td>Activation volume in yielding (nm$^3$).</td>
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<td>$V_{ca}^<em>$, $V_{cf}^</em>$</td>
<td>Activation volumes in compressive yielding (nm$^3$).</td>
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<td>$V_{ia}^<em>$, $V_{i\phi}^</em>$</td>
<td>Activation volumes in tensile yielding (nm$^3$).</td>
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<tr>
<td>$v$</td>
<td>Loading speed (mm/min or m/s).</td>
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<td>$w_e$</td>
<td>Specific essential work of fracture in EWF approach (kJ/m$^2$).</td>
</tr>
<tr>
<td>$w_f$</td>
<td>Specific total work of fracture in EWF approach (kJ/m$^2$).</td>
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<tr>
<td>$w_p$</td>
<td>Specific non-essential plastic work in EWF approach (MJ/m$^3$).</td>
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\( \beta \)  
Shape factor in Equations (4-1), (4-2).

\( \Delta H \)  
Activation energy in yielding (kJ/mol).

\( \Delta H_f \)  
Activation energy in fracture (kJ/mol).

\( \Delta H_{\alpha}, \Delta H_{\beta} \)  
Activation energies in yielding for \( \alpha \) and \( \beta \) process respectively (kJ/mol).

\( \Delta L_y \)  
Tensile yield elongation (mm).

\( \Delta S \)  
Activation entropy in yielding (J/mol/K).

\( \Delta S_f \)  
Activation entropy in fracture (J/mol/K).

\( \Delta \sigma_y \)  
Increase of yield stress after aging (in compression or in tension) (MPa).

\( \delta \)  
Displacement at the loading point in fracture test (mm).

\( \delta_H \)  
Excess enthalpy in DSC measurements (J/g).

\( \varepsilon \)  
Strain (mm/mm).

\( \dot{\varepsilon} \)  
Strain rate (sec\(^{-1}\)).

\( \dot{\varepsilon}_f \)  
Pre-exponential factor for strain rate in fracture (sec\(^{-1}\)).

\( \dot{\varepsilon}_o, \dot{\varepsilon}_{\alpha}, \dot{\varepsilon}_{\alpha\beta} \)  
Pre-exponential factors for strain rate in yielding (sec\(^{-1}\)).

\( \dot{\varepsilon}_\beta \)  
Variable in Equation (3-7) (sec\(^{-1}\)).

\( \sigma \)  
Stress (MPa).

\( \sigma_y \)  
Yield stress in general (in compression or in tension) (MPa).

\( \sigma_{yc} \)  
Compressive yield stress (MPa).

\( \sigma_{yt} \)  
Tensile yield stress (MPa).

\( \nu_0 \)  
Frequency factor in Equations (3-3), (4-8) (sec\(^{-1}\)).
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BPA-PC</td>
<td>Bisphenol A-based Polycarbonate</td>
</tr>
<tr>
<td>DENT</td>
<td>Double Edge Notched Tension</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EWF</td>
<td>Essential Work of Fracture</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transformed Infrared Spectroscopy</td>
</tr>
<tr>
<td>IFPZ</td>
<td>Inner Fracture Process Zone</td>
</tr>
<tr>
<td>MDSC</td>
<td>Modulated Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>OPDZ</td>
<td>Outer Plastic Deformation Zone</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
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<td>PSC</td>
<td>Plane Strain Compression</td>
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<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>SENB</td>
<td>Single Edge Notched Bending</td>
</tr>
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<td>SENT</td>
<td>Single Edge Notched Tension</td>
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CHAPTER 1

INTRODUCTION

1.1 Aging effects on the thermal and mechanical properties of polymers

Thermal transitions in polymers include melting ($T_m$), glass transition ($T_g$), secondary relaxation transition ($T_D$), among others. These transitions show different sensitivities to various properties and may be the best indicators of change and degradation during use. Bershtein and co-worker [1] has reported that the area of sub-$T_g$ transitions can be considered the "activation barrier" for solid-phase reactions, flow of creep, deformation, physical aging change, acoustic damping because the activation energy for the transition and these processes is similar. The $T_g$ represents the major transition for many polymers, defining one end of the operating range. In addition, the thermal and mechanical histories of the material affect the value of the $T_g$. Changes in the temperature of the $T_g$ are commonly used to monitor changes in the polymers, such as increased cross-linking from thermal or UV aging [2].

1.1.1 Thermal properties of polymers

The thermal behavior of glassy polymers can be understood in terms of their structure which are formed typically by substances containing long chains, networks of linked atoms or those that possess a complex molecular structure. Normally such materials have a high viscosity in the liquid state. When rapid cooling occurs to a temperature at which the crystalline state is expected to be the more stable, molecular movement is too sluggish or the geometry too awkward to take up a crystalline conformation. Therefore the random arrangement characteristic of the liquid persists down to temperatures at which the viscosity is so high that the material is considered to be solid. The term glassy has come to be synonymous with a persistent non-equilibrium state. In fact, a path to the state of lowest energy might not be available.
To become more quantitative about the characterization of the liquid-glass transition phenomenon and the glass transition temperature, $T_g$, we note that in cooling an amorphous material from the liquid state, there is no abrupt change in volume such as occurs in the case of cooling of a crystalline material through its freezing point, $T_f$. Instead, at the glass transition temperature, $T_g$, there is a change in slope of the curve of specific volume vs. temperature, moving from a low value in the glassy state to a higher value in the rubbery state over a range of temperatures. This comparison between a crystalline material (1) and an amorphous material (2) is illustrated in the Figure 1-1. Note that the intersections of the two straight line segments of curve (2) defines the quantity $T_g$.

![Diagram](image)

Figure 1-1: Specific volume measurements of polymers by dilatometric method.

The specific volume measurements shown here, made on an amorphous polymer (2), are carried out in a dilatometer at a slow heating rate. In this apparatus, a sample is placed in a glass bulb and a confining liquid, usually mercury, is introduced into the bulb so that the liquid surrounds the sample and extends partway up a narrow bore glass capillary tube. A capillary tube is used so that relatively small changes in polymer volume caused by changing the temperature produce easily measured changes in the height of the mercury in the capillary.

The determination of $T_g$ for amorphous materials, including polymers as mentioned above, by dilatometric methods (as well as by other methods) are found to be rate dependent. This is
schematically illustrated in the Figure 1-2, again representing an amorphous polymer, where the higher value, $T_{g2}$, is obtained with a substantially higher cooling rate than for $T_{g1}$.

Figure 1-2: Effect of cooling rate on the $T_g$ measurement by dilatometric method.

We can understand this rate dependence in terms of intermolecular relaxation processes. Since a glass is not an equilibrium phase, its properties will exhibit a time dependence, or physical aging. The primary portion of the relaxation behavior governing the glass transition in polymers can be related to their tangled chain structure where cooperative molecular motion is required for internal readjustments. At temperatures well above $T_g$, 10 to 50 repeat units of the polymer backbone are relatively free to move in cooperative thermal motion to provide conformational rearrangement of the backbone. Below $T_g$, the motion of these individual chains segments becomes frozen with only small scale molecular motion remaining, involving individual or small groups of atoms. Thus a rapid cooling rate or "quench" takes rubbery material into glassy behavior at higher temperatures (higher $T_g$).

While the dilatometer method is the more precise method of determining the glass transition temperature, it is a rather tedious experimental procedure and measurements of $T_g$ are often made in a differential scanning calorimeter (DSC). In this instrument, the heat flow into or out of a small (10 – 20 mg) sample is measured as the sample is subjected to a programmed linear temperature change. This will be discussed in the next section. There are other methods of
measurement such as density, dielectric constant and elastic modulus which are treated in
texts on polymers. These methods are, of course, also rate dependent.

In differential scanning calorimetry (DSC), the thermal properties of a sample are compared
against a standard reference material which has no transition in the temperature range of
interest, such as powdered alumina. Each is contained in a small holder within an adiabatic
enclosure as illustrated in Figure 1-3.

![DSC Schema](image)

Figure 1-3: Schema of differential scanning calorimetry.

The temperature of each holder is monitored by a thermocouple and heat can be supplied
electrically to each holder to keep the temperature of the two equal. A plot of the difference in
energy supplied to the sample against the average temperature, as the latter is slowly increased
through one or more thermal transitions of the sample yields important information about the
transition, such as latent heat or a relatively abrupt change in heat capacity.

1.1.2 DSC responses around the glass transition

The thermal glass transition is observed when a melt that is not able to crystallize undergoes
supercooling. This phenomenon can be explained by assuming that during cooling, the
characteristic time for the cooperative rearrangements approaches the same order of
magnitude as the time determined by the measurement conditions (i.e. by the cooling rate).
The movements specific to the liquid state "freeze" (vitrification). This results in a reduction
of the heat capacity. The temperature at which this effect is observed shifts to lower values
with decreasing cooling rate. The glass transition is a dynamic transition of the supercooled melt from a state of metastable equilibrium to a nonequilibrium state (glass).

On heating, the molecular processes “thaw” (devitrification), but at a temperature that is a little higher than that at which they “froze” on cooling. This leads to overheating or enthalpy relaxation peaks in the heating curve.

Figure 1-4 shows the theoretical change of the enthalpy (the integral of the heat capacity curve) during a thermal glass transition.

\[ egin{align*}
\text{Enthalpy} & \quad \text{Liquid} \\
\text{Glass} & \quad \text{D} \\
T_{g1} & \quad T_{g2} \\
\text{Temperature} & \quad \text{T}_{ag}
\end{align*} \]

Figure 1-4: Theoretical enthalpy curve at the thermal glass transition.

The sample is cooled from A to C at a constant rate. Around B it passes through the region of the glass transition with the glass transition temperature \( T_{g1} \). If the sample is then immediately heated up to the point A again, then the same glass transition temperature is measured. Any differences that arise between the glass transition temperature measured in this way on heating or cooling are due to effects of thermal conductivity within the sample. If the sample is held for some time at a temperature \( T_{ag} \), then it ages and the enthalpy becomes smaller. It attains the state designated by the point D. On heating again, the enthalpy intersects the liquid line at the temperature \( T_{g2} \) (point E). The glass temperature has changed through aging.
In DSC, the glass temperature $T_{g2}$ can also be attained by cooling from the melt at a lower cooling rate. Figure 1-5 shows the differences between the heating and cooling curves in the enthalpy versus temperature diagram. Curve 1 is a cooling curve. No overheating effects occur. The glass temperature $T_{g1}$ is the point of intersection of the extrapolated curves of the liquid and the glass. Curve 2 is the corresponding heating curve when the heating and cooling rates are the same. In this curve, relatively small overheating effects occur with the glass temperature $T_{g1}$. Curve 3 differs from Curve 2 only in a more rapid heating rate. This leads to larger overheating effects but the glass temperature remains the same. If the heating rate is lower than the cooling rate, the glass temperature does not change, but the overheating effect is reduced. Curve 4 represents the measurement of a sample that was heated at the same rate as in curve 2, but which was stored for some time at a temperature $T_{ag}$ below the glass temperature. Two effects occur: the glass temperature is lower ($T_{g2}$) and the overheating peak is larger by an amount equal to the value of the enthalpy relaxation $\delta_H$. The process of storage below the glass transition temperature is also known as physical aging.

![Figure 1-5: Theoretical enthalpy curves at the glass transition to illustrate the differences between cooling and heating curves.](image)

Various quantities can be used to characterize the glass transition. Besides the glass transition temperature ($T_g$), the height of the heat capacity step ($\Delta C_p$), and the width of the glass transition ($\Delta T_g = T_2 - T_I$) are often determined. Other quantities that are used are the height of
the overheating peak \( (h_p) \) and its maximum temperature (i.e. peak temperature, \( T_p \)). In Figure 1-6, a number of characteristic quantities are shown.

![Glass transition diagram](image)

Figure 1-6: A number of characteristic quantities at the glass transition of the DSC curve.

Various methods are used to determine the glass transition temperature. Each method gives a somewhat different result, which is why both the evaluation method and the measurement parameters should always be stated. The following is a short summary of the evaluation methods:

- **Bisector method:** \( T_g \) is the temperature at which the bisector of the angle between the two tangents intersects the measurement curve.

- **Point of inflection:** \( T_g \) is the temperature of the point of inflection of the DSC curve.

- **Half step height:** A straight line extrapolation is performed on the \( C_p \) curves of the liquid \( (C_l) \) and the glass \( (C_g) \). \( T_g \) is the temperature at which the measurement curve attains a height equal to half the value of the step height:

  \[
  C_p(T_g) = \frac{C_l(T_g) - C_g(T_g)}{2} + C_g(T_g)
  \]

- **Richardson method:** Determination of the fictive temperature, \( T_f \), of the glass as the glass transition temperature. This temperature corresponds to the intersection of the
extrapolated enthalpy curves of the glass and the liquid in the enthalpy-temperature diagram shown in Figure 1-4. The determination of $T_f$ is done by means of an area calculation in the heat capacity-temperature diagram (see Figure 1-7).

![Graph showing heat capacity vs. temperature with areas A1, A2, A3, and T_f highlighted.]

Figure 1-7: Determination of fictive temperature by means of a method based on area calculations in the heat capacity-temperature diagram.

The heat capacity-temperature response of a material is an important thermodynamic and physical characteristic. The heat capacity, $C_p$, refers to the ability of a material to store heat and is given by the following expression:

$$C_p = \frac{q/t}{\Delta T/t}$$

In this expression, $C_p$ is the sample’s heat capacity (J/g°C), $q/t$ is the heat flow (W/g), $\Delta T/t$ is the heating rate (°C/s).

The enthalpy, around the glass transition in Figure 1-4, can be determined by DSC through integrating the heat capacity-temperature curve. With the Perkin-Elmer software installed in the DSC Pyris 1 machine, the enthalpy function can be accomplished after generating heat capacity data. The appearance in the glass transition on the enthalpy curve is seen to be a change in slope. The fictive temperature, $T_f$, can be seen as the intersection of the extrapolated
pre-transition and post-transition baselines on the enthalpy curve shown in Figure 2-13 (chapter 2). The fictive temperature, $T_f$, describes the actual state of the glass. The glass transition temperature determined in this way thereby includes information about the history of the material and its structure. The half step height glass temperature, $T_g$, the peak temperature, $T_p$, and the fictive temperature, $T_f$, will be more discussed in the next section.

Enthalpy relaxation or excess enthalpy in a glass depends on the mechanical and thermal conditions during manufacture and storage. It affects the overheating peak of the heating curves. A method that is frequently used to determine the enthalpy relaxation is to first heat the sample up (generating the heating curve $C_{p1}(T)$), then cool it down and afterwards immediately heat it a second time (generating the heating curve $C_{p2}(T)$). The subtraction of the second heating curve from the first yields the enthalpy relaxation:

$$\delta_H = \int_{T_i}^{T_f} \left( C_{p1}(T) - C_{p2}(T) \right) dT$$

A direct determination of the enthalpy relaxation from the area of the overheating peak may lead to large errors. Different methods measuring the enthalpy relaxation, $\delta_H$, will be evaluated and discussed in the next section (chapter 2).

1.1.3 Aging effects on the mechanical properties of polymers

The mechanical properties are most important in the design and selection of engineering plastics because all the applications require necessarily a certain degree of mechanical loading. Natural mechanical testing is necessary for quality control and assurance, comparison and selection of materials, design calculations, prediction of service performance, and as a starting point for the formulation of theories in material sciences [3].

Several large-strain mechanical properties, such as yielding behavior, fracture toughness, can be more changed after a period of a heat treatment that is often called physical aging or annealing. Typically, polymers degrade due to prolonged exposure to non-ambient temperature and/or an aggressive media, and then fail prematurely under mechanical stresses.
For example, if only toughness is considered, polymers deform easily at elevated temperatures as the polymer chain segments become more mobile and lose their rigidity, resulting in a ductile fracture behavior. At low temperatures, the molecular segments are frozen-in, resulting in poor impact resistance.

During the last decades a great deal of attention has been focused on the phenomenon of physical aging in glassy amorphous polymers. It is well known that polymer glasses exist in a non-equilibrium state and for that reason significant changes in the physical properties of the polymer occur as it approaches equilibrium [4].

Annealing of amorphous polymers at temperatures $T_{ag}$ near and below the glass transition temperature, $T_g$, causes aging phenomena which can be accomplished over a short time scale. Sub-$T_g$ annealing affects a large number of the mechanical properties of polymer, for example impact strength, Young’s modulus, tensile strength, hardness, etc. Changes in these properties are governed by two major parameters, the aging temperature $T_{ag}$ and the aging time $t_{ag}$. It has also been shown that the enthalpy relaxation $\delta H$, which is measured by the endothermic peaks observed on the $T_g$ area by differential scanning calorimetry (DSC), is an increasing linear function of logarithm of $t_{ag}$ at a given $T_{ag}$ [5-6].

Intuitively, there should be a correlation between enthalpy relaxation and mechanical properties in bulk polymers since they are both energy dissipation processes. Adam et al. [7] reported that the extra mechanical energy required to deform the annealed polymer is similar in magnitude to the thermal energy associated with the DSC peak. Bauwens [8] attempted to correlate the increase of yield stress and the decrease of enthalpy relaxation.

It would also appear that the fracture toughness of a viscoelastic material should also be a time-temperature dependent parameter. While the fracture behavior of polymers has been studied in-depth, the time-temperature dependence as well as the aging time-aging temperature dependence of fracture is less adequately studied in spite of the interest for their engineering applications.
1.2 Materials for the study

An unmodified Bisphenol A-based polycarbonate (BPA-PC) was used in this study. The excellent properties of PC (transparency, toughness, heat resistance, etc) have been attributed to its unique structure with the repeat units consisting of a bulky bisphenylene group attached to a “flexible” carbonate group [9]. However, the impact strength of PC is extremely dependent on the testing temperature, sample thickness or thermal history.

Injection molded PC samples, with low- and high-molecular weights, were tested. The impact strength of PC is also thickness-dependent, with thin parts more likely to show ductile behavior due to plane stress conditions. A sample thickness of about 3.2 mm is proposed, based on the existing literature [10]. The thinner extruded PC samples were also investigated.

1.2.1 Polycarbonate: history and applications

Polycarbonate is a relatively young member of the large and widespread family of thermoplastics. The earliest significant report on the synthesis of aromatic polycarbonates was published by Einhorn in 1898 [11]. Later, Bischoff and Hedenstroem [12] reported the synthesis of these same polymers by transesterification* with diphenyl carbonate (Figure 1-8). H. Schnell and D.W. Fox who synthesized it independently commercialized this polymer in the 1950’s. In fact, in 1953 Schnell [13], a German researcher at Farbenfabriken Bayer, first synthesized polycarbonate with Bayer resins. The process was quickly tested in an experimental plant and upscaled for industrial production as early as 1958. Otherwise, Fox [14] of General Electric discovered polycarbonate by chance as a viscous compound in a storage flask. Here too, systematic testing soon culminated in industrial-scale production with the G.E Lexan products released in 1959.

Polycarbonate is extremely translucent and has excellent strength and toughness. It possesses good dimensional stability, dielectric strength, flame retardancy, and impact resistance. It is

* The diol often used for this reaction is Bisphenol A, produced from the reaction of phenol and acetone. The phenols are better leaving groups that aliphatic alcohols - and so are more reactive in transesterification reactions
also non-toxic and thus safe for use in the food sector. Further applications include medicine devices, compact disks, safety helmets, window glazing, safety glass, etc (Figure 1-9). But polycarbonate has some disadvantages, that is, it is susceptible to stress cracking with aromatic solvents, and it is difficult to machine.

Figure 1-8: Polycarbonate is produced by transesterification reactions.

Figure 1-9: Current applications of polycarbonate.
1.2.2 Physical aging and DSC analysis of polycarbonate

In general, most theoretical work has focused on volumetric and DSC data rather than mechanical and dielectric data in order to explain the physical aging phenomenon. In fact, the early DSC results of Petrie [5] and the more recent works of Hodge [15] and Bair [16] have served as the primary database for model development and/or testing. Nairn et al. [6] studied the effects of the sample thickness and the sample-cutting preparation technique on the excess enthalpy value measured for aged PC. Bauwens-Crowet and Bauwens [17] proposed that the kinetics of yield and annealing processes as well as enthalpy relaxation were identical in polycarbonate. Recently, Oreddy and Rincon [18] established a correlation between the aging enthalpy at equilibrium state and the change of specific heat at $T_g$. Hutchinson et al. [19] studied the effects of physical aging on the kinetics of enthalpy relaxation, creep response and yield behavior of polycarbonate. They found that the yield stress of annealed samples depends on $\log(\text{aging time})$ in quite a different way from its dependence on $\log(\text{strain rate})$, and showed a disagreement with the results found in [17].

1.2.3 Physical aging and mechanical properties of polycarbonate

The mechanical properties of polycarbonate (PC) and other amorphous thermoplastics are a function of their molecular structure, molecular weight, end-groups, methods of fabrication, secondary finishing operations including physical-aging [20-45].

The impact behavior of PC has long intrigued investigators because it was the first high-temperature amorphous thermoplastic to exhibit ductile behavior in a notched Izod impact test. The first reports on this in the technical literature were in 1967 by Golden et al. [20-21], who focused on the effects of thermal pre-treatment, molecular weight and strain rate on the strength of PC. Subsequently, LeGrand [22] reported on the combined effects of molecular weight, annealing times, and annealing temperatures. The data were correlated by an empirical equation that would be used to predict the influence of these various parameters [22-23]. LeGrand [22] as well as Key and Katz [24] noted that a critical flaw was formed at the tip of the notch in notched samples. Paravin and Williams [25] reported on the brittle-ductile
transition in PC, whereas Mills [26] discussed the mechanism of brittle fracture in this material. Ryan [23] presented an extensive study of the impact and yield properties as a function of strain rate, molecular weight, thermal history, and temperature similar to previous works. Recently, Chang and Hsu [27] have discussed the precrack hysteresis energy in regard to brittle-ductile transition.

The first detailed study of the temperature dependence of stress-strain behavior of PC was reported by Ekvall and Low [28]. Their study was conducted on films rather than injection-molded samples. They observed that the material underwent shear yielding similar to that observed in some metals and that at very low temperatures the samples underwent a ductile-to-brittle transition. Mears and Pae [29] studied the deformation and fracture of this material as a function of hydrostatic pressure and demonstrated that brittle fracture was suppressed by the application of pressure. Wu and Turner [30] reported on the strain response to complex stress histories but failed to take into account thermal and processing histories in their work. They determined the thermal activation parameters for the large strain deformation of polycarbonate. LeGrand [22] reported on the effects of thermal annealing on yield behavior. Bauwens [31] attempted to correlate the yield processes above and below the glass transition using a modified Eyring model, whereas Heymans [32] proposed a model to explain the development of orientation at large strains. Titomanlio and Rizzo [33] studied the large strain compressive behavior of PC. Brown and Windle [34] presented a model to interpret the stress-orientation-strain in amorphous glassy polymers. The large strain-stress behavior at high temperatures was reported by Nied et al. [35].

The other mechanical properties of polycarbonate such as dynamic mechanical analysis, stress relaxation, creep, fatigue, etc, which are outside the scope of the study, were also reported in literature [36-45].
1.3 Objective and scope of the study

The objective of this thesis is threefold: i) to investigate the effects of time and temperature on physical aging of PC from the viewpoint of thermal behavior, ii) to investigate the effects of physical aging on the kinetics of yielding in PC over various loading rates and temperatures, iii) to investigate the effects of physical aging and time-temperature on fracture behavior of PC and to analyze the validity of different approaches of fracture characterization that are currently used.

The scope and methodology of experimental work to be performed are as follows:

(a) To accelerate the aging process of the thermoplastic, the samples were exposed in an oven for different times at various temperatures below the glass transition, $T_g$.

(b) To determine the thermal transitions of the thermoplastic, DSC analysis for a select number of two parameters, the aging temperature and the aging time, was carried out. The concept of lateral cohesional entanglement has been used to explain the observed changes in excess enthalpy.

(c) To measure the time-temperature dependence and the aging time-aging temperature dependence of yielding, tensile tests and plane-strain compression tests were performed on a universal-testing machine. The yielding kinetics has been analyzed based on thermodynamic theory of macromolecular segments.

(d) The changes of activation entropy in yielding $\Delta S_{t_{ag}}$ and enthalpy relaxation $\delta H_{t_{ag}}$ have been used to determine an analytical correlation in various aging temperature, $T_{ag}$.

(e) To determine the fracture toughness of the injection molded samples, low-speed bending fracture tests and impact tests have been analyzed according to the recently proposed fracture models [46-48]. The essential work of fracture method (EWF) has been discussed in studying fracture toughness of the extruded samples.
(f) To determine the time-temperature dependence of the fracture performance, the brittle-ductile transition temperature, $T_{b-d}$, were investigated. The Arrhenius-type equation has been used to correlate $T_{b-d}$ and the loading rate.

1.4 Interest and valuation of the study

In addition from being theoretically interesting, the phenomenon of aging is very important from a practical point of view. Several large-strain mechanical properties (yielding behavior, fracture toughness, etc) of glassy polymers undergo marked changes and strongly depend on the aging time as well as aging temperature. In the testing of such plastics, the aging time and the aging temperature are just as important as other parameters such as temperature, loading speed, humidity, etc. Furthermore, a good understanding of the aging behavior of a material is necessary to the forecast of its long-term behavior from short-term tests.
CHAPTER 2

EFFECTS OF TIME AND TEMPERATURE ON PHYSICAL AGING
OF POLYCARBONATE

2.1 Introduction

It is well known that glassy polymers are in a non-equilibrium thermodynamic state. On cooling from the equilibrium liquid, the transformation to glass occurs at a temperature $T_g$ when the molecular rearrangements, that are need for the polymer to accommodate to the temperature change, slow down to such an extent that they requires a time-scale longer than that imposed by the cooling rate. If the cooling is arrested at a temperature below $T_g$, the polymer will have excess thermodynamic quantities such as volume, enthalpy, and entropy, and there will be a driving force to reduce these quantities towards equilibrium. Thus, at a constant temperature, as time is allowed for the previously frozen-in molecular motions to be released, these thermodynamic quantities will decrease, leading to the phenomenon of physical aging.

Annealing of amorphous polymers at temperatures $T_{ag}$ near and below the glass transition temperature $T_g$, causes aging phenomena which can be accomplished over a short time. Physical aging should not be confused with annealing above $T_g$. The latter improves crystallinity or relieves internal stresses while the molecular rearrangements that take place in physical aging leads to embrittlement. Some glassy polymers such as polycarbonate are relatively tough and are used as fracture-resistant substitute for glass. Aging in polycarbonate is therefore a serious concern. Presently, the understanding of the physical aging on a molecular level is very limited. Many investigations have suggested that aging is a completely morphological effect, that is, a result of the polymer chains attempting to reach an equilibrium, low energy conformation [5-6,8,15-16,18-19,49-50].
Sub-$T_g$ annealing affects a large number of mechanical properties of the polymer, for example impact strength, Young's modulus, tensile strength, hardness, etc. Changes in these properties are governed by two major parameters, the aging temperature $T_{ag}$ and the aging time $t_{ag}$. In this work, the effects of annealing time and temperature on physical aging of polycarbonate have been investigated. Differential scanning calorimetry (DSC) was used to analyze the aging mechanisms. DSC is a means of recording the exothermic and endothermic changes when a material is heated or cooled. The DSC trace of an aged polymer has a peak or overshoot associated with the glass transition. The area of this overshoot represents the extra energy required to convert the aged polymer into rubber and is often used as a measure of aging. It has been shown that the enthalpy relaxation $\delta H_2$ measured by the endothermic peaks observed in the $T_g$ area and the temperature at this peak are increasing linear functions of logarithm of aging time at a given aging temperature [5-6,8,15,19,51]. Other parameters recorded by DSC scans such as fictive temperature and glass transition temperature are also analyzed and their relationships with physical aging are discussed.

2.2 Experimental

A Bisphenol A-based polycarbonate film, Makrofol DE 1-1D, supplied by the Tekra Corporation, was studied in this work. The thermal characteristics were determined with a Perkin-Elmer Differential Scanning Calorimeter, Model Pyris 1. All the samples were first heated in the DSC (at 10 °C/min) to a temperature of 180 °C, well above the glass transition of polycarbonate ($T_g \approx 150$ °C), to eliminate their previous thermal history. The samples were then quenched at a rate of 100 °C/min to the aging or annealing temperature $T_{ag}$, which was chosen in the region from 60 °C to 120°C, i.e., approximately from 85 °C to 25 °C below the nominal $T_g$ of polycarbonate. After the thermal treatment, the sample was heated at 10 °C/min from 60 °C to 180 °C to obtain the first scan of the aged or annealed state. The same sample was then quenched at 100°C/min to 60 °C and reheated again at the same rate to 180 °C to obtain the second scan of the unaged or reference state.
2.3 Results and discussions

Figure 2-1 shows the DSC heat flow diagram of PC samples annealed at a temperature $T_{ag} = 120^\circ$C for different aging times $t_{ag}$. It can be seen that with longer aging time, the excess enthalpy, represented by the magnitude of the endothermic peak, becomes more and more important. The location of this peak also changes with aging time. Figure 2-2 shows the temperature at the endothermic peak, $T_p$, as a function of aging time. As the annealing time at 120$^\circ$C increases, $T_p$ first decreases before shifting to higher temperature. The result is rather surprising because $T_p$ has always been reported to increase with annealing time and temperature [19,52]. It has been shown that $T_p$ depends upon the whole previous thermal history of the sample, i.e. the cooling rate, annealing temperature, annealing time, and heating rate [53]. From the reported data in the literature [19,52-53], both the peak temperature and the excess enthalpy increase linearly with log(aging time). For the case of short aging time, it has also been suggested that the poorly annealed glass display what is called an upper peak during the heating scan, and has been shown theoretically to remain invariant on annealing but not decreasing with aging time. The plot of excess enthalpy versus $\log(t_{ag})$ has been shown to rise linearly even for very short annealing times because enthalpy is being continuously lost during aging. To verify this effect, the excess enthalpy was calculated. Presently, there are two methods of determining the area of overshoot that can be used to calculate the excess enthalpy. The simplest method is to extrapolate the base line of the DSC trace above $T_x$, back in temperature until it touches the peak and take the area enclosed, divided by the sample mass, as the excess enthalpy (see Figure 2-3a). The results measured by this method are shown in Figure 2-3b. It can be seen that the rise in excess enthalpy $\delta H$ with $\log(t_{ag})$ is not linear. As opposed to what observed for $T_p$, the excess enthalpy $\delta H$ does not drop in the lower aging time region but also increases with aging time at this temperature. For shorter aging times, the rate of increase in excess enthalpy is lower than that observed in the longer aging time region, suggesting that several aging mechanisms took place over the range of aging times investigated. The interaction of several mechanisms in aging can be clearly demonstrated in Figure 2-4 that shows the DSC scan for samples annealed at 100$^\circ$C for different times. As the aging time increases, a second peak at lower temperature appears on the DSC trace and it become more and more dominant with aging time. Because of the
appearance of this second peak, $T_p$, no longer reflects the same phenomenon. Consequently, the drop of the endothermic peak with $t_{ag}$ observed above for short aging times is only due to the change in molecular conformation process during aging. This effect can also be observed when the aging temperature is varied as shown in Figure 2-5 for samples aged at various temperatures for 95 hours. The DSC scans show that for an annealing time of 95 hours, the second peak at lower temperature appears when the annealing temperature reaches around 100°C and it becomes predominant with a strong shift to higher temperature with increasing annealing temperature.
Figure 2-1: DSC scans for PC samples annealed at 120°C for different times.

Figure 2-2: Variation of temperature at endothermic peak, $T_p$, as a function of aging time at 120°C.
Figure 2-3: (a) Measurement of excess enthalpy; and (b) Plot of excess enthalpy, $\delta_H$, versus $\log(t_{ag})$ for PC samples annealed at 120°C.
Figure 2-4: DSC scans for PC samples annealed at 100°C for different times.

Figure 2-5: DSC scans for PC samples annealed for 95 hours at various temperatures.
For polycarbonate, the behavior of samples aged at very high temperature (but still below $T_g$) has been found to differ from that of samples aged at lower temperatures. Two distinct phenomena having their own kinetics have thus been proposed to occur in PC; aging and annealing [8,32]. In this approach, the temperature range where the process of aging takes place is bounded between $T_g - 50^\circ$K as the upper limit and by $T_\beta$ as the lower limit. It has also been suggested that in this process, the polymer never reaches its equilibrium structural state. For annealing, it is believed that the range of temperatures where the process takes place is limited between about $T_g - 50^\circ$K and $T_g$, and the polymer may reach its equilibrium. The proposed distinction between aging and annealing cannot explain the change in the aging process observed above because the thermal treatment this case was within the annealing region and was maintained constant during the treatment.

The effects observed above results suggest that aging of PC is a progressive process involving several mechanisms. It is a result of the polymer chains attempting to reach an equilibrium, low energy conformation. Jones [54] has proposed a molecular model for local chain dynamics of glassy polycarbonate (PC). It has been suggested that the diphenyl carbonate group of a PC chain shows trans-trans (T-T) and trans-cis (T-C) conformations through rotations of the phenyl group. In the amorphous phase, both of these two conformations exist. One of the unique features of these different conformations is that the $T$-$T$ conformation is longer than the $T$-$C$ conformation, which the latter prefers the amorphous arrangement. This difference in conformation may interpret the aging effects on PC, losing amorphous properties (decrease in toughness, transparency) and developing crystalline properties (increase in yielding, hardness, etc.). Heymans [32], and Lu and co-workers [55] have also shown that upon sub-$T_g$ annealing, the population of low-energy $T$-$T$ conformation increases, while the population of high-energy $T$-$C$ conformation decreases. By employing Fourier transformed infrared spectroscopy (FTIR), these authors measured the energy absorbed during the conformational change and during aging. Lu et al. [55] compared this energy change with the relaxation enthalpy due to aging by modulated differential scanning calorimetry (MDSC). They found that the energy absorbed by conformational change contributes some, but only small amount of the energy of the endothermic peak in the MDSC measurement. They explained this difference by the concept of cohesional entanglement of neighbouring chain
segments [55-56], a kind of interchain cohesion with local parallel alignment of neighbouring chain segments as physical crosslinks. Rapid quenching of the sample from the rubbery state to the temperature below \( T_g \) does not allow sufficient time for the quenched sample to form new cohesive entanglement along the chain. Sub-\( T_g \) annealing will lead to the increase of the trans-trans conformation, which allows more local parallel alignment of chain segments. This may result in the formation of new cohesive entanglements along the chain. When the linear density of cohesive entanglements along the chain is high, they will hinder the conformational changes in some locations along the chain in the glassy state. Heating the sample to a temperature around \( T_g \) will disentangle some cohesive entanglements. The breaking of cohesive entanglements leads to a sudden conformation change and the absorption of heat as manifested in an endothermic peak in the DSC curve. It has also been suggested that the number of the binding energy of the cohesive entanglements formed during sub-\( T_g \) annealing should depend on the duration of annealing. The longer the sub-\( T_g \) annealing time is, the more the binding energy of the cohesive entanglements is. This explanation is consistent with the results observed in this work. The progressive change in the slope of excess enthalpy versus aging time suggest that aging begin with a conformational change and when there are sufficiently local parallel alignment of chain segments, cohesive entanglements along the chain are progressively formed, resulting in a stronger increase in excess enthalpy with aging time. It is worth mentioning that the concept of lateral entanglements is also consistent with the shift of \( T_p \) toward higher temperature for longer aging times. An increase in the density of cohesive entanglement with aging will lead to a stronger morphology that will require a higher temperature and a higher energy to disentangle. The location at the minimum value of \( T_p \) would thus probably correspond to the onset of lateral cohesive entanglements.
Figure 2-6 shows the effect of aging time at two lower annealing temperatures (100°C and 80°C) on $T_p$. At 100°C, as the aging time increases, $T_p$ remains relatively constant before beginning to drop after about 95 hours, whereas at 80°C, $T_p$ does not change at all after 360 hours. As $t_{ag}$ increases the constant region of $T_p$ becomes shorter as can be seen in Figure 2-2 for the case of annealing at 120°C above. The results clearly show that at the earlier stage of physical aging, the temperature at the endothermic peak $T_p$ does not change with annealing time. This reflects the characteristic of the upper peak, composed of poorly stabilized glass with large value of excess enthalpy before heating as suggested in [19].

![Graph showing variation of temperature at endothermic peak $T_p$, as a function of aging time at 80°C and 100°C.](image)

Figure 2-6: Variation of temperature at endothermic peak, $T_p$, as a function of aging time at 80°C and 100°C.

Figures 2-7 and 2-8 show respectively the variation of excess enthalpy as a function of aging time at 100°C and 80°C respectively. The results revealed that at 100°C, several increasing and decreasing periods of excess enthalpy with $t_{ag}$ take place. At a later stage (longer $t_{ag}$) a strong rise in $\delta H$ with aging time can be observed. Furthermore the plot of excess enthalpy versus log($t_{ag}$) is not linear, confirming again that aging is not a simple process with a single
kinetics but it involves a complex interaction of various mechanisms. At 80°C, even though the scatter of the experimental data is relatively large, it can be seen that $\delta_{H}$ drops continuously over the range of aging times investigated (up to 360 hours). The drop in $\delta_{H}$ with $t_{ag}$ suggests that de-aging or rejuvenation takes place since the enthalpy increases. It should be noted that at short aging times and low aging temperatures, the excess enthalpy measured by this method (see Figure 2-3) favours the upper endothermic peak. The result in Figure 2-8 for the annealing temperature of 80°C reflects therefore mostly the change of poorly stabilized PC with large value of excess enthalpy before heating [19].

Figure 2-7: Plot of excess enthalpy, $\delta_{H}$, versus $\log(t_{ag})$ for PC samples annealed at 100°C.
Figure 2-8: Plot of excess enthalpy, $\delta_H$, versus $\log(t_{ag})$ for PC samples annealed at 80°C.

In fact the relaxation time of the polymer for responding to thermal change during the heating scan can have a confusing effect on the $T_g$ region of the DSC curve as shown in Figure 2-9. The effect of aging is expected to lower the glass transition temperature. However, the results show that when scanned at 10°C/min, the $T_g$ of samples annealed at 120°C for more than 3 hours is displaced to a higher temperature. Consequently the enthalpy change associated with the increased heat capacity above $T_g$ is also displaced in time to a higher temperature. To overcome this problem, a more complicated method has been proposed to evaluate the real excess enthalpy. In this method, after the first heating scan of the aged sample above its glass transition temperature, the sample is held at that temperature to remove the aging effect and then quenched. The same sample is then scanned again to measure a reference curve of the unaged state. Subtraction of the DSC curves between the aged and quenched (unaged) state will give the excess enthalpy. This method is considered to be more accurate than the first method because it takes into account the increase in $T_g$ caused by aging. However experimental overlapping curves also involves subjective data manipulation and related experimental errors.
Figure 2-9: Variation of glass-transition temperature, \( T_g \), as a function of aging time at 120\(^\circ\)C.

Figures 2-10 to 2-12 show the data obtained with the second method to measure the excess enthalpy for the three aging temperatures (80, 100, 120\(^\circ\)C). It can be seen that scatter of the experimental data is much larger for the second method. The scatter is more important for lower aging temperature, due to the smaller values of excess enthalpy involved. The results suggest that each method may lead to a different interpretation of the aging process. For instance with the aging temperature of 100\(^\circ\)C, the second method (Figure 2-11) shows a more significant rise in excess enthalpy with aging time from 0 to about 100 hours whereas the first method (Figure 2-7), \( \delta_H \) shows a much lesser change with two decreasing periods with aging time (before the onset of a strong rise after about 100 hours). This discrepancy could be explained by the fact that in the second method, the subtraction between the DSC scans of aged and de-aged samples would include the change in both the upper and the lower peaks even if the latter is small at low annealing times or temperatures, whereas when the lower peak is not significant, the second method would indicate only the change in the upper peak (at short aging times and/or low aging temperatures). This effect is further confirmed by the difference in the DSC scans of the samples aged at 120\(^\circ\)C and 80\(^\circ\)C. At 120\(^\circ\)C, the first
method shows a continuous rise in the slope of $\delta_t$ versus $\log(t_{ag})$ (Figure 2-3), reflecting an earlier stage in the aging process, whereas the second method (Figure 2-10) indicates an advanced state of aging with a linear correlation between $\delta_t$ and $\log(t_{ag})$. At the annealing temperature of 80°C, measurements by the second method (Figure 2-12) indicate that after a decreasing period, $\delta_t$ starts to rise after an aging time of about 11 hours, suggesting that aging becomes more dominant. Conversely, as shown in Figure 2-8, measurements by the first method show a continuous reduction of $\delta_t$ up to 360 hours of aging time. The negative values of excess enthalpy recorded by this method confirm again that rejuvenation takes place under certain range of annealing times and temperatures observed above. The results also suggest that rejuvenation would preferably take place in the poorly stabilized PC with high excess enthalpy since it is more reflected by the upper peak. Conversely, aging would occur in the more stabilized and order PC as it manifests mostly in the lower endothermic peak. Since these peaks change simultaneously under annealing, the processes of rejuvenation and aging would also take place simultaneously. At the early stage of annealing, rejuvenation is more dominant and can be detected by the DSC scan but at a later annealing stage, aging becomes predominant and outweighs the rejuvenation process.
Figure 2-10: (a) Subtraction method to measure excess enthalpy $\delta_H$; and (b) Plot of excess enthalpy, $\delta_H$, versus $\log(t_{ag})$ for PC samples annealed at 120°C.
Figure 2-11: Variation of $\delta_H$, measured by subtraction method, as a function of $\log(t_{ag})$ for PC samples annealed at 100°C.

Figure 2-12: Variation of $\delta_H$, measured by subtraction method, as a function of $\log(t_{ag})$ for PC samples annealed at 80°C.
From the DSC scans, the concept of fictive temperature has also been introduced to account quantitatively for the various effects produced by quenching and annealing [17,57-59]. This parameter is directly related to the state of aging of glassy materials. The fictive temperature, $T_f$, of a glass in an aged state at time $t$ is defined as the temperature at which the volume would be equal to the equilibrium volume at $T_f$ if the sample were instantaneously removed to that temperature. The fictive temperature at the start of aging is thus equal to $T_g$. During aging, the fictive temperature will be reduced in a manner that characterizes the kinetics of the relaxation. From the relative enthalpy curve, generated by integrating the specific heat data, the appearance of the glass transition is seen to be a change in slope. The fictive temperature can be determined as the intersection of the extrapolated pre-transition and post-transition baselines on this enthalpy curve as shown in Figure 2-13. Figures 2-14 to 2-16 show respectively the variation of fictive temperature as a function of aging time at 120°C, 100°C and 80°C. It can be seen that at 120°C (Figure 2-14), $T_f$ continuously decreases with $t_{eq}$, reflecting the aging process as discussed above. For the case of 80°C (Figure 2-16), it can be seen that $T_f$ continuously increases up to 360 hours, confirming that rejuvenation take place at this temperature. For the case of 100°C (Figure 2-15), $T_f$ seems to remain relatively constant before dropping when aging becomes sufficiently severe. Unlike the result shown in Figure 2-7, the regions in which rejuvenation takes place (and consequently a rise in $T_f$) cannot be observed, due to relative large scatter of the experimental data.

![Figure 2-13: Determination of fictive temperature.](image-url)
Figure 2-14: Variation of fictive temperature, $T_f$, as a function of aging time at 120°C.

Figure 2-15: Variation of fictive temperature, $T_f$, as a function of aging time at 100°C.
Figure 2-16: Variation of fictive temperature, $T_f$, as a function of aging time at 80°C.

2.4 Conclusion

The results have shown that the rise in excess enthalpy $\delta_H$ with log (aging time) is not linear, suggesting that several aging mechanisms took place over the range of aging times investigated. As the aging time increases, a second peak at lower temperature appears on the DSC trace and it become more and more dominant with aging time. Because of the appearance of this second peak, the temperature at the endothermic peak $T_p$ no longer reflects the same phenomenon. The drop of the $T_p$ with $t_{ag}$ observed for short aging times is only due to the change in the mechanism of molecular conformation with increasing aging time. This leads to the appearance of a second peak at lower temperature. With increasing annealing time or temperature the lower peak becomes predominant and shifts to higher temperature. The concept of lateral entanglements can explain the observed changes in excess enthalpy and agrees with the shift of $T_p$ toward higher temperature with increasing aging time. An increase in the density of cohesional entanglement with aging stage will lead to a stronger morphology that will require a higher temperature and a higher energy to disentangle. At the earlier stage
of physical aging, the temperature at the endothermic peak $T_p$ does not change with annealing time due to the upper endothermic peak. The location at the minimum value of $T_p$ would probably correspond to the onset of lateral cohesional entanglements. The effect of aging is expected to lower the glass transition temperature $T_g$. However, the result show that when scanned at 10°C/min, the $T_g$ of samples annealed at 120°C for more than 3 hours is displaced to a higher temperature. The results of measurements and interpretation of the aging process strongly depends on the method used to calculate the excess enthalpy from the DSC scan. The subtraction between the DSC scans of aged and de-aged samples would include the change in both the upper and the lower endothermic peaks. However the method of extrapolating the base line of the DSC trace above $T_g$ back in temperature until it touches the peak and take the area enclosed, would indicate only the change in the upper peak when the lower peak is not significant, i.e. at short aging times and/or low aging temperatures. Conversely, the former method reflects a more advanced state of aging. The results suggest that during annealing, both rejuvenation and aging occur. Rejuvenation is more reflected by the upper peak whereas aging manifest in the lower endothermic peak. Since these peaks change simultaneously under annealing, the processes of rejuvenation and aging would also take place simultaneously. At the early stage of annealing, rejuvenation is more important and can be detected by the DSC scan but at a later annealing stage, aging becomes predominant and outweighs the rejuvenation process.
CHAPTER 3

EFFECTS OF PHYSICAL AGING ON YIELDING KINETICS
OF POLYCARBONATE

3.1 Introduction

On cooling amorphous polymers from the equilibrium liquid, the transformation to glass occurs at a temperature \( T_g \) when the molecular rearrangements, that are need for the polymer to accommodate to the temperature change, slow down to such an extent that they requires a time-scale longer than that imposed by the cooling rate. If the cooling is arrested at a temperature below \( T_g \), the polymer will have excess thermodynamic quantities such as volume, enthalpy, and entropy, and there will be a driving force to reduce these quantities towards equilibrium. Thus, at a constant temperature, as time is allowed for the previously frozen-in molecular motions to be released, these thermodynamic quantities will decrease, leading to the phenomenon of physical aging. Physical aging has been known for many years as an inherent property of glassy materials. Annealing polymers in a temperature range below their glass transition temperature (below \( T_g \)) results in changes in their structure and their mechanical properties. In several studies on physical aging of polycarbonate [19] as well as in polyvinylacetate [60], factors such as: enthalpy, creep and yielding have been analyzed and discussed in terms of the relationship between structure and properties due to physical aging.

In tensile tests, yielding and cold-drawing of polycarbonate (PC) has been considered to be a double transition, first as a transition from an isotropic glass to an isotropic rubbery state at yield, and then, on unloading after stretching of a rubbery mesophase, a transition from an oriented rubber to an oriented glass [61]. Physical aging strongly affects the characteristic features of the stress-strain curve of PC. In unaged condition, PC is hard and tough, but after aging, the curve becomes more brittle. For example, after annealing for more than 300 hours at 120°C, the tensile stress-strain curve becomes brittle and drawing entirely disappears in PC. In terms of molecular movement, the yielding process of a polymer is usually regarded as a
momentary condition of viscous flow because it denotes the point at which the change of stress with strain is zero for a given strain rate. It is thus considered to be a thermally activated process involving inter- and intra-molecular motion. Ree-Eyring’s viscosity theory [62] has therefore been used in this case. Although this theory was developed for shear-induced viscous liquid flow, it has been successfully used to describe the yielding behavior of a number of polymers: polycarbonate (PC) [63], polymethyl methacrylate (PMMA) [64], polyethylene terephthalate (PET) [65], isotactic polypropylene (iPP) [66].

The purpose of this work was to investigate the effects of physical aging on the kinetics of yielding in polycarbonate. PC samples were annealed over a wide range of aging times and temperatures. Both tensile and compressive tests were performed over various loading rates and temperatures to analyze the effects of aging time and aging temperature on yielding kinetics.

3.2 Experimental

Two grades of polycarbonate of different molecular weights, Makrolon 2608 (low-molecular-weight $M_w \approx 26,000$), and Makrolon 3208 (high-molecular-weight $M_w \approx 32,000$), supplied by Bayer were analyzed in this study. Tensile tests were performed on M1 type tensile samples according to the ASTM Standard D 638-01 [67]. All the samples were injection molded. Compression tests were also carried out because PC became too brittle at very low temperatures and very high loading rates [68] and the yield stress could not be determined by tensile tests. These tests were carried out over a wide range of crosshead speeds from 0.2 up to 100 mm/min, and a wide range of temperatures from $-80^\circ$C to $60^\circ$C, using an Instron Automated Material Testing System, Model 4206. At least three samples were done for each testing condition. The technique adopted in this work was a plane strain compression (PSC), introduced by Ikeda [69]. The advantage of this test is that the loaded area is constant and that instability due to reduction in area or buckling cannot occur. The dimensions of the PSC samples were 3.18 mm thick, 12.7 ± 0.2 mm wide, and 60 ± 15 mm long (see Figure 3-1).
3.3 Results and discussions

From the Ree-Eyring's viscosity theory [62], the yield stress has been expressed as:

\[
\frac{\sigma_y}{T} = V^* \left( \frac{\Delta H}{RT} + 2.303 \log \left( \frac{2 \dot{\varepsilon}}{\dot{\varepsilon}_o} \right) \right)
\]  

where \(\Delta H\) is the activation energy of the yielding process, \(T\) is the absolute temperature, \(\dot{\varepsilon}\) is the strain rate (proportional to the cross-head speed), \(V^*\) is called the activation volume, \(\dot{\varepsilon}_o\) is the pre-exponential factor and \(R\) is the universal gas constant.

In order to verify this theory, tensile tests were performed over a range of high temperatures from 22°C to 60°C and a range of strain rates from \(6.67 \times 10^{-5}\) s\(^{-1}\) to \(6.67 \times 10^{2}\) s\(^{-1}\). For lower temperatures and higher loading rates, the tensile behavior of PC became so brittle so that yielding could not be observed. The plots of tensile data \(\sigma_y/T\) as a function of \(\log \dot{\varepsilon}\),
according to Equation (3-1), are shown in Figure 3-2 for the unaged and annealed samples at 120°C for 96 hours. The activation energy $\Delta H_a$ and the activation volume $V_a^*$ determined from these tensile data are shown in Table 3-1.

**Table 3-1: Activation Energy and Activation Volume of Unaged and Heat-Aged Samples at 120°C for 96 Hours.**

<table>
<thead>
<tr>
<th>Type of yielding</th>
<th>$\Delta H_a \ (kJ \ (mol))$</th>
<th>$V_a^* \ (nm^3 \ (segment))$</th>
<th>$A_a = \frac{R}{V_a^*} \ (10^{-3} \ M Pa \ K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unaged and aged</td>
<td>279-286</td>
<td>3.51-3.73</td>
<td>3.7-3.9</td>
</tr>
<tr>
<td>Bauwens <em>et al.</em> [63]</td>
<td>316</td>
<td>3.21</td>
<td>4.3</td>
</tr>
</tbody>
</table>

It can be seen that the activation energies $\Delta H_a$ obtained from tensile tests are almost the same before and after aging whereas there is a discrepancy in the values of the pre-exponential factor $\dot{\varepsilon}_{\alpha}$. The latter reflects the jump frequency of the polymer segments. In the previous investigation (in chapter 2), it has been shown that annealing strongly affect the excess of enthalpy in PC. The observed unchanged in $\Delta H_a$ after a relatively severe thermal treatment (120°C for 96 hours) suggest that the effect of physical aging on yielding differs to that on enthalpy excess in PC.
Figure 3-2: Variation of $\sigma_y / T$ versus $\log \dot{\varepsilon}$, for unaged samples (solid lines) and aged samples at 120°C for 96h (dashed lines), for: a) Makrolon 2608, and b) Makrolon 3208.
The Eyring’s model assumes that, in moving from one equilibrium position to another, a molecule (or a segment of a macromolecule for polymers) must pass over an energy barrier. In the absence of stress, the segments of the polymer jump over the barrier very infrequently and they do so in random directions. The rate of jump between two equilibrium positions is expressed by an Arrhenius-type equation as:

\[
\text{jump rate} = \dot{e}_o \exp\left[-\frac{\Delta H}{RT}\right]
\]

(3-2)

where \( \dot{e}_o \sim \) Forward jump rate = Backward jump rate at equilibrium

After aging, the fact that only the parameter \( \dot{e}_{oa} \) significantly decreases suggests a slower jump rate of segments of macromolecules between two equilibrium positions. The result suggests therefore that aging reduces the flexibility of the macromolecules and thus, makes the polymer more brittle. In fact, Bauwens [70] has proposed that the parameter \( \dot{e}_{oa} \) contains an entropy term, \( \Delta S \), that varies with physical aging. In the above equations, the activation energy \( \Delta H \) corresponds to the height of a potential energy barrier over which a molecular segment has to pass when it makes a single step of displacement, whereas the activation entropy \( \Delta S \) is a measure of the change in structural disorder of the molecular segment taking place when it jumps over the barrier \( \Delta H \).

According to [70], the parameter \( \dot{e}_{oa} \) can be expressed by:

\[
\dot{e}_{oa} = \frac{1}{2} \nu_o \exp\left(\frac{\Delta S}{R}\right)
\]

(3-3)

where \( \nu_o \), frequency factor, may be taken to be equal to the Debye frequency, as a first approximation [17]:

\[
\nu_o = 10^{13.8975} T_{ag}
\]

(3-4)

with \( \nu_o \) in \( h^{-1} \) and \( T_{ag} \) in K.

Combining Equations (3-3) and (3-4), the activation entropy \( \Delta S \) in yielding can be estimated and shown in Table 3-2. The parameter \( \dot{e}_{oa} \) shown in this Table was deduced from the
experiment data shown in Figures 3-2 to 3-4. Heat-aging causes a decrease of the entropy in polycarbonate, and this decrease is more important for the lower-weight PC sample. Figure 3-5 shows the effect of aging time on the activation entropy that was deduced from the experiment data shown in Figure 3-8. Increasing the annealing time and temperature results in a continuous reduction of activation entropy $\Delta S$.

**Table 3-2: Activation entropy of unaged and heat-aged samples at 120°C for 96 hours.**

<table>
<thead>
<tr>
<th>Type of yielding</th>
<th>Material</th>
<th>$\dot{\varepsilon}_{\text{oa}}$ (sec$^{-1}$)</th>
<th>$\Delta S$ (J/mol/K)</th>
<th>$\Delta S_{\text{aged}} / \Delta S_{\text{unaged}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tension</td>
<td>unaged PC-2608</td>
<td>1.49 E +25</td>
<td>233</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>aged PC-2608</td>
<td>7.25 E +18</td>
<td>112</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>unaged PC-3208</td>
<td>4.57 E +23</td>
<td>204</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>aged PC-3208</td>
<td>1.70 E +19</td>
<td>119</td>
<td>0.58</td>
</tr>
<tr>
<td>Compression</td>
<td>unaged PC-2608</td>
<td>4.67 E +23</td>
<td>204</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>aged PC-2608</td>
<td>5.62 E +20</td>
<td>148</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>unaged PC-3208</td>
<td>2.64 E +26</td>
<td>257</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>aged PC-3208</td>
<td>8.63 E +24</td>
<td>229</td>
<td>0.89</td>
</tr>
</tbody>
</table>
Figure 3-3a: Plot of $\sigma_{yc}/T$ as a function of $\log \dot{\varepsilon}$ for unaged samples of Makrolon 2608.
Figure 3-3b: Plot of $\sigma_{yc}/T$ as a function of $\log \dot{\varepsilon}$ for aged samples of Makrolon 2608 (aged at 120°C for 96 hours).
Figure 3-4a: Plot of $\sigma_{yc}/T$ as a function of log $\dot{\varepsilon}$ for unaged samples of Makrolon 3208.
Figure 3-4b: Plot of $\sigma_{yc}/T$ as a function of $\log \dot{\varepsilon}$ for aged samples of Makrolon 3208 (aged at 120°C for 96 hours).
Figure 3-5: Changes of activation entropy $\Delta S$ with aging time for Makrolon 2608.

It has also been shown that the enthalpy relaxation $\delta H$, which is measured by the endothermic peaks observed on the $T_g$ area by differential scanning calorimetry (DSC), is an increasing linear function of logarithm of $t_{ag}$ at a given $T_{ag}$ [5-6]. Intuitively, there should be a correlation between enthalpy relaxation and mechanical properties in bulk polymers since they are both energy dissipation processes. Struik [71] also suggested that a close relation exists between the tensile yield peak and the well-known endothermic DSC peak at $T_g$. Adam et al. [7] reported that the extra mechanical energy required to deform the annealed polymer is similar in magnitude to the thermal energy associated with the DSC peak. Bauwens [8] attempted to correlate yield stress and enthalpy relaxation.

The DSC results in chapter 2 shows a continuous increase, except $T_{ag} = 80^\circ$C, of the subtracted excess enthalpy $\delta H$ when log($t_{ag}$) increases as shown in Figure 3-6. This variation of $\delta H$ trends inversely to that of activation entropy in yielding $\Delta S$. To visualize the correlation between $\Delta S$ and $\delta H$, the experiment data of the same aging conditions, $t_{ag}$ and $T_{ag}$, are plotted.
in Figure 3-7. This figure represents a well correlated fitting straight line between $\Delta S$ and $\delta_H$ at aging temperatures near below $T_g$ (from 100 to 120°C). But for aging temperatures far below $T_g$ such as 80°C, there seems not to exist a close relation between $\Delta S$ and $\delta_H$. More work is needed before we can speculate on why the correlation is only appropriate for the aging temperatures near below $T_g$. A possible reason is that rejuvenation (or deaging) and aging take place simultaneously during annealing; rejuvenation is more important at the lower temperature, while aging becomes predominant and outweighs the rejuvenation process at a higher temperature of annealing. For PC, in the range below or around 80 °C, the rejuvenation or deaging process grows earlier and becomes dominant in thermal behavior, hence $\delta_H$ becomes negative and unchanged (Figure 3-6); whereas the aging process grows faster in yielding behavior, consequently $\Delta S$ continuously decreases in the same temperature range (Figure 3-5).

![Graph](image)

Figure 3-6: Changes of subtracted enthalpy relaxation $\delta_H$ with aging time for PC samples annealed at 80-120°C.
Figure 3-7: A cross-plot of $\Delta S$ as a function of $\delta_H$ for PC samples annealed at 80-120°C.
In fact, it has been shown that over a very large range of temperatures and loading rates, the yielding behavior of polymers can be controlled by two processes of molecular motion acting in parallel [63-66]. Equation (3-1) has been modified from the theory of Ree-Eyring and expressed by:

\[
\frac{\sigma_{yt}}{T} = \frac{\sigma_{\alpha}}{T} + \frac{\sigma_{\beta}}{T} = \frac{R}{V_{*}} \left[ \frac{\Delta H_{\beta}}{RT} + 2.303 \log \left( \frac{2\dot{\varepsilon}}{\dot{\varepsilon}_{\alpha}} \right) \right] + \frac{R}{V_{*}} \sinh^{-1} \left[ \frac{\dot{\varepsilon}}{\dot{\varepsilon}_{\beta}} \exp \left( \frac{\Delta H_{\beta}}{RT} \right) \right]
\]

(3-5)

and:

\[
\frac{\sigma_{yc}}{T} = \frac{\sigma_{\alpha}}{T} + \frac{\sigma_{\beta}}{T} = \frac{R}{V_{*}} \left[ \frac{\Delta H_{\beta}}{RT} + 2.303 \log \left( \frac{2\dot{\varepsilon}}{\dot{\varepsilon}_{\alpha}} \right) \right] + \frac{R}{V_{*}} \sinh^{-1} \left[ \frac{\dot{\varepsilon}}{\dot{\varepsilon}_{\beta}} \exp \left( \frac{\Delta H_{\beta}}{RT} \right) \right]
\]

(3-6)

where \( V_{*}, V_{*}, V_{*}, \Delta H_{\alpha}, \Delta H_{\beta}, \dot{\varepsilon}_{\alpha}, \) and \( \dot{\varepsilon}_{\beta} \) have the same meanings as in Equation (3-1) but are related to the \( \alpha \) and the \( \beta \) process. It has been suggested that the \( \alpha \) process is controlled by the main-chain motion whereas the \( \beta \) process is rather controlled by localized or lateral chain motions. The subscripts \( t \) and \( c \) refer to the tensile and compression tests respectively. Equations (3-5) and (3-6) have been shown to agree with experimental data for a number of polymers [63-66].

In order to further verify the effect of aging on more localized molecular motions in PC, compression tests were performed at different temperatures ranging from -80°C to 60°C, over two decades of loading speed ranging from 0.2 mm/min to 100 mm/min (corresponding to the strain rates ranging from 0.001 sec\(^{-1}\) to 0.5 sec\(^{-1}\)). The tests were performed on both Makrolon 2608 and Makrolon 3208 (low and high molecular weight respectively), in the unaged state and after the same heat treatment at \( T_{ag} = 120^\circ\text{C} \) for \( t_{ag} = 96 \) hours. Figures 3-3 to 3-4 show the plots of \( \sigma_{yc}/T \) versus logarithm of strain rate \( \dot{\varepsilon} \) for both unaged and heat-aged PC. It can be seen from these figures that the diagram of \( \sigma_{yc}/T \) versus \( \log(\text{strain rate}) \) can be separated into two regions: in the region I (corresponding to high temperatures and low loading rates) a primary molecular motion process \( \alpha \) dominates and in the region II (corresponding to low temperatures and high loading rates) a secondary motion (\( \beta \)) also contributes so that the controlling process becomes \( (\alpha + \beta) \). In Table 3-3, the values of the parameters
\[ V_\alpha^*, \Delta H_\alpha, \dot{\varepsilon}_\alpha, V_\beta^*, \Delta H_\beta, \text{ and } \dot{\varepsilon}_\beta \] of the \( \alpha \) and \( \beta \) processes, characterizing the compressive yielding behavior in polycarbonate are calculated from the best fit of Equation (3-6) with the measured variation of \( \sigma_{yc}/T \) versus \( \log(\text{strain rate}) \), using the same non-linear multivariable regression procedure described in [72].

Between the regions I and II, the curve of \( \sigma_{yc}/T \) as a function of logarithm strain rate shows a noticeable change in slope. This change can be used to find the transition boundary between these two regions by standard mathematics. The transition between the two regions can be expressed as a function of strain rate as follows [66]:

\[ \dot{\varepsilon}_\beta = \frac{\dot{\varepsilon}_\beta}{\sqrt{3}} \exp \left( -\frac{\Delta H_\beta}{RT} \right) \] (3-7)

From the values of \( \dot{\varepsilon}_\beta \) and \( \Delta H_\beta \), a set of points \((\dot{\varepsilon}_\beta, T)\) can be calculated by Equation (3-7). These point constitute a slanting straight-line \( d_c \), separating the two regions I and II (Figures 3-3 to 3-4). Below \( d_c \), the Ree-Eyring theory reduces to the Eyring theory in terms of a single simply activated process and in this case, the plots of yield stresses versus \( \log(\text{strain-rate}) \) or versus temperature give straight lines. Above \( d_c \), due to the existence of the \( \beta \) process in the region of low temperatures and high strain rates, two activated processes are involved. The results obtained from the Ree-Eyring model shown in Table 3-3 also suggest that only the parameter \( \dot{\varepsilon}_\alpha \), corresponding to the jumping frequency in the \( \alpha \) process, varies significantly and reflects the effect of thermal history. The other parameters do not change after aging. Furthermore, according to this model, heat treatment does not affect localized molecular motions during yielding as reflected by the \( \beta \) process. The present results also agree with that reported in [73].
### Table 3-3: Eyring Parameters for Polycarbonate in Compression.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\Delta H_\alpha$ ((kJ/mol))</th>
<th>$V_{c^*}$ ((nm^3/segment))</th>
<th>$\dot{\epsilon}_{o\alpha}$ ((1/sec))</th>
<th>$\Delta H_\beta$ ((kJ/mol))</th>
<th>$V_{c^*}$ ((nm^3/segment))</th>
<th>$\dot{\epsilon}_{o\beta}$ ((1/sec))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-2608</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unaged</td>
<td>267.8</td>
<td>2.58</td>
<td>4.67 E+23</td>
<td>68.8</td>
<td>0.73</td>
<td>1.75 E+13</td>
</tr>
<tr>
<td>Aged(^a)</td>
<td>271.0</td>
<td>2.68</td>
<td>5.62 E+20</td>
<td>68.6</td>
<td>0.81</td>
<td>0.86 E+13</td>
</tr>
<tr>
<td>PC-3208</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unaged</td>
<td>272.4</td>
<td>2.35</td>
<td>2.64 E+26</td>
<td>46.7</td>
<td>0.40</td>
<td>2.12 E+09</td>
</tr>
<tr>
<td>Aged(^a)</td>
<td>278.4</td>
<td>2.44</td>
<td>8.63 E+24</td>
<td>46.6</td>
<td>0.35</td>
<td>2.80 E+09</td>
</tr>
</tbody>
</table>

\(^a\): samples aged at 120°C for 96 hours.

To study the effects of aging time $t_{ag}$ and aging temperature $T_{ag}$ on the yielding kinetics of PC, Makrolon 2608 were annealed at different thermal treatment conditions as shown in Table 3-4. Since the above results show no effect of aging on localized molecular motions of the $\beta$ process, compression tests were carried out only in the region corresponding to the $\alpha$ process, under various temperatures and loading speeds.

### Table 3-4: Thermal Treatment and Compressive Testing Conditions.

<table>
<thead>
<tr>
<th>Group</th>
<th>Annealing conditions</th>
<th>Testing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{ag}$ (°C)</td>
<td>$t_{ag}$ (hours)</td>
</tr>
<tr>
<td>L60</td>
<td>60</td>
<td>6; 12; 24; 48; 96(^a)</td>
</tr>
<tr>
<td>L80</td>
<td>80</td>
<td>6; 12; 24; 48; 96(^a)</td>
</tr>
<tr>
<td>L100</td>
<td>100</td>
<td>6; 12; 24; 48; 96(^a)</td>
</tr>
<tr>
<td>L120</td>
<td>120</td>
<td>6; 12; 24; 48; 96(^a)</td>
</tr>
</tbody>
</table>

\(^a\): the aged-96h samples tested at all temperatures, the rest tested at 22°C only.
In considering that the activation energy $\Delta H_a$ and the activation volume $V_a^*$ are almost unchanged after aging, the values of $\dot{\varepsilon}_{oa}$ have been estimated from the linear relationship between $\sigma_y$ and $\log(\text{strain rate})$ at room temperature using Equation (3-1). The values of $\Delta H_a$ and $V_a^*$ were taken from the values of unaged samples given in Table 3-3. Figure 3-8 shows the plots of $\log(\dot{\varepsilon}_{oa})$ as a function of $\log(t_{ag})$ for Makrolon 2608 annealed at different aging temperatures. The results suggest a linear correlation between $\log(\dot{\varepsilon}_{oa})$ and $\log(t_{ag})$ that can be expressed by:

$$\log(\dot{\varepsilon}_{oa}) = C_2 - C_1 \log(t_{ag})$$  \hspace{1cm} (3-8)

where $C_1$, $C_2$ are two experimental constants. For each aging temperature $T_{ag}$, with $\dot{\varepsilon}_{oa}$ in $\text{sec}^{-1}$ and $t_{ag}$ in hours, the values of $C_1$ and $C_2$ corresponding to different aging times $t_{ag}$ were obtained with the least-squares linear regression technique and are shown in Table 3-5. The results suggest that $C_2$ remain relatively constant, regardless of annealing temperature. However, $C_1$ strongly decreases with annealing temperature, suggesting a decrease of aging rate with temperature. Figure 3-9 shows the plot of $C_1$ against $T_{ag}$. The result suggests a relatively linear correlation. The extrapolation of this plot intersects the $T_{ag}$ axis at about 30°C, suggesting that below this temperature, no aging takes place.

<table>
<thead>
<tr>
<th>Group</th>
<th>Material</th>
<th>$T_{ag}$ (°C)</th>
<th>$t_{ag}$ (hours)</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$R^2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L60</td>
<td>PC-2608</td>
<td>60</td>
<td>6-96</td>
<td>0.32</td>
<td>23.09</td>
<td>98.1</td>
</tr>
<tr>
<td>L80</td>
<td>PC-2608</td>
<td>80</td>
<td>6-96</td>
<td>0.50</td>
<td>23.22</td>
<td>98.9</td>
</tr>
<tr>
<td>L100</td>
<td>PC-2608</td>
<td>100</td>
<td>6-96</td>
<td>0.58</td>
<td>22.64</td>
<td>96.6</td>
</tr>
<tr>
<td>L120</td>
<td>PC-2608</td>
<td>120</td>
<td>6-96</td>
<td>0.91</td>
<td>22.31</td>
<td>98.0</td>
</tr>
</tbody>
</table>
Figure 3-8: Plots of $\log(\dot{e}_{\text{od}})$ vs. $\log(t_{ag})$ for Makrolon 2608 (groups L60-L120).

Figure 3-9: Variation of experimental constant $C_1$ as a function of $T_{ag}$ for Makrolon 2608.
From a practical viewpoint, it might also be useful to estimate the yield stress after a certain aging time at a given temperature. For this purpose, Equation (3-1) can be rearranged as:

$$\frac{\sigma_y}{T} = 2.303 \frac{R}{V^*} \left[ \frac{\Delta H_a}{2.303RT} + \log(2\dot{\varepsilon}) - \log(\dot{\varepsilon}_{oa}) \right]$$  \hspace{1cm} (3-9)

in which the parameters $V^*$, $\Delta H_a$ are the values of unaged samples. At a given temperature and strain rate, the change in yield stress $\Delta \sigma_y$ can be expressed by:

$$\frac{\Delta \sigma_y}{T} = \left( \frac{\sigma_y}{T} \right)_{\text{aged}} - \left( \frac{\sigma_y}{T} \right)_{\text{unaged}} = 2.303 \frac{R}{V^*} \left( \log(\dot{\varepsilon}_{oa})_{\text{unaged}} - \log(\dot{\varepsilon}_{oa})_{\text{aged}} \right)$$  \hspace{1cm} (3-10)

By combining with Equation (3-8), a linear relationship between $\frac{\Delta \sigma_y}{T}$ and $\log(t_{ag})$ for each aging temperature can be simply deduced by:

$$\frac{\Delta \sigma_y}{T} = N_1 \log(t_{ag}) + N_2$$  \hspace{1cm} (3-11)

in which:

$$N_1 = 2.303 \frac{R}{V^*} C_1$$  \hspace{1cm} (3-12)

$$N_2 = 2.303 \frac{R}{V^*} \left( \log(\dot{\varepsilon}_{oa})_{\text{unaged}} - C_2 \right)$$  \hspace{1cm} (3-13)

In the reported investigations on the effect of aging on yielding behavior of polycarbonate, there are two opposite opinions on the yielding kinetics (represented by $d\sigma_y/d(\log \dot{\varepsilon})$) and the aging kinetics (represented by $d\sigma_y/d(\log t_{ag})$). Bauwens and co-worker [8,17] suggested that the kinetics of both yielding and aging processes in polycarbonate are identical. An increase in the strain rate by a factor of 10 has the same effect on the yield stress as an increase in the aging time by a factor of 10. However, Hutchinson et al. [19] disagreed with this idea and suggested that these kinetics are different.

This controversy can be verified using the above Equations. The ratios of change in yielding to that of loading rate and aging time can be determined from Equations (3-9) and (3-11) respectively:
\[
\frac{d(\sigma_y/T)}{d \log(\dot{\varepsilon})} = 2.303 \frac{R}{V_a^*} \tag{3-14}
\]

and

\[
\frac{d(\sigma_y/T)}{d \log(t_{ag})} = N_1 = 2.303 \frac{R}{V_a^*} C_1 \tag{3-15}
\]

Since the constant \(C_1\) varies with aging temperatures as shown in Table 3-5, these two kinetics could not be identical. The above ratios shown in Equations (3-14) and (3-15), \(d(\sigma_y/T)/d \log(\dot{\varepsilon})\) and \(d(\sigma_y/T)/d \log(t_{ag})\), for different aging conditions are also presented in Table 3-6. It can be seen that the first ratio is constant, whereas the second ratio varies with aging temperatures. The results suggest that the variations of yield stress with loading rate and aging time are controlled by two different kinetics.

**Table 3-6: Values of \(d(\sigma_{ye}/T)/d(\log \dot{\varepsilon})\) and \(d(\sigma_{ye}/T)/d(\log t_{ag})\) in Compression.**

<table>
<thead>
<tr>
<th>Group</th>
<th>Material</th>
<th>(T_{ag}) (°C)</th>
<th>(t_{ag}) (hours)</th>
<th>(d(\sigma_{ye}/T)/d(\log \dot{\varepsilon})) (kPa/K per decade)</th>
<th>(d(\sigma_{ye}/T)/d(\log t_{ag})) (kPa/K per decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L60</td>
<td>PC-2608</td>
<td>60</td>
<td>6-96</td>
<td>12.33</td>
<td>3.93</td>
</tr>
<tr>
<td>L80</td>
<td>PC-2608</td>
<td>80</td>
<td>6-96</td>
<td>12.33</td>
<td>6.10</td>
</tr>
<tr>
<td>L100</td>
<td>PC-2608</td>
<td>100</td>
<td>6-96</td>
<td>12.33</td>
<td>7.14</td>
</tr>
<tr>
<td>L120</td>
<td>PC-2608</td>
<td>120</td>
<td>6-96</td>
<td>12.33</td>
<td>11.27</td>
</tr>
</tbody>
</table>
3.4 Conclusion

Physical aging strongly affects the mechanical properties of PC. In unaged condition, PC is hard and tough, but after aging, it becomes more brittle. After annealing for more than 300 hours at 120°C, the tensile stress-strain curve becomes brittle and drawing entirely disappears in PC. In terms of molecular movement, the yielding process is a thermally activated process involving inter- and intra-molecular motions. The time-temperature dependence of yielding behavior can be separated into two regions: in the region corresponding to high temperatures and low loading rates, a primary molecular motion process $\alpha$ dominates. In the region corresponding to low temperatures and high loading rates, a secondary motion $\beta$ also contributes so that the controlling process becomes $(\alpha + \beta)$. Aging does not affect localized molecular motions of the $\beta$ process during yielding. Physical aging in PC results in a slower jump rate of the main segments of macromolecules between two equilibrium positions. It reduces the flexibility of the macromolecules and thus, makes the polymer more brittle. Heat aging also causes a decrease of the entropy ($\Delta S$) in polycarbonate, and this decrease is more important when the molecular weight is reduced. Increasing the annealing time and temperature results in a continuous reduction of $\Delta S$. The rate of aging decreases with decreasing annealing temperature and below about 30°C, no aging takes place. There exists a well-seeming correlation between the activation entropy in yielding, $\Delta S$, and the subtracted enthalpy relaxation, $\delta_{HT}$, for aging temperatures near below $T_g$. The kinetics of yielding and aging processes in polycarbonate are different. An increase in the strain rate does not have the same effect on the yield stress as an increase in the aging time by a same factor.
CHAPTER 4

EFFECTS OF PHYSICAL AGING AND TIME-TEMPERATURE
ON THE FRACTURE PERFORMANCE OF POLYCARBONATE

4.1 Introduction

Physical aging has been known for many years as an inherent property of glassy materials. Annealing polymers in a temperature range below their glass transition temperature (below $T_g$) results in changes in their structure and their mechanical properties. Polycarbonate (PC) is an amorphous plastic with very high impact strength, good ductility and fair stiffness. However, these advantages can be suppressed by physical aging. The mechanical characteristics of polycarbonate products can be altered during service. The changes of mechanical performance due to physical aging can lead to important variations between the short-term data used to characterize the material and its long-term performance. From the reported studies on physical aging of polycarbonate [19] as well as on polyvinylacetate [60], factors such as enthalpy, creep and yielding have been analyzed and discussed in terms of the relationship between structure and properties due to physical aging. However, little attention has been paid to the effect of aging on fracture behavior.

For polymeric film, the Essential Work of Fracture (EWF) method is presently widely used to characterize fracture. The EWF method was originally Broberg's idea [74] and then developed by Cotterell and Reddel [75] for ductile metals. It has been recently used to investigate the toughness of different polymers [76-81], but this technique still remains controversial [82-83]. It has also been shown that fracture performance of polymers depends on both the initiation and the propagation of a defect in the material [84-88]. Depending on the loading rate and temperature, a given polymer can break in a brittle, semi-ductile or ductile manner [46-48,89]. A single fracture toughness parameter is insufficient to evaluate fracture performance.
The objective of this work is twofold: a) to investigate the effects of physical aging on fracture behavior of extruded films and injection molded bars of PC, with the emphasis on brittle-ductile transition in fracture behavior; and b) to analyze the validity of different approaches for fracture characterization currently used.

4.2 EWF theory

The essential work of fracture (EWF), proposed by Broberg [74], assumes that the non-elastic region at the tip of a crack may be divided into two regions: an inner region where the fracture process takes place, and the outer region where the plastic deformation takes place. The total work of fracture, $W_f$, has been thus partitioned into two components: the work that is expanded in the inner fracture process zone (IFPZ) to form a neck and subsequent tearing; and the work that is dissipated in the surrounding outer plastic deformation zone (OPDZ), which is assumed to be proportional to the plastic work dissipation per unit volume of the material (see Figure 4-1). The former is referred to as the essential work of fracture $W_e$ (which is assumed to be a material property for a given sheet thickness and is independent of the sample geometry). The latter is called the non-essential work of fracture $W_p$ (which is a geometry dependent). When both IFPZ and OPDZ are contained in the ligament, the work $W_e$ is proportional to the ligament length $L$ and the work $W_p$ is proportional to the square of the ligament, $L^2$. Hence,

$$W_f = w_e L t + \beta w_p L^2 t$$  \hspace{1cm} (4-1)

and

$$w_f = w_e + \beta w_p L$$  \hspace{1cm} (4-2)

where $w_f$ is the specific total work of fracture ($= W_f / L t$), $w_e$ is the specific essential work of fracture ($= W_e / L t$), $w_p$ is the specific non-essential plastic work ($= W_p / L t$), $\beta$ is a shape factor representing the size of the plastic-zone for a given sample geometry, $t$ is the sample thickness. To obtain $w_e$, a series of samples, with different ligament lengths, can be tested to fracture and the total work, $w_f$, can be plotted against the ligament length, $L$. The essential work of fracture, $w_e$, is then derived from a “best-fit” linear regression analysis of the data (see Figure 4-2). Sample geometries such as the double edge notched tension (DENT) and the
single edge notched tension (SENT) are commonly used for this purpose. But the DENT geometry is generally favored, as its symmetry prevents the sample from twisting, which could be a problem in non-symmetrical geometries such as SENT.

Figure 4-1: Schematic representation of the inner fracture process zone (IFPZ) and the outer plastic deformation zone (OPDZ) in a DENT sample.

\[ w_f = w_e + \beta w_p L \]

Figure 4-2: Graphical determination of \( w_e \) and \( \beta w_p \) parameters from the plot of \( w_f \) vs. \( L \).
4.3 Experimental

The Bisphenol A-based polycarbonate, investigated in this work, included two groups: extruded PC films (thickness of 0.25 mm) and injection molded PC bars (thickness of 3.18 mm). The first group, Makrofol PCVM, was supplied by Tekra Corporation at New Berlin, Wisconsin. The second group, with two grades Makrolon 2608 (low molecular-weight $M_w \approx 26,000$) and Makrolon 3208 (high molecular-weight $M_w \approx 32,000$), was supplied by the Polymer Research Group of Bayer Corporation at Pittsburgh, Pennsylvania. The PC samples were annealed in a Gruenberg bench oven, Model B45C40, at various temperatures, $T_{\text{ann}}$, ranging from 60 to 120°C for different times, $t_{\text{ann}}$, varying from 0 to 240 hours, i.e., approximately from 85°C to 25°C below the nominal $T_g$ (glass transition temperature) of polycarbonate.

For the EWF tests, rectangular samples were cut from Makrofol film sheets and then razor notched to produce a series of DENT samples, with varying ligament lengths, $L$, ranging from 4 to 16 mm (Figure 4-1). The DENT samples were tested on an Instron Automatic Material Testing System, Model 4206; with a grip distance of 70 mm, at room temperature (RT) and a constant crosshead speed of 10 mm/min.

The single edge notched bending sample (SENB), in Figure 4-3, was used for the fracture tests of PC bars (ASTM D5045-99 [90]). The length of the initial crack created in these samples was about 40-50 % of the sample width. A pre-notch was first made by a saw cut and the final crack was created by a razor blade. For low loading speeds ($\leq 200$ mm/min) the fracture tests were performed on the same Instron System 4206, and the dimensions of samples were 3.18-mm thick, $12.8 \pm 0.1$ mm wide and $70 \pm 5$ mm long. The impact tests (2.5 m/sec) were performed on an instrumented Monsanto Plastic Impact Machine. The dimensions of the impact samples were 3.18 mm thick, $10\pm 0.1$ mm wide and $50 \pm 2$ mm long.

The tensile tests were performed on dog-bone samples according to the ASTM standard D638-01 [67], at room temperature and constant loading speed of 10 mm/min for the PC film and 2 mm/min for the PC bars. The tensile engineering stress was calculated from the tensile
force divided by the original cross-sectional area, and the tensile engineering strain was calculated as crosshead displacement divided by the original gauge length of the samples (Figure 4-4).

![Diagram](image)

**Figure 4-3:** Single edge notched bending (SENB) sample for the fracture tests of PC bar.

![Graph](image)

**Figure 4-4:** Typical tensile curve of PC and illustration of strain energy density ($dW/dV$).

The thermal characteristics were determined with a Perkin-Elmer Differential Scanning Calorimeter (DSC), Model Pyris 1. All the samples were first heated in the DSC at 20°C/min to a temperature of 180°C, well above the glass transition of polycarbonate ($T_g \approx 150°C$), to eliminate their previous thermal history. The samples were then quenched at a rate of 100°C/min to the aging or annealing temperature, $T_{aq}$, which was chosen in the region from 60°C to 120°C. After the thermal treatment, the samples were reheated at 10°C/min from 60°C to 180°C to obtain the DSC scan of the aged or annealed state. The same sample was then quenched at 100°C/min to 60°C and reheated again at the same rate to 180°C to obtain the second scan of the unaged state (i.e. state of $t_{aq} = 0$ hours and $T_{aq} = 23°C$).
4.4 Results and discussion

The effect of aging time, $t_{ag}$, on the EWF parameters in PC film aged at 120°C, is shown in Figures 4-5 and 4-6. The results show that the essential work of fracture, $w_f$, and the non-essential work of plastic deformation, $\beta w_p$, show opposite changes with increasing $t_{ag}$. Furthermore, $w_f$ and $\beta w_p$ exhibit respectively a minimum and a maximum value around $t_{ag} = 6$ hours.

Since rejuvenation and aging can take place simultaneously [91], it is important to verify whether these inversions of change in $w_f$ and $\beta w_p$ around $t_{ag} = 6$ hours are due to a rejuvenation effect. The rejuvenation effect can be verified by DSC analysis of the thermal behavior of PC bars and PC films. From the DSC scans, the concept of fictive temperature, $T_f$, has been introduced to take account of the effects produced by quenching and annealing [57-59]. This parameter directly relates to the state of aging of glassy materials. $T_f$ of a glass in an aged state at time $t$ is defined as the temperature at which the volume would be equal to the equilibrium volume at $T_f$ if the sample were instantaneously removed to that temperature. The fictive temperature at the start of aging is thus equal to $T_g$. During aging, the fictive temperature will be reduced in a manner that characterizes the kinetics of the relaxation. From the relative enthalpy curve, generated by integrating the specific heat data, the appearance of the glass transition is seen to be a change of slope. The fictive temperature can be determined as the intersection of the extrapolated pre-transition and post-transition baselines on this enthalpy curve as shown in Figure 2-13 of chapter 2. The effects of aging time on fictive temperature are shown in Figures 4-7 for the PC film. The result revealed that $T_f$ continuously decreases with increasing aging time at 120°C, suggesting that no rejuvenation took place at this temperature.
Figure 4-5: Effect of aging time at 120°C on essential work of fracture ($w_e$) of PC film.

Figure 4-6: Effect of aging time at 120°C on non-essential work ($\beta w_p$) of PC film.
To further verify the result in Figure 4-5, measurements of fracture performance by strain energy density were carried out. In this theory, the parameters governing crack propagation have been proposed by Sih and co-workers [85-87]. The strain energy density function, $dW/dV$, in front of the crack tip has been expressed in the form:

$$\frac{dW}{dV} = \frac{S}{r}$$  \hspace{1cm} (4-3)

where $S$ is the strain energy density factor and $r$ is the distance from the crack tip. The crack growth condition has been established by:

$$\left( \frac{dW}{dV} \right)^* = \frac{S_1}{r_1} = \frac{S_2}{r_2} = \ldots = \frac{S_j}{r_j} = \ldots = \frac{S_c}{r_c} = \text{const.}$$  \hspace{1cm} (4-4)

where $(dW/dV)^*$ is the available energy density that is released when a unit of macro-volume fails as $(dW/dV)^*$ becomes critical. The strain energy density, $(dW/dV)^*$, can be determined by the area under the tensile stress-strain curve to break (see Figure 4-4). The variation of $(dW/dV)^*$ with aging time at 120°C is shown in Figure 4-8 for PC film. As opposed to what observed when the EWF concept is used, the toughness of PC, as measured by the strain energy density theory, continuously decreases with aging time, suggesting again that rejuvenation did not occur at 120°C.

Measurements on injection molded PC bars also confirm that rejuvenation does not take place at 120°C. Figure 4-9 shows that $T_f$ also continuously decreases with aging time at this temperature. The result agrees with the continuous reduction of $(dW/dV)^*$ with aging time as shown in Figure 4-10.
Figure 4-7: Effect of aging time at 120°C on fictive temperature ($T_f$) of PC film.

Figure 4-8: Effect of aging time at 120°C on strain energy density ($dW/dV$) of PC film.
Figure 4-9: Effect of aging time at 120°C on fictive temperature ($T_f$) of PC bar.

Figure 4-10: Effect of aging time at 120°C on strain energy density ($dW/dV$)* of PC bar.
In order to further verify the aging effects on fracture behavior of PC, three-point-bend were also performed on injection molded bars of PC. Low speed fracture tests and impact tests \( (v = 2.5 \text{ m/s}) \) were performed. Two grades of different molecular weights, Makrolon 2608 and Makrolon 3208, were analyzed. These samples were annealed at \( T_{ag} = 120^\circ \text{C} \) for various aging times. The results revealed that, when aging takes place, fracture changes from ductile to brittle behavior. This is consistent with the increase in both yield stress and drawing stress discussed previously (chapter 3 or [92]). The results in Figures 4-11 and 4-12 show that Makrolon 3208 breaks with a ductile behavior at \( v = 200 \text{ mm/min} \) for aging times below 100 hours. With the same thermal history (annealed at 120^\circ \text{C} for 96 hours) Makrolon 2608 breaks in a ductile manner at a loading speed of 2 mm/min, but becomes entirely brittle at 200 mm/min.

The effects of aging temperature, \( T_{ag} \), on the EWF parameters are presented in Figures 4-13 and 4-14. The essential work of fracture \( w_f \) and the non essential work due to plastic deformation \( \beta w_p \) also show two inversions in tendency around \( T_{ag} = 60^\circ \text{C} \) and 100^\circ \text{C}. Figure 4-15 (for PC film) and Figure 4-16 (for PC bar) show that these inversions are not observed by the measurements of \( (dW/dV)^* \) versus aging temperature. The results suggest again that, as opposed to what observed when the EWF method is used, the toughness of PC, as measured by the strain energy density \( (dW/dV)^* \), continuously decreases with aging temperature. Figure 4-17 shows the effect of aging temperature, \( T_{ag} \), on impact fracture energy of the injection-molded bars of the low molecular weight sample, tested at room temperature. These samples were annealed for 96 hours at various temperatures ranging from 60^\circ \text{C} to 120^\circ \text{C}. The results confirm that fracture toughness of PC continuously decreases in this range of aging temperatures. Before aging, Makrolon 2608 has an average impact strength \( G_c^{\text{anneal}} \approx 21.5 \text{ kJ/m}^2 \), but after aging at \( T_{ag} = 60^\circ \text{C} \) for 96 hours the value of \( G_c \) decreases to about 60% its value. If \( T_{ag} \) increases to 120^\circ \text{C} the value of \( G_c \) is reduced to only about 20% its original toughness. This is in agreement with that measured by the strain energy density and invalidates the effects observed by the essential work of fracture approach.
Figure 4-11: Effect of aging time at 120°C on low-speed fracture energy ($G_f$ or $G_i$) of PC bar.

Figure 4-12: Effect of aging time at 120°C on impact fracture energy ($G_c$) of PC bar.
Figure 4-13: Effect of aging temperature (after 96 hours) on essential work of fracture ($w_e$) of PC film.

Figure 4-14: Effect of aging temperature (after 96 hours) on non-essential work ($\beta w_p$) of PC film.
Figure 4-15: Effect of aging temperature (after 96 hours) on strain energy density \((dW/dV)^*\) of PC film.

Figure 4-16: Effect of aging temperature (after 96 hours) on strain energy density \((dW/dV)^*\) of PC bar.
Figure 4-17: Effect of aging temperature (after 96 hours) on impact fracture energy \( (G_c) \) of PC bar.

According to the EWF approach, the non-essential work \( \beta W_p \) relates to the plastic work dissipation in the surrounding zone of the fracture surface. However, the strain energy density theory suggests that fracture performance depends on two parameters, crack initiation resistance and crack propagation resistance. It has also been found that crack initiation resistance tends to vary inversely with crack propagation resistance when the test temperature is varied [89]. The observed variations of \( \beta W_p \) with aging time and aging temperature are probably due to the energy of crack propagation and do not represent only the non-essential plastic work. Figure 4-18 shows that the yield stress of PC films increases and the yield strain remains relatively constant with increasing aging temperature. The results invalidate the observed variation of non-essential work dissipated by plastic deformation \( \beta W_p \) in the outer plastic zone as suggested by the EWF method. The above results suggest that \( \beta W_p \) does not reflect the change in plastic work with aging and suggest that the EWF parameters can be misleading in studying fracture behavior. It is worth noting that Liu and Nairn [93] have also used the EWF test to study the effects of aging on ductile polymeric bottles made of polyester and copolyester resins. Very unusual variations in the essential work of fracture have also
been observed in these polymers. Only in changing the grade of the polyester resin, aging has been reported to either increase or decrease the essential work of fracture. Some inconsistencies between the data obtained by the EWF method and that measured by bottle-drop impact tests have also been remarked. These authors believed consequently that the EWF is a very sensitive technique that can detect unusual effects of aging. This is in contradiction with the well-known brittleness effect of aging on polymers.

![Graph](image-url)

Figure 4-18: Effect of aging temperature (after 96 hours) on tensile yield stress ($\sigma_y$) and yield elongation ($\Delta L_y$) of PC film.

The results in this work suggest that the EWF method cannot be used to characterize fracture performance. The work dissipated in the outer plastic zone is a simplistic consideration of the fracture process, that involves both crack initiation and crack propagation energies. A single fracture parameter is not sufficient to characterize fracture performance and can lead to risky conclusions in studying material failure. Fracture performance of polymers depends on both the initiation and the propagation of a defect in the material. Depending on the loading rate and temperature, a given polymer can break in a brittle, semi-ductile or ductile manner. An increase in the strain rate or a decrease in temperature reduces the mobility of polymers
segments, leading to a brittle behavior. Polymers can exhibit the same fracture energy at crack initiation over a large range of loading speeds and temperatures [83,89]. However, the fracture performances of polymers are not the same at low temperatures and high temperatures, or under low speeds and impact loading. At low temperatures or high loading speeds, fracture is unstable, indicating that catastrophic failure of the part occurs after crack initiation. At lower velocities or higher temperatures, fracture is stable, the crack cannot propagate without additional supply of energy from external loads and the part could still perform its structural function in terms of fracture resistance.
In chapter 3 or the previous work [92], it has been found that the entropy of PC decreases with physical aging. Consequently, this should also alter the fracture behavior of the polymer, especially its brittle-ductile transition. To investigate this transition, fracture tests were carried out on the three-point-bend sample at various loading speeds ranging from 0.2 mm/min to 200 mm/min. Figures 4-19 and 4-20 present the temperature dependence of the fracture energies of PC before and after aging at 120°C for 96 hours, at a loading rate of 200 mm/min. The results show that as the temperature increases, a transition in fracture behavior from brittle to ductile behavior occurs, with a peak in crack initiation energy and a semi-ductile behavior below the peak, in the transition region. Table 4-1 shows that, when the velocity of loading increases, the brittle-ductile transition shifts to a higher temperature. The results also show that aging increases the brittle-ductile transition temperature, \( T_{b-d} \), and the effect is more pronounced for the lower molecular-weight sample. This shift is in agreement with the principle of time-temperature superposition for mechanical properties of polymers. The increase in \( T_{b-d} \) after aging also agrees with the decrease of entropy observed previously [92]. This transition has been shown to relate to the molecular relaxation of the polymer [94-96] and has also been found [84,97] to be controlled by an energy-activated process, expressed by the Arrhenius equation:

\[
\dot{\varepsilon} = \dot{\varepsilon}_f \exp \left( -\frac{\Delta H_f}{RT} \right) \tag{4-5}
\]

where \( \dot{\varepsilon} \) is the strain rate, \( \dot{\varepsilon}_f \) is a pre-exponential factor, \( \Delta H_f \) is the activation energy, \( R \) is the universal gas constant, and \( T \) is the absolute temperature. For three-point-bend samples, by ignoring the effect of the crack, the nominal strain rate can be estimated by:

\[
\dot{\varepsilon} = 6 \frac{vD}{S^2} \tag{4-6}
\]

where \( v \) is the loading speed, \( D \) is the sample width, and \( S \) is the span. Equation (4-5) can be rearranged as:

\[
\ln \dot{\varepsilon} = \ln \dot{\varepsilon}_f - \frac{\Delta H_f}{RT} \tag{4-7}
\]
Figure 4-19: Variation of fracture energy at crack initiation as a function of temperature for Makrolon 2608.

Figure 4-20: Variation of fracture energy at crack initiation as a function of temperature for Makrolon 3208.
Table 4-1: Temperature at Brittle-Ductile Transition for Unaged and Aged PC Bars.

<table>
<thead>
<tr>
<th>Loading speed</th>
<th>$T_{b-d}$ (°C) of PC-2608</th>
<th>$T_{b-d}$ (°C) of PC-3208</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unaged</td>
<td>Aged</td>
</tr>
<tr>
<td>0.2 mm/min</td>
<td>-20 ± 5</td>
<td>20 ± 5</td>
</tr>
<tr>
<td>2 mm/min</td>
<td>-15 ± 5</td>
<td>20 ± 5</td>
</tr>
<tr>
<td>20 mm/min</td>
<td>-15 ± 5</td>
<td>28 ± 5</td>
</tr>
<tr>
<td>200 mm/min</td>
<td>-10 ± 5</td>
<td>30 ± 5</td>
</tr>
</tbody>
</table>

*: Aged at temperature $T_{ag}$ = 120°C for aging period $t_{ag}$ = 96 hours.

Figures 4-21 and 4-22 show the plots of $ln(\dot{\varepsilon})$ as a function of $1/T_{b-d}$ for the unaged and the aged samples of low and high molecular-weight respectively (Makrolon 2608 and Makrolon 3208). In the range of loading speeds ranging from 0.2 mm/min to 200 mm/min, the results suggest a relatively linear relationship between $1/T_{b-d}$ and $ln(\dot{\varepsilon})$. From the slope and the intercept of the plots of $ln(\dot{\varepsilon})$ vs. $1/T_{b-d}$, the energy barrier, $\Delta H_f$, and the pre-exponential factor, $\dot{\varepsilon}_f$, controlling the time-temperature dependence of fracture behavior, can be determined and the data are shown in Table 4-2. It can be seen that $\Delta H_f$ obtained from fracture tests are almost the same before and after aging, whereas the pre-exponential factor $\dot{\varepsilon}_f$ is strongly reduced by aging. It has been shown [92] that the $\dot{\varepsilon}_f$ contains an entropy term, $\Delta S_f$, that varies with physical aging. The activation entropy $\Delta S_f$ is a measure of the change in structural disorder of the molecular structure and is related to $\dot{\varepsilon}_f$ by:

$$\dot{\varepsilon}_f = \frac{1}{2}V_o \exp \left( \frac{\Delta S_f}{R} \right)$$ (4-8)

where $V_o$, frequency factor, may be calculated from Equation (3-4) in chapter 3.
Figure 4-21: Plots of $\ln(\dot{\varepsilon})$ vs. $1/T_{b \cdot d}$ for Makrolon 2608 in case of: unaged (solid line); and aged at 120°C for 96 hours (dotted line).

Figure 4-22: Plots of $\ln(\dot{\varepsilon})$ vs. $1/T_{b \cdot d}$ for Makrolon 3208 in case of: unaged (solid line); and aged at 120°C for 96 hours (dotted line).
Table 4-2: Parameters of Equation (4-5) in Fracture for PC Bars.

<table>
<thead>
<tr>
<th>Material</th>
<th>PC-2608</th>
<th>PC-3208</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H_f$</td>
<td>$\dot{\epsilon}_f$</td>
</tr>
<tr>
<td></td>
<td>(kJ/mol)</td>
<td>(1/sec)</td>
</tr>
<tr>
<td>Unaged</td>
<td>382</td>
<td>7.16 E +74</td>
</tr>
<tr>
<td>Aged$^a$</td>
<td>388</td>
<td>3.98E + 65</td>
</tr>
</tbody>
</table>

$^a$: aged at temperature $T_{ag} = 120^\circ$C for aging period $t_{ag} = 96$ hours.

Combining Equations (4-8) and (3-4), the activation entropy, $\Delta S_f$, can be estimated from the fracture tests and is shown in Table 4-3. The results show that heat aging causes a decrease of the activation entropy in polycarbonate, and this decrease is more pronounced for the lower molecular-weight sample. This confirms the results obtained previously by tension and compression tests [92].

Table 4-3: Activation Entropy in Fracture for PC Bars.

<table>
<thead>
<tr>
<th>Type of loading</th>
<th>Material</th>
<th>$\Delta S$ (J/mol/K)</th>
<th>$\Delta S_{aged} / \Delta S_{unaged}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-P fracture</td>
<td>unaged PC-2608</td>
<td>1182</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>aged$^a$ PC-2608</td>
<td>1003</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>unaged PC-3208</td>
<td>782</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>aged$^a$ PC-3208</td>
<td>700</td>
<td>0.89</td>
</tr>
</tbody>
</table>

$^a$: aged at temperature $T_{ag} = 120^\circ$C for aging period $t_{ag} = 96$ hours.
4.5 Conclusion

The effects of aging time ($t_{ag}$) and aging temperature ($T_{ag}$) on fracture performance of polycarbonate have been investigated over the ranges of $T_{ag} = 23-120^\circ$C and $t_{ag} = 0-96$ hours. The fracture toughness of PC continuously decreases in the ranges of aging times and temperatures investigated. Measurements of the strain energy density showed a continuous reduction with aging time and aging temperature. This reduction is almost the same in comparison with the change of fracture energy measured by three-point bending tests. The variation of the fictive temperature, $T_f$, of the glass transition was also analyzed to determine the degree of aging in the samples. The effects of aging on the shift in fictive temperature are in agreement with both the changes in strain energy density and fracture energy at crack initiation. The variations of $T_f$ show the same trends when $t_{ag}$ changes. These trends are also in agreement with both the strain energy density measurement and three-point bending tests. The results contradict the effects of aging on fracture toughness observed by the essential work of fracture (EWF) approach that showed several regions of increasing fracture toughness with aging time and aging temperature. This is in contradiction with the well-known brittleness effect of aging in polymers. EWF parameters can be misleading in studying fracture behavior and cannot be used to characterize fracture performance.

The work dissipated in the outer plastic zone is only a simplistic consideration of the fracture process, that involves both crack initiation and crack propagation energies. The transition in fracture behavior with loading rate and temperature has also been analyzed by an activation energy approach, using the Arrhenius equation. The results revealed that aging increases the brittle-ductile transition temperature, $T_{bd}$, and the effect is more pronounced in the lower molecular weight PC. The results of fracture tests suggest that heat aging causes a decrease of the activation entropy in polycarbonate. This decrease is also more pronounced for the lower molecular-weight sample. The results are in agreement with the decrease in entropy observed previously by tension and compression tests.
CHAPTER 5

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions:

During the last decades a great deal of attention has been focused on the phenomenon of physical aging in glassy amorphous polymers. It is well known that polymer glasses exist in a non-equilibrium state and for that reason significant changes in the physical properties of the polymer occur as it approaches equilibrium [4]. Some glassy polymers such as polycarbonate (PC) are relatively tough and are used as fracture-resistant substitute for glass. Aging in polycarbonate is therefore a serious concern.

Presently, the understanding of the physical aging on a molecular level is limited. Many investigations have suggested that aging is a completely morphological effect, that is, a result of the polymer chains attempting to reach an equilibrium, low energy conformation [5-6,15-16,18-19,49-50]. Two distinct phenomena having their own kinetics have also been proposed to occur in PC; aging and annealing [8,32]. The primary aim of this thesis is to study the aging mechanisms of polycarbonate by using differential scanning calorimetry (DSC). The effects of aging temperature, $T_{ag}$, and aging time, $t_{ag}$, on the enthalpy relaxation, $\delta_H$, are investigated. Other parameters recorded by DSC scans such as fictive temperature, $T_f$, and endothermic peak temperature, $T_p$, are also analyzed and their relationships with physical aging are discussed.

In the recently reported investigations on the effect of aging on yielding behavior of polycarbonate, there are two opposite opinions on the yielding kinetics (represented by $d\sigma_y/d(\log \dot{\varepsilon})$) and the aging kinetics (represented by $d\sigma_y/d(\log t_{ag})$). Bauwens and co-worker [8,17] suggested that the kinetics of both yielding and aging processes in polycarbonate are identical. An increase in the strain rate by a factor of 10 has the same effect on the yield stress as an increase in the aging time by a factor of 10. However, Hutchinson et al. [19] disagreed with this idea and suggested that these kinetics are different. The second purpose of this thesis is to
investigate the effects of physical aging on the kinetics of yielding in polycarbonate. PC samples were annealed over a wide range of aging times and temperatures. Both tensile and compressive tests were performed over various loading rates and temperatures to analyze the effects of aging time and aging temperature on yielding kinetics.

It would also appear that the fracture toughness of a viscoelastic material should also be a time-temperature dependent parameter. While the fracture behavior of polymers has been studied in-depth, the time-temperature dependence as well as the aging time-aging temperature dependence of fracture is less adequately studied in spite of the interest for their engineering applications. For polymeric film, the Essential Work of Fracture (EWF) method is presently widely used to characterize fracture. The EWF method was originally Broberg's idea [74] and then developed by Cotterell and Reddel [75] for ductile metals. It has been recently used to investigate the toughness of different polymers [76-81], but this technique still remains controversial [82-83]. It has also been shown that fracture performance of polymers depends on both the initiation and the propagation of a defect in the material [84-88]. Depending on the loading rate and temperature, a given polymer can break in a brittle, semi-ductile or ductile manner [46-48,89]. A single fracture toughness parameter is insufficient to evaluate fracture performance. The third objective of this thesis is twofold: a) to investigate the effects of physical aging on fracture behavior of extruded films and injection molded bars of PC, with the emphasis on brittle-ductile transition in fracture behavior; and b) to analyze the validity of different approaches for fracture characterization currently used.

The effects of time and temperature on physical aging of PC have been firstly investigated from the viewpoint of thermal behavior. Aging of PC is a progressive process involving several mechanisms. The results agree with the concept of lateral cohesional entanglement. An increase in the density of cohesional entanglement with aging stage leads to a stronger morphology that requires a higher temperature and a higher energy to disentangle. The method used to calculate the excess enthalpy from the DSC scan affects the measurement results and the interpretation of the aging process. The subtraction between the DSC scans of aged and de-aged samples would include the change in both the upper and the lower endothermic peaks. The method of extrapolating the base line above $T_g$ back in temperature until it touches the peak would indicate
only the change in the upper endothermic peak at the early stage of annealing, when the lower peak is small. During annealing, rejuvenation and aging take place simultaneously. At the early stage of annealing, rejuvenation is more important and can be easily detected by DSC analysis. At a later annealing stage, aging becomes predominant and outweighs the rejuvenation process.

The second conclusion deals with the effects of physical aging on the kinetics of yielding in polycarbonate. The time-temperature dependence of yielding behavior can be separated into two regions (α and β). Aging does not affect localized molecular motions of the β process during yielding. Physical aging in PC results in a slower jump rate of the main segments of macromolecules between two equilibrium positions. It reduces the flexibility of the macromolecules and thus, makes the polymer more brittle. Heat aging also causes a decrease of the entropy (ΔS) in polycarbonate, and this decrease is more important when the molecular weight is reduced. Increasing the annealing time and temperature results in a continuous reduction of ΔS. The rate of aging decreases with decreasing annealing temperature and below about 30°C, no aging takes place in yielding behavior. The kinetics of yielding and aging processes in polycarbonate are different. An increase in the strain rate does not have the same effect on the yield stress as an increase in the aging time by a same factor.

The third conclusion concerns the effects of physical aging and time-temperature on fracture behavior of polycarbonate. Measurements of the strain energy density showed a continuous reduction when aging time and aging temperature increase in the ranges investigated. These aging effects are confirmed by the change in fracture toughness, as measured by three-point bending tests. The variation of fictive temperature, T_f, with aging time is in agreement with both the strain energy density measurement and the three-point bending tests. These results contradict the effects of aging on fracture toughness observed by the essential work of fracture (EWF) approach. The latter showed anomalous regions of increasing fracture toughness with aging, leading to spurious conclusions. The brittle-ductile transition in fracture behavior is analyzed by an activation energy approach. Aging increases the brittle-ductile transition temperature, T_b-d, and the effect is more pronounced for the lower molecular-weight sample. Fracture tests also show a decrease in the fracture entropy (ΔS_f) with aging, confirming the results observed previously from tension and compression tests.
For polycarbonate, there exists a well-seeming correlation between the activation entropy in yielding, $\Delta S$, and the DSC subtracted enthalpy, $\delta_H$, for aging temperatures near below $T_g$ only. More work is needed before we can speculate on why the correlation is not appropriate for temperatures far below $T_g$. A possible reason is that: in the range below or around 80 °C, the rejuvenation or deaging process grows earlier and becomes dominant in thermal behavior, hence $\delta_H$ becomes negative and unchanged; whereas the aging process grows faster in yielding behavior, consequently $\Delta S$ continuously decreases in the same temperature range. This also confirms that not all of the properties of glassy polymers reach equilibrium simultaneously.
5.3 Future work:

An interesting problem of glassy polymers is the determination of aging mechanisms. Accelerated aging or annealing glassy polymers in a temperature range below their glass transition temperature (below \( T_g \)) results in changes in their structure and their mechanical properties. However, there have been some observations related to altering the state of aging. Accelerated aging is observed in many experiments, but in some cases temporary deaging or rejuvenation is also detected. Haidar and Smith [98] studied deaging in tensile stress-strain curves of PC film from applying a stress nearly below the yield point of the annealed samples. Othmezouri-Decerf [36] investigated deaging in mechanical damping spectra of PC after various aging and mechanical deformation histories. Struik [71] described the deaging in creep of PVC that occurs with an increase in aging temperature. The DSC results of PC in [91] also show that rejuvenation or deaging is more important at the early stage of annealing. McHerron and Wilkes [99] reported that PS, PMMA, PC can be deaged, as measured by enthalpy and yield strength, by electron beam irradiation. Risch and Wilkes [100] found that the absorption of \( \text{CO}_2 \) can also affect to deaged PC.

The temperature range over which aging occurs is also the matter under discussion so far. Physical aging below \( T_g \) takes place for all glassy polymers, but does it occur at all temperatures below \( T_g \) or only in a narrow range just below \( T_g \)? Struik [101] suggested that aging tends to disappear at low temperature, below the \( \beta \) relaxation. Bauwens [8] proposed that there exists two distinct phenomena called “annealing” and “aging”: the former extends from \( T_g \) to \( T_g -50\text{K} \), and the latter extends from \( T_g -50\text{K} \) to \( \beta \) relaxation. Recent FTIR investigation on low-temperature aging of PC [102] also supported the conclusion of Bauwens. The results in [92] show that no aging takes place in yielding behavior of PC at temperatures below 30°C.

Another question of interest is whether of not all of the properties of glassy polymers reach equilibrium simultaneously. The answer seems to be no; various properties reach their equilibrium values at different times. But, as to the sequence of property arrival times at equilibrium, the situation remains cloudy [103].
REFERENCES


