Modeling the Time-Temperature Dependency of Thermoplastics Used in Solid-Phase Thermoforming Process

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Abstract

Many constitutive theories, hyperelastic and viscoelastic have been proposed for modeling materials used in solid-phase forming processes such as thermoforming and blow molding. The phenomenological hyperelastic models were developed based purely on mathematical interpretation whereas physically base hyperelastic models were established from the formalism of macromolecular conformation as a thermodynamically reversible process. It has been shown earlier that materials being thermoform experienced rate-temperature dependent deformation ranges from constant width (CW) through to equal biaxial (EB)[1]. Modeling this complex deformation behavior is widely recognized to be un-feasible with typical hyperelastic model, where the fulfillment of energy conservation would renders these models time independent. In order to account for time-temperature dependency, viscoelastic model that encompass the linking of hyperelastic laws and viscous flow theories have been proposed by numerous researchers. This paper revisited and analyzed a number of the rate-temperature-equivalent viscous flow theories commonly used in material modeling, includes the Williams-Landel-Ferry (WLF)[2], Arrhenius[3], and Vogel-Fulcher-Tammman (VFT)[4,5,6], in term of their effectiveness in interpreting the time-temperature dependent relaxation behavior of polypropylene (PP) and high impact polystyrene (HIPS).

1 Introduction

In molding processes such as thermoforming and blow molding, thermoplastic undergoes large multi-axial stretches while exposed to elevated, spatial and time varying strain rates, pressures and temperatures. Accurately modeling the material response under these processing conditions proved to be difficult. Further complications would arise as a result of the complex thermal and time dependent mechanical response of polymers. At temperature below glass transition, molecular movements other than the micro-Brownian motion are very limited and thermoplastics appear as glass-like solid structure. At this stage, most thermoplastics undergo brittle fracture at small strain upon stretching. Above glass transition, molecular mobility increases as internal energy is rises. When subjected to an externally applied stress exceeding the intra- and inter-molecular resistance to chain segmental rotation, the material deforms linearly and viscoelastically at the smallest strain (typically less than ≈ 5% strain for most thermoplastics). At larger strain, permanent deformation develops and the behavior is non-linear viscoelastic. Depending on the molecular weight and chemical structure, a range of constitutive nonlinear viscoelasticity such as yielding, strain softening, flow and orientation hardening can commonly be observed. This series of viscoelastic deformation is both time and temperature dependent, whereby the deforming material exhibits rate dependent stiffening, temperature dependent softening, creeping of strain under constant applied load and stress relaxation when the strain is held constant over a period of time.

The principle of energy conservation that forms the underlying concept of hyperelasticity renders hyperelastic models time independent, i.e. the state of deformation stress depends only on the current state of strain but not affected by the history of straining or the rate the strain is achieved. This well-known limitation of hyperelastic laws has restricted them from being used alone in the modeling of time-temperature dependent viscoelastic properties of polymers. In constitutive modeling of polymer viscoelasticity, the limitation of hyperelastic models being time independent may be solved by linking them with one or more viscous dissipation functions such that any change in viscosity and relaxation time as a result of the variation in time and/or temperature can be accounted for.
The initial part of this article outlined experimental work carried out for the characterization of time-temperature dependent relaxation master curve of a semi-crystalline PP and an amorphous HIPS. Brief outlines of the variety of available hyperelastic models will be presented but greater attention is given to a number of the classical time-temperature-superposition (TTS) viscous flow functions frequently adopted to describe the rate and thermal dependency of polymer deformation. They are the WLF, Arrhenius and VFT functions. These viscous dissipation functions were analyzed in term of their capability to reproduce the time-temperature dependent relaxation response of PP and HIPS obtained experimentally.

2 Materials
The polymers used in this work were commercially available pre-extruded HIPS and nucleated isotactic PP sheets with an average thickness of 1.51 and 1.42 ± 0.01mm, respectively. The MFI as quoted by the company was 3 (230°C/2.16kg, g/10 min) for the PP and 4.5 (200°C/5kg, g/10 min) for the HIPS. DSC scans at 10°C/s revealed that the \( T_g \) of the HIPS sample is \( \approx 95°C \) whereas the peak \( T_m \) of the PP sample is recorded at \( \approx 165°C \).

3 Experimental
Experimental characterization of time dependent thermal-mechanical properties of the materials was conducted on a Rheometric Scientific™ DMTA V instrument. In all cases, rectangular specimens with length \( \times \) width \( (l \times w) \) dimensions of 20 \( \times \) 12.5 \( \pm \) 0.05mm were analyzed under dynamic dual cantilever bending, where both ends of the specimen are securely clamped to a rigid frame and a drive shaft that oscillate upward and downward at a controlled frequency is gripped to the center of the specimen. The entire fixture is located within a heating chamber equipped with nitrogen purge gas in which a polymer specimen can be heated or cooled to desired temperature (i.e. constant, sweep or step change) during the analysis. Figure 1 shows the setting of dual cantilever bending fixture within DMTA V instrument.

![Figure 1](image)

*Figure 1: Experimental set-up of dual cantilever bending fixture in DMTA V instrument.*

The oscillatory movement of the center drive shaft generates a dynamic alternating displacement on the specimen, with maximum deflection being at the specimen center. The typical mode of deformation experienced by a rectangular sheet of specimen exposed to dynamic dual cantilever bending can be shown in figure 2.
Figure 2: Typical deformation under dynamic dual cantilever bending.

The specimen stress, $\sigma$ and strain, $\varepsilon$ can be related to the drive shaft displacement, $D$ and force, $F$ of the motor through equations 1 and 2 respectively\cite{7}.

$$
\varepsilon = K_\varepsilon \cdot D \quad \text{and} \quad K_\varepsilon = \frac{12 \cdot h}{l^2}
$$

$$
\sigma = K_\sigma \cdot F \quad \text{and} \quad K_\sigma = \frac{3 \cdot l}{4 \cdot w \cdot h^2}
$$

where $l$, $w$ and $h$ are the specimen length, width and thickness respectively while $K_\varepsilon$ and $K_\sigma$ are the strain and stress constants for dual cantilever bending geometry.

During an analysis, the applied strain is introduced in a periodic sinusoidal fashion and the amount of oscillatory applied force or stress required to sustain the commanded periodic strain is measured and evaluated for the frequency and temperature dependent properties such as moduli and stiffness. Given the frequency, $\omega$, the periodic time, $t$ as well as the periodic strain, $\varepsilon_p$ and stress, $\sigma_p$ can be expressed as:

$$
\frac{t}{\omega} = \frac{2 \pi}{\omega}
$$

$$
\varepsilon_p = \varepsilon \cdot \sin(\omega \cdot t)
$$

$$
\sigma_p = \sigma \cdot \sin(\omega \cdot t + \delta)
$$

where $\delta$ denote the phase difference between periodicical applied stress and strain, i.e. both periodicical applied stress and strain will be in-phase ($\delta = 0$) for a perfectly elastic Hookean material and out-of-phase ($\delta = 90^\circ$) for a perfectly viscous Newtonian liquid. For typical thermoplastics such as PP and HIPS exhibiting viscoelastic properties, the periodic stress and strain will be out-of-phase with the phase angle $\delta$ fall between $0^\circ$ and $90^\circ$.

Employing trigonometry identity, the periodic applied stress might be re-written as:

$$
\sigma_p = \sigma \cos \delta \cdot \sin(\omega \cdot t) + \sigma \sin \delta \cdot \cos(\omega \cdot t)
$$
Depending on the oscillatory sinusoidal strain and the measured phase angle, equations 5 and 6 can be further evaluated to give the complex modulus, $E^*$ of the material as a summation of an in-phase ‘real’ component (the storage or elastic modulus $E'$ - represents energy storage) and an out-of-phase ‘imaginary’ component (the loss or viscous modulus $E''$ - represents energy loss), mathematically expressed as:

$$E^* = E' + iE''$$

with

$$i = \sqrt{-1}$$

…….(7)

where

$$E' = \frac{\sigma \cos \delta}{\varepsilon}$$

…….(8)

and

$$E'' = \frac{\sigma \sin \delta}{\varepsilon}$$

…….(9)

The relationship between $E^*$, $E'$, $E''$ and $\delta$ may be represented by an Argand diagram as shown in figure 3.

![Figure 3: Argand diagram relating complex, storage and loss moduli.](image)

It is therefore by analyzing the temperature and frequency (hence time) dependent response in terms of the storage (elastic) and loss (viscous) moduli in DMTA analysis, the viscoelastic properties of a material may be quantified.

### 3.1 Dynamic mechanical strain sweep analysis

Preliminary dynamic strain sweep analyses were carried out to ensure the imposed strain does not exceed the specimens’ linear viscoelastic limit. This precaution is crucial in DMTA analysis as the underlying concept will hold only if the material is tested within its linear viscoelastic region, i.e. region where ratio of stress to strain yields a constant value of modulus and the modulus is a function only of temperature and frequency or time. Any deviations beyond this limit signified that the material undergoes plastic deformation and a non-recoverable energy loss due to plastic strain will be imposed on the material. The additional energy loss may be mistakenly treat as viscous dissipation and thus renders the analysis results invalid.

Both PP and HIPS specimens were subjected to dynamic strain sweep from 0.001 to 0.3%, with a linear strain increment of 0.005%, at 25°C and frequency commonly standardized at convenient for DMTA analysis, 1 Hz or $2\pi$ rad/s$^{[8]}$. Three tests were performed for each material and their average was evaluated. The dynamic strain sweep results, plotted as storage modulus against percentage strain can be shown in figure 4.
Figure 4: Dynamic strain sweep results of PP and HIPS.

It can be seen from figure 4 that the storage modulus of both HIPS and PP remain unchanged up to a critical strain of 0.10% and 0.12% respectively. Above this limit, an increase in strain is no longer associated with the proportional increase in stress and the analysis reveals a drop in the measured storage modulus, indicating the initiation of plastic deformation.

3.2 Dynamic mechanical frequency-temperature sweep analysis

Classical experimental characterizations of the time and temperature dependent mechanical properties of polymer viscoelasticity are routinely based on analyses such as hot tensile creep and relaxation. These standard analyses are time consuming and an alternative yet effective technique, the dynamic mechanical frequency-temperature sweep analysis was employed in the current work. Within the test, a polymer specimen is subjected to periodical sinusoidal strain amplitude of 0.05%, pre-programmed in a logarithmic frequency sweep from 0.1 to 100 rad/s ($2\pi$ rad/s = 1 Hz) and under a range of controlled temperatures sweep. The PP samples were subject to temperatures sweep from -10 to 160°C while the HIPS samples were analyzed from 30 to 135°C. In all cases, nitrogen purge gas was used in the cryogenic cooling system to achieve a higher accuracy in temperature control and a temperature ramp rate of 5°C was used to avoid possible thermal lag between the sample surface and its center core. For every 5°C increment, these analyses simultaneously captured the variation of the materials’ storage and loss moduli over the pre-programmed frequency sweep range. Figure 5 shows the log storage modulus vs. log frequency plots at every 10°C interval for the PP and HIPS samples.

Figure 5: Dynamic mechanical frequency-temperature dependent results of PP (left) and HIPS (right).
It is clear from figure 5 that the frequency (hence time) and temperature dependent profile of the polymers can be visualized through the use of dynamic mechanical frequency-temperature sweep analysis. As expected, the storage modulus of both PP and HIPS declines with increasing specimen temperature and decreasing sinusoidal strain frequency. A higher drop in storage modulus was found at the PP specimen as its temperature is increased above \( \approx 150^\circ C \), in the region where an aggregated crystalline melting takes place. For HIPS, it was observed that the storage modulus was almost unchanged and frequency insensitive up to \( \approx 80^\circ C \), generally due to the fact that its polymer chain back-bone is largely immobilize below \( T_g \) and apart from the micro-Brownian motion, all higher degrees of molecular movement are restricted. At temperature between 90 and 130\(^\circ\)C, the HIPS exhibited a rapid drop in storage modulus, denoting the occurrences of a transition event in this temperature regime. This finding is in agreement with Birley and co-workers\(^9\), where the authors found that strain rate sensitivity (hence frequency) is particularly severe in the vicinity of a primary or secondary thermal transition. As temperature is further increase above 130\(^\circ\)C, the storage modulus of HIPS became relatively stable and once again insensitive to variation in sinusoidal strain frequency, indicating the completion of the transition event.

The dynamic mechanical data shown in figure 5 were subsequently converted to the equivalent relaxation modulus and relaxation time through a methodology developed by Ninomiya and Ferry\(^10\). While it is natural to question and compare the accuracy of such conversion, Henning Winter\(^11\) observed that the determination of relaxation modulus from dynamic storage and loss moduli data is extremely accurate and might actually be more precise to determine relaxation modulus from dynamic mechanical data than to measure it directly in a step strain analysis. Figure 6 depicts the converted relaxation modulus and relaxation time of the PP and HIPS specimens.

![Figure 6: Dynamic mechanical time-temperature dependent relaxation modulus of PP (left) and HIPS (right).](image)

As expected, the relaxation moduli were found to decay with increasing temperature and time. It can be noted from figure 6 that the DMTA generated time-temperature dependent relaxation modulus covered only a time span of less than 26s and it is indeed not sufficient to be served as a good representation of the material’s long-term relaxation behavior. It is however that a relaxation master curve could be constructed from the short-term DMTA data through TTS, where it is assumed that a relaxation process that occurs rapidly at elevated temperatures will occur to the same degree over longer period of time at lower temperature\(^12\). In this context, a short-term relaxation modulus curve at temperature \( T_{\text{ref}} \) was chosen as reference while all other curves were horizontally shifted (along the log time axis) with respect to the chosen
reference, with modulus curves at temperature higher than $T_{ref}$ being shifted to the right and modulus curves at temperature lower than $T_{ref}$ being shifted to the left, until these shifted curves coincide to form a final relaxation master curve. The amount of horizontal shift, $H(T)$ was tabulated in table 1 and a new variable, $a_T$, customary called the ‘shift factor’ can be quantified through relationship $H(T) = -\log a_T$. For example, for the reference modulus curve, $H(T) = 0$ and $a_T = 1$; for modulus curves at $T > T_{ref}$, $H(T) > 0$, $a_T < 1$ whereas for modulus curves at $T < T_{ref}$, $H(T) < 0$ and $a_T > 1$.

<table>
<thead>
<tr>
<th>PP</th>
<th>Temp. T (C)</th>
<th>$H(T_{ref} - 20^\circ C)$</th>
<th>$H(T_{ref} - 30^\circ C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>255</td>
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<td>-0.10</td>
<td>-0.25</td>
</tr>
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<td>-0.10</td>
<td>-0.25</td>
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<tr>
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<td>0.00</td>
<td>-0.10</td>
<td>-0.25</td>
</tr>
<tr>
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<td>0.00</td>
<td>-0.10</td>
<td>-0.25</td>
</tr>
<tr>
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<td>-0.25</td>
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<tr>
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<td>-0.25</td>
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</tr>
<tr>
<td>241</td>
<td>0.00</td>
<td>-0.10</td>
<td>-0.25</td>
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</table>

<table>
<thead>
<tr>
<th>HIPS</th>
<th>Temp. T (C)</th>
<th>$H(T_{ref} - 90^\circ C)$</th>
<th>$H(T_{ref} - 110^\circ C)$</th>
</tr>
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<td>-0.25</td>
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<tr>
<td>336</td>
<td>0.00</td>
<td>-0.10</td>
<td>-0.25</td>
</tr>
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</table>

Table 1: Amount of horizontal shift, $H(T)$ for the construction of master curves

Based on the data shown in table 1, it can be observed that despite the chosen $T_{ref}$, the amount of $H(T)$ required for relaxation modulus curves at temperatures $T_1$ and $T_2$ to overlap one another is dependent only at their temperature different. At present, the shift factor, $a_T$ appears to be an empirical parameter, however, it will be shown later that the value of $a_T$ may be evaluated from one of the many viscous flow functions proposed to capture the time-temperature dependent response of viscoelastic polymers.

Figure 7 demonstrates the $TTS$ shifted relaxation master curves of the PP specimens with $T_{ref}$ chosen at $20^\circ C$ and $120^\circ C$, and HIPS specimens with $T_{ref}$ chosen at $90^\circ C$ and $110^\circ C$ respectively.

Figure 7: Dynamic mechanical time-temperature dependent relaxation modulus of PP and HIPS
It can be seen from figure 7 that at lower temperatures, the relaxation modulus took longer time to decay to the same level of modulus found at a higher temperature, referred to as the principle of rate-temperature equivalent\[13\]. When long-term relaxation master curve is generated through TTS principle, it is always tempting to validate its reliability and accuracy compared to the classical single step tensile creep or relaxation analysis. The outcome is promising as Sepe\[12\] analyzed the variation between three conventional tensile creep results span over 125 hours with the first 125 hours of a DMTA master curve and observed that their difference is actually smaller than the random variation exists between the triplicate creep tests.

4 Constitutive material modeling

Over the past decades, many attempts have been made to construct constitutive model capable of describing the full range of features of a deforming polymer. Early efforts focused primarily on the modeling of nonlinear elastic or hyperelastic deformation of rubbers, built on the concept of the conservation in strain (Helmholtz) energy. In this context, two main approaches, a phenomenological approach where mathematical functions are generated by fitting empirical deformation stress-strain data and a more physically based approach that is established at the macro-molecular level are widely used.

The Mooney-Rivlin\[14, 15\], Isihara\[16\], Biderman\[17\], Hart-Smith\[18\], Alexander\[19\] and Ogden\[20\] are among the most noticeable phenomenological hyperelastic models. These models relate strain energy function, \( W \) to either principal stretch ratios, \( \lambda_i \) or invariants of strain, \( I_i \). Given the strain energy, \( W \); the principal nominal stresses, \( \sigma_i \) can be evaluated through a differentiation procedure operate on \( W \).

\[
W = f(\lambda_i) \quad \text{or} \quad W = f(I_i)
\]  
\[
\sigma_i = \frac{\partial W}{\partial \lambda_i} + P \quad \text{or} \quad \sigma_i = \left( \sum_i \frac{\partial W}{\partial I_i} \cdot \frac{\partial I_i}{\partial \lambda_i} \right) + P
\]

where \( P \) is an arbitrary hydrostatic pressure arising due to the absent of an incompressibility constraint in equation 11. This arbitrary pressure can commonly be resolved from the known boundary conditions of the deformation, i.e. one of the principal plane is usually stress free and \( \sigma_i \) can be written in terms of \( \sigma_1 - \sigma_2, \sigma_2 - \sigma_3 \) and \( \sigma_3 - \sigma_1 \).

Unlike phenomenological hyperelastic models, the physically based hyperelastic models were derived principally from the first and second laws of thermodynamic, where the most probable chain configuration of an entropy elastic polymeric chain, in its unstrained and strained states were studied through statistical mechanics and assuming that the deformation process is always thermodynamically reversible\[21, 22\]. These hyperelastic models loosely can be classified into two categories, they are: (a) ‘phantom’ network models, where molecular chains are assumed to be held only at numerous cross-linkages points and these network chains are capable of moving through one another as ‘phantoms’ and (b) a more realistic approach which in addition to the afore mentioned cross-linkages, these models treat an aggregate of molecular chains to be feasible to encounter a series of chains imperfections such as chains with only one end attached to the network, linkage of two points on a single chain and entanglement between neighboring chains.

The neo-Hookean\[23, 24\], 3-chain\[25\], full-network\[26\] and 8-chain\[27\] hyperelastic are among the most popular ‘phantom’ network models while the Ball et. al.\[28\] and Edwards-Vilgis\[29, 30\] models are the among the most widely use physically based hyperelastic models that take into account chain imperfections. Although many forms of phenomenological and physical network hyperelastic models have been proposed to date, these models are neither capable of capturing the time dependency nor their inherent thermal dependent variable can sufficiently reproduce
the influences of temperature variation on material behavior. These models however was found useful in defining the large deformation of polymer under elevated strain rates where the time frame is so short that there may be assumed virtually no viscous dissipation taken place during the deformation process.

In constitutive modeling of polymer viscoelasticity, the classical approach of introducing additional viscous flow function into rate independent elastic or hyperelastic model has achieved considerable success in simulating time-temperature dependent behavior of a range of polymers. A number of the early viscoelastic models employed the combination of perfectly elastic component with ideal viscous Newtonian fluid, includes the well-known Maxwell, Kelvin or Voigt and Zener models. It is however these earlier form of viscoelastic models are confined to the small strain linear viscoelastic region, due to the fact that the mechanical properties of viscoelastic polymers are neither linear Hookean elastic nor Newtonian ideal fluid, but appear somewhere in between them. Later development in line with such linking approach put forward the coupling of nonlinear hyperelastic theories to one or more time-temperature dependent viscosity functions. The typical viscosities functions commonly use in the principle of TTS, include the WLF, Arrhenius and VFT were analyzed in term of their capability in reproducing the shift factor, \( \alpha_T \) of PP and HIPS shown in table 1. These viscous flow functions describe the temperature dependent viscosity, \( \eta \) of a polymer at temperature \( T \), with respect to its value at a reference temperature, \( T_{ref} \), in the form which can be expressed as:

\[
WLF: \quad \log \left( \frac{\eta_T}{\eta_{T_{ref}}} \right) = \frac{-C_1(T - T_{ref})}{C_2 + T - T_{ref}} \quad \ldots (12)
\]

\[
Arrhenius: \quad \log \left( \frac{\eta_T}{\eta_{T_{ref}}} \right) = \frac{1}{2.303} \left( \frac{E_a}{R \cdot T} - \frac{E_a}{R \cdot T_{ref}} \right) \quad \ldots (13)
\]

\[
VFT: \quad \log \left( \frac{\eta_T}{\eta_{T_{ref}}} \right) = \frac{1}{2.303} \left( \frac{B}{T - T_{\infty}} - \frac{B}{T_{ref} - T_{\infty}} \right) \quad \ldots (14)
\]

where parameters \( C_1, C_2, B, T_{\infty} \) and \( E_a \) are material constants while \( R \) is the universal gas constant.

Relating these viscous flow functions (equations 12 – 14) to the free volume theory of Doolittle\(^{[32]} \) suggested that the temperature dependence viscosity arise primarily from its dependence on free volume, which emphasized that the viscosity of polymeric fluids, in particular supercooled glass forming liquid, decreases as temperature increases (i.e. at \( T > T_{ref} \) \( \rightarrow \eta_T < \eta_{T_{ref}} \)), typically due to the increase in free volume\(^*\).

It was shown in figure 6 that the modulus of polymeric materials decreases as temperature and relaxation time increases. At lower temperature, the modulus relaxes at a slower rate compared to those occur at a higher temperature; hence a shorter time would be required for a material to relax to the same level of modulus at a higher temperature. Indeed, the modulus of a material at temperature \( T \), at a particular relaxation time \( t \), could be evaluated from a known behavior of the same material at reference temperature \( T_{ref} \), at a specific relaxation time \( t/t_{ref} \), shown schematically in figure 8. Remember from the construction of relaxation master curve

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\(^*\) Free volume is associated with the space not occupied by molecule segments in a sample.
that the shift factor, $a_T$ possess a value of 1 if $T = T_{ref}$; $a_T < 1$ if $T > T_{ref}$ and $a_T > 1$ if $T < T_{ref}$.

Figure 8: The evaluation of relaxation modulus at temperature $T$, relaxation time $t$ from a known behavior of the material at temperature $T_{ref}$, where $T > T_{ref}$.

The evaluation technique above, generally known as the concept of ‘reduced time’ may be expressed as:

$$[E(t)]_{ref} = \left[ E\left( \frac{t}{a_T} \right) \right]_{T_{ref}} \quad \cdots\cdots(15)$$

It can be observed from figure 8 that a same value of modulus may be evaluated at different temperatures if the appropriate value of the shift factor, $a_T$ is chosen, it follows that:

$$E(T, t_T) = E\left( T_{ref}, t_{ref} = \frac{t_T}{a_T} \right)$$

$$\Rightarrow a_T = \frac{t_T}{t_{ref}} \quad ; \quad \log a_T = \log \left( \frac{t_T}{t_{ref}} \right) = \log t_T - \log t_{ref} \quad \cdots\cdots(16)$$

Here, the shift factor, $a_T$ reflect the difference in logarithmic of two ‘times’, $t_T$ and $t_{ref}$ associated with two ‘temperatures’, $T$ and $T_{ref}$. In flow analysis of polymeric melt, the viscosity is proportional to such a time (i.e. viscosity is inversely proportional to shear rate in a simple shear experiment) and it follows that $\log a_T = \log \left( \frac{t_T}{t_{ref}} \right) = \log \left( \eta_T / \eta_{ref} \right)$.

Prior to the generation of shift factor, $a_T$, a number of the material constants are required to be characterized from the viscous flow functions shown in equations 12 – 14, they are the parameters $C_1$ and $C_2$ in WLF, $E_a$ (commonly termed the Arrhenius activation energy) in Arrhenius as well as $B$ and $T_x$ in VFT. The characterization of these material constants were carried out by organizing the WLF, Arrhenius and VFT functions into structure where plot of shift factor against temperature would yield a linear graph with gradient $y'$ and intercept $C$, expressed as:
WLF:
\[
\frac{1}{\log a_T} = \frac{C_2}{C_1} \left( \frac{1}{T_{\text{ref}} - T} \right) - \frac{1}{C_1}
\] ......(17)

Arrhenius:
\[
\log a_T = \frac{E_a}{2.303 \cdot R} \cdot \frac{1}{T} - \frac{E_a}{2.303 \cdot R \cdot T_{\text{ref}}}
\] ......(18)

VFT:
\[
\log a_T = \frac{B}{2.303} \left( \frac{1}{T - T_\infty} \right) - \frac{B}{2.303} \left( \frac{1}{T_{\text{ref}} - T_\infty} \right)
\] ......(19)

From the amount of horizontal shift, \( H(T) \) employed in the construction of master curve (table 1), the experimental shift factor, \( a_T \) was evaluated. Suppose that reference temperatures of 393K and 363K were chosen for PP and HIPS respectively, plots of \( 1/\log a_T \) against \( 1/(T_{\text{ref}} - T) \) and \( \log a_T \) against \( 1/T \) should yield linear graphs (show in figures 9 and 10) that allow the constants \( C_1 \), \( C_2 \) and \( E_a \) to be evaluated from their gradients and intercepts. For the VFT function, it can be shown that both WLF and VFT are equivalent to one another (appendix A) and the parameters \( B \) and \( T_\infty \) can in fact be evaluated from the characterized constants \( C_1 \) and \( C_2 \) from WLF equation. On the other hand, when parameter \( T_\infty \) in VFT function is vanishingly small, it resemble the Arrhenius equation with \( B = E_a / R \). It is therefore depends on the constant \( T_\infty \), the VFT function capable of demonstrate the WLF or Arrhenius type of TTS behavior.

Figure 9: Graphs of shift factor against temperature plot for PP with \( T_{\text{ref}} \) at 120°C.
It can be seen from figures 9 and 10 that while a linear graph could be well established for PP, plot of shift factor against temperature for HIPS fails to achieve linearity over the entire range of temperatures from 30 to 150°C, with discontinuity being occurred at the region where secondary transition (glass-rubber transition) took place, at ≈ 95°C for the HIPS under studied. This observation suggested that the TTS principle may fail if one attempt to apply this technique over temperature range crossover region where highly nonlinear change in physical structure of the material take place, in particularly glass and melting transitions.

The material constants as characterized from the gradient and intercept of the graphs are:

**PP:**
\[ C_1 = 72.95, \quad C_2 = 665.17 \quad (WLF) \]
\[ E_a = 278.33 \text{ kJ/mol} \quad (Arrhenius) \]
\[ B = 111747.1 \text{ K}, \quad T_x = -272.17 \text{ K} \quad (VFT-WLF \text{ equivalent}) \]
\[ B = 33475.02 \text{ K}, \quad T_x = 0 \text{ K} \quad (VFT-Arrhenius \text{ equivalent}) \]

**HIPS:**
\[ C_1 = 11.77, \quad C_2 = 45.7 \quad (WLF) \]
\[ E_a = 378.31 \text{ kJ/mol} \quad (Arrhenius) \]
\[ B = 1238.48 \text{ K}, \quad T_x = 317.3 \text{ K} \quad (VFT-WLF \text{ equivalent}) \]
\[ B = 45499.89 \text{ K}, \quad T_x = 0 \text{ K} \quad (VFT-Arrhenius \text{ equivalent}) \]

Having characterized the material parameters, it is of course the question arise whether these viscous flow functions would generate a series of the desired shift factor, \( a_T \) with respect to the temperature different between \( T \) and \( T_{\text{ref}} \). Supposes \( T_{\text{ref}} \) of 120°C (393K) and 90°C (363K) were chosen for PP and HIPS respectively and employing the characterized material parameters, the shift factor evaluated from the WLF and Arrhenius functions can be shown in table 2. It has been demonstrated earlier that depend on the values of constants \( B \) and \( T_x \), the VFT equation may appear as a form similar to the WLF or Arrhenius function. When the constants \( B \) and \( T_x \) are characterized to the VFT-WLF and VFT-Arrhenius equivalent forms, it is indeed that the generated shift factor would be similar to that of the WLF and Arrhenius respectively and hence will not be shown in table 2.
Table 2: The evaluated shift factor from WLF and Arrhenius functions

In the ideal case where the evaluated shift factor (such as those tabulated in table 2) capable of matching those used to construct a smooth relaxation master curve*, the relevant viscous flow function is said to be able to manifest the material’s time-temperature dependent relaxation behavior via the principle of TTS. In fact, the calculated shift factor could be used to horizontally shift a relaxation master curve† whereby its accuracy may be compared to those obtained experimentally. Figure 11 reveal the results of the relaxation response predicted from WLF and Arrhenius viscous flow functions, plotted against empirically results of PP while figure 12 shows similar plot for HIPS (full-line denotes empirical data while symbol denotes TTS shifted response).

![Figure 11: Modulus relaxation response of PP, empirical vs. those evaluated from WLF and Arrhenius functions.](image-url)

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* Shift factors used to construct the relaxation master curves of PP and HIPS, at chosen reference temperature can be found in table 1 while the resultant master curves are depicted in figure 7.

† Here, it is referred to relaxation master curve constructed from experimental data. It will be shown later that within constitutive material modelling, a series of generalized Maxwell function may be used to capture such empirical master curve.
Figure 12: Modulus relaxation response of HIPS, empirical vs. those evaluated from WLF and Arrhenius functions.

From figures 11 and 12, it can be observed that the WLF function out-performed Arrhenius in describing the relaxation response of both PP and HIPS. Discrepancies were found in the details where both WLF and Arrhenius poorly predicted the modulus relaxation of PP at 160°C. In addition, there also a large different in between the empirical relaxation behavior of HIPS and those calculated from Arrhenius function in the temperature region in between 100 and 120°C.

The analysis so far was concerned on the effectiveness of a number of TTS shift functions in term of their capability in evaluating the time and temperature dependent response of PP and HIPS. It is however in constitutive modeling of polymer viscoelasticity via TTS, an additional function would be required to capture the modulus relaxation master curve as a function of time. This may be done by utilizing a series of generalized Maxwell function, as schematically shows in figure 13, where $\xi_i$ and $\eta_i$ are the spring (elastic) and dashpot (viscous) constants of the $i^{th}$ Maxwell element.

![Figure 13: Generalized Maxwell function with $i$ parallel Maxwell elements](image)

Each Maxwell element represents a unique contribution to a material’s relaxation behavior. If one considering the model in shear, the generalized Maxwell function may be mathematically expressed as:

$$G(t) = G_0 \left[ 1 - \sum_{i=1}^{n} g_i \left(1 - e^{-\frac{t}{\tau_i}}\right) \right]$$  \hspace{1cm} ......(20)

where $G(t)$ is the relaxation modulus at time $t$, $G_0$ is the initial un-relaxed modulus, $n$ denotes the number of individual Maxwell elements while $g_i$ and $\tau_i$ are material parameters,
with parameter $g_i$ capturing the relative amount of modulus relaxation while parameter $\tau_i$ defining the relaxation time constant of any individual ‘$i’ Maxwell element.

Characterization of the constants $g_i$ and $\tau_i$ were carried out within MathCAD® and it was found that a 10-terms and 5-terms generalized Maxwell functions are sufficient to effectively reproduce the relaxation master curve of the PP and HIPS specimens used in this work, respectively. Table 3 tabulates the characterized values of the material parameters while figure 14 depicts a comparison between the empirically constructed relaxation master curve and those calculated from the generalized Maxwell function.

| Characterized constants of 10-terms generalized Maxwell function for PP |  |
|---|---|---|---|---|---|---|---|---|
| $g_1$ | $g_2$ | $g_3$ | $g_4$ | $g_5$ | $g_6$ | $g_7$ | $g_8$ |
| 0.131 | 6.124 | 0.1104 | 0.1059 | 0.0603 | 0.0575 | 0.0544 | 0.0585 | 0.0654 |
| $\tau_1$ | $\tau_2$ | $\tau_3$ | $\tau_4$ | $\tau_5$ | $\tau_6$ | $\tau_7$ | $\tau_8$ |
| 0.9486 | 4.9389 | 3.9296 | 3.3197 | 4.2269 | 4.2408 | 4.2336 | 4.2307 |

| Characterized constants of 5-terms generalized Maxwell function for HIPS |  |
|---|---|---|---|---|
| $g_1$ | $g_2$ | $g_3$ | $g_4$ | $g_5$ |
| 0.2497 | 6.773 | 0.2300 | 3.9750 | 0.0174 |
| $\tau_1$ | $\tau_2$ | $\tau_3$ | $\tau_4$ | $\tau_5$ |
| 0.8526 | 6.1424 | 4.1035 | 22.250 | 150.7 |

**Table 3**: The characterized constants of generalized Maxwell function for PP and HIPS

**Figure 14**: Relaxation master curves calculated from generalized Maxwell function, plotted against empirically constructed relaxation master curve

The results shown in figure 14 clearly demonstrated that the generalized Maxwell function, when accurately characterize capable of capturing the long-term relaxation master curve of PP and HIPS materials used in this work.

### 5 Discussion and Conclusions

To date, modeling of the mechanical relaxation response of polymers under varying deformation rate and temperature domains has been widely studied through the use of the TTS concept. The TTS theory in principle allows the evaluation of time-temperature dependent viscous dissipation and relaxation time of ‘thermally and rheologically simple’ material such as strong glass-forming liquids and amorphous solids by establishing an equivalent in between the materials’ properties at short elapsed time, high temperature to those obtained at low temperature, long elapsed time.

From the current analyses, it has been demonstrated that a long-term relaxation master curve of typical thermoformable materials such as semi-crystalline PP and amorphous HIPS could be obtained by horizontally shifting a series of short-term relaxation curves (with respect to a reference curve at temperature $T_{ref}$, see figure 7) whose data were obtained at different temperature interval until the relevant curves superimposed. The amount of applied horizontal
shift in turn provides a convenience mean to calculate the long-term relaxation response at a particular temperature $T$, relevant to a reference temperature $T_{\text{ref}}$, at which the relaxation master curve was constructed. It follows that if one can determine the value of the applied shift factor, $a_T$, in between temperatures $T$ and $T_{\text{ref}}$, the long-term relaxation modulus at temperature $T$ may be predicted.

Williams, Landel and Ferry\textsuperscript{[2]} investigated the temperature dependent relaxation processes of a wide variety of polymers, polymer solutions, organic glass-forming liquids and inorganic glasses proposed a function for the evaluation of shift factor, $a_T$, known as the WLF function (equation 12). The resultant WLF function was found useful in describing the time-temperature dependent relaxation response of polymers in application such as thermoforming\textsuperscript{[33]} and blow molding\textsuperscript{[34]}. Arrhenius\textsuperscript{[35]} is his work on investigating the influence of temperature on the reaction rate of sucrose formulated the well-known Arrhenius equation (equation 13) and researchers\textsuperscript{[36, 37]} have found that the temperature dependent relaxation time and viscosity properties of strong glass forming liquids exhibit behavior similar to that of the Arrhenius reaction rate process. Vogel\textsuperscript{[4]}, Fulcher\textsuperscript{[5]} and Tammann\textsuperscript{[6]} on the other hand proposed the VFT equation (equation 14) on their analyses on supercooled glass forming liquids in the temperature range adjacent and above to the $T_g$ of the materials.

Current analyses on the three viscous flow functions (WLF, Arrhenius and VFT) commonly used in the evaluation of TTS shift factor revealed that the WLF out-performed Arrhenius in term of its accuracy in predicting the modulus relaxation response of PP and HIPS (figures 11 and 12) whereas the VFT function may appears as an equivalent form to the WLF or Arrhenius, depends on the characterized material constants. It is however that non of the viscous dissipation function being analyzed capable of capturing the modulus relaxation response of HIPS at temperature lower than 80°C, as can be seen from figure 10 that a linear plot could not be established at regime below this temperature. In addition, poor prediction was also found at the modulus relaxation of PP at 160°C. This may appear to be the limitation of these viscous flow functions in predicting the time-temperature dependent material properties over a wide temperature range involving highly nonlinear variation in viscosity, in particular at the glass-rubber and melting transitions regime.

From the analyses results demonstrated in the current work, it is indeed that the time and temperature dependency of materials typically used in thermoforming application, such as PP and HIPS could be modeled through the linking of properly characterized viscous flow function (to evaluate an accurate TTS shift factor) and generalized Maxwell function (to capture the long-term relaxation master curve) within constitutive material model. In the case where large deformation is considered, the viscous flow function and generalized Maxwell model in turn could be linked with one of the many hyperelastic laws to create a nonlinear elastic + linear viscoelastic\footnote{An assumption is made here that the polymer nonlinear viscoelasticity at large strain may be effectively approximated through the use of small strain linear viscoelastic theory.} model which ideally would capture the time-temperature dependent response of material subjected to large deformation.

6 References


**Appendix A**

*VFT function:*

\[
\log a_T = -\frac{1}{2.303} \left( \frac{B}{T-T_a} - \frac{B}{T_{ref}-T_a} \right)
\]

\[
\Rightarrow \log a_T = \frac{1}{2.303} \left( \frac{B(T_{ref}-T_a)-B(T-T_a)}{(T-T_a)(T_{ref}-T_a)} \right) \Rightarrow \log a_T = \frac{1}{2.303} \left[ \frac{B(T_{ref}-T_a)-T+T_a}{(T-T_a)(T_{ref}-T_a)} \right]
\]

\[
\Rightarrow \log a_T = \frac{1}{2.303} \left[ \frac{-B(T-T_{ref})}{(T-T_a)(T_{ref}-T_a)} \right] \Rightarrow \log a_T = \left[ -\frac{B}{2.303(T_{ref}-T_a)} \right] \left( T-T_{ref} \right)
\]

Hence, *VFT* equivalent to *WLF* with \( C_1 = \frac{B}{2.303(T_{ref}-T_a)} \) and \( C_2 = \left( T_{ref}-T_a \right) \).